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SYNTHESIS AND ADSORPTION OF FUNCTIONALIZED POLYSTYRENES

A Dissertation Presented

by

DHAMODHARAN R. IYENGAR

Submitted to the Graduate School of the
University of Massachusetts in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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Polymer Science and Engineering Department

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DEDICATION

Dedicated to my parents, my eldest brother Narayanan, my wife Rama and my other brothers and sisters whose support, motivation and encouragement made it all possible.

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Several people contributed to my education and development and I acknowledge their efforts. The most important contribution was from Professor Thomas J. McCarthy whose inspiration, guidance and support enabled the successful completion of this dissertation. His commitment to research, tireless work, vast knowledge, the impressive correlations that he could draw between different disciplines of science and his boundless enthusiasm was an example of leadership to me. I thank my committee members Professors Hsu and Archer for their critical review of the research work presented and their support throughout my programme at the University. Special thanks to Professor S. P. Srinivasan of the chemistry department at A. M. Jain College, Madras without whose support and help I would not have known that chemistry was more fun than mathematics.

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I also like to thank many fellow students who made this research work enjoyable. In particular I acknowledge the friendship and support of Brant Kolb, David Waldman, Eric Kendal, Joan Brennan and Jack Hirsch. I enjoyed numerous discussions with Brant, Eric, Jack and Dave and thank them for teaching me a lot. Jack is a special friend who in addition to his invaluable help in the laboratory also kept the instruments running. I thank the other members of the McCarthy group for their help and criticism. I also like to thank some of my friends who encouraged and helped me throughout the course of this work: Jack Shea, Howard Schild, Anand and Vijayasarathi.

Finally, I thank the folks of the glass shop (Larry, Tim and Sally), the chemistry stockroom and the members of the radiation safety division led by James Tocci (Bob, Linda and Alecia) for their help and kindness.

ABSTRACT

SYNTHESIS AND ADSORPTION OF FUNCTIONALIZED POLYSTYRENES

SEPTEMBER 1992

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The effect of specifically interacting functional groups (sticky foot) located at the chain ends of polystyrene on the adsorption rate, adsorbance, graft density and surface excess are discussed from cyclohexane, a theta solvent and toluene, a good solvent, the substrate under investigation being glass. Polystyrenes with hydroxyl and carboxylic acid end-groups (PS-OH, PS-COOH, HO-PS-OH and HOOC-PS-COOH) in narrow molecular weight distribution are synthesized by anionic polymerization of styrene followed by suitable termination reactions. Thin layer chromatography (TLC) is developed as an analytical technique to predict trends in the adsorption of the polymers in a range of solvents. In particular the information about the location of the end-group and therefore different chain architectures at the interface are inferred from this simple technique.

Adsorption isotherms are obtained for each of the functionalized polymers of four different molecular weights, the selection of which was based on the TLC results. Kinetics of adsorption and the adsorbance data are determined by liquid scintillation counting of tritium labelled polymers. Graft density and surface excess data are calculated from the adsorbance data and other known parameters.

It is shown, from these data, that polystyrenes with a carboxylic acid end-group form weakly stretched brushes at the glass-cyclohexane interface and mushrooms at the glass-toluene interface a result consistent with the higher osmotic repulsions towards packing in good solvents. Polystyrenes with functional groups at both the chain ends are hypothesized to form a range of structures from those dominated by tails at higher concentrations to those dominated by loops (in a good solvent) and trains (in a theta solvent) at lower solution concentrations. At higher molecular weights it is shown that functionalized polystyrenes behave as though they are not functionalized a result consistent with the TLC predictions. Hydroxyl end-group is shown to be an ineffective sticky foot from its adsorbance vis-a-vis polystyrene.

The segment density distribution away from a polished silicon surface for a carboxylic acid end-functionalized polystyrene adsorbed from cyclohexane is determined by neutron reflection technique. The dry film thicknesses of polymer modified glass surfaces are determined by x-ray photoelectron spectroscopy. It is shown from the water contact angle data that a highly hrdrophilic surface of glass is converted to a completly hydrophobic surface by the adsorption of the functionalized polystyrenes.

In summary it is mentioned that carboxylic acid and hydroxyl end-functionalized polystyrenes weakly perturb the system, polystyrene and a high energy surface. A range of polymer configurations from that dominated by tails to loops to trains is obtained, the dynamics of which is shown to be dependent on factors such as end-group concentration, location of the end-group, solvent nature, molecular weight and the enthalpies of the functional group-surface and surface-segment interaction energies. No particular theory convers such a dynamic range except the Scheutjens-Fleer theory. Their prediction of segment density distribution away from the surface is closer to what is observed by neutron reflection experiments in a moderately good solvent.

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CHAPTER 1

INTRODUCTION

1.1 Significance of Polymer Adsorption

Adsorption of polymers at interfaces is pivotal to a range of technologies including lubrication,[1] colloid stabilization,[2] corrosion inhibition,[3] and adhesion.[4] Areas of critical technological importance impacted by polymer adsorption are summarized in Table 1. Adsorption of an isolated macromolecule to an "attractive" wall has been the subject of numerous theoretical investigations since 1945.[5-7] A large amount of experimental work on the adsorption of homopolymers and copolymers to particulate (porous and non-porous) and "flat" substrates has been performed as well. Theoretical and experimental work on polymer adsorption is reviewed extensively in many articles.[7-11] Presently there is abundant interest (theoretical and experimental) in the adsorption of functionalized homopolymers and block copolymers to surfaces in contact with the polymer solution. This is largely due to the development of new experimental techniques such as the surface force balance,[12-14] evanescent wave-induced fluorescence,[15,16] in situ ATR IR measurements,[17-21] second harmonic generation,[22,23] neutron reflection,[24,25] dynamic scanning angle reflectometry,[26] evanescent wave ellipsometry,[27,28] in situ ellipsometry,[29] NMR spin-spin relaxation time measurements,[30,31] in situ ATR UV measurements,[32] surface plasmon oscillations,[33,34] high resolution ion scattering,[35] thin layer chromatography[36-38], streaming potential measurements[39] and neutron scattering.[40] These techniques enable a better understanding of the structure of adsorbed polymers, in terms of the forces involved in bringing two adsorbed layers together, the segment density distribution away from the surface, the hydrodynamic thickness, the root-mean-square thickness, the adsorption enthalpy, the bound fraction and the kinetics of adsorption in short time scales and aid in the critical evaluation of the large number of theoretical

Table 1.1 Area's of Practical Interest Involving Polymer Adsorption

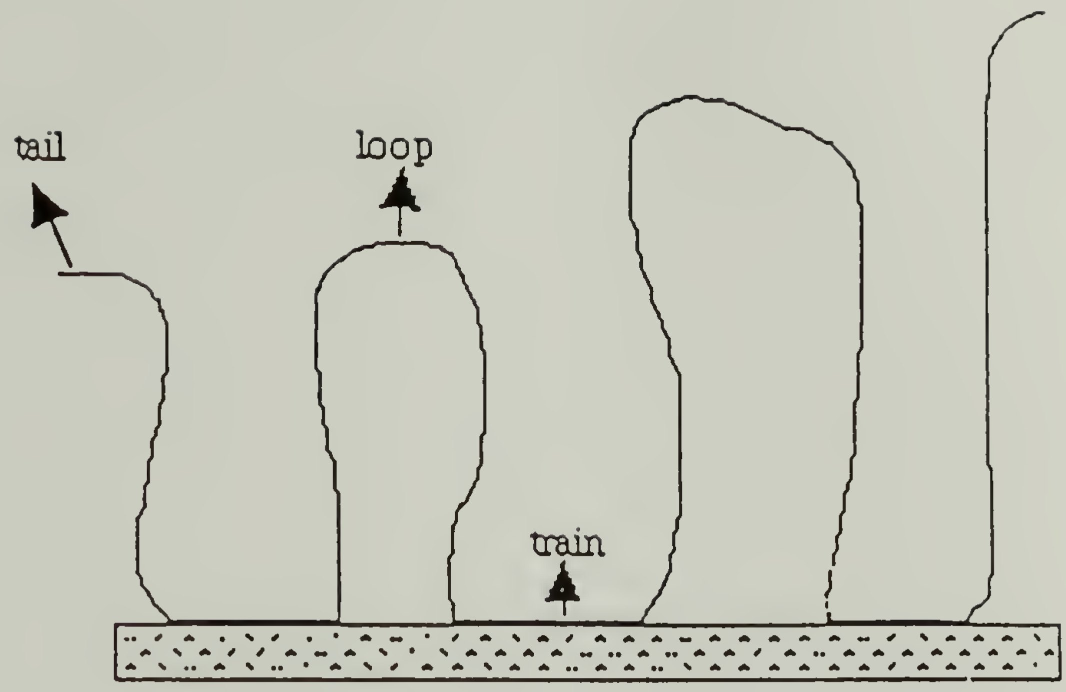
- Adhesive films
- Paints and Coatings
- Sealing
- Lamination
- Reinforcement
- Corrosion inhibition
- Polymer protected and modified electrodes
- Particle separation by flotation
- Marine fouling by polysaccharide / protein adsorption
- Enhanced packing of magnetic recording materials
- Detergent action
- Immune reactions
- Textile finishing
- Rheology of polymer-stabilized systems
- Cell adhesion and growth
- Solid lubricants
- Protective and dispersive colloids
- Flocculation
- Drag reduction
- Chromatography
- Solid propellants
- Adsorbents as crystallization inhibitors
- Wetting of fibres by prepreg in composites and reinforcement
- Soil structure and dewatering of clay
- Blood/endothelial interactions and bio-compatibility of artificial implants.
- Groundwater treatment to remove sub-microscopic particles.
- Precipitation
- Genetic reproduction
- Stabilization of drugs
- Flow of water through soil containing adsorbed humic acids
- Tertiary oil recovery

Note: The above collection was obtained from several review articles on polymer adsorption quoted in the text and the information learned from recent American Chemical Society meetings.

predictions published by many research groups whose attention is currently focused on this problem.[41-54]

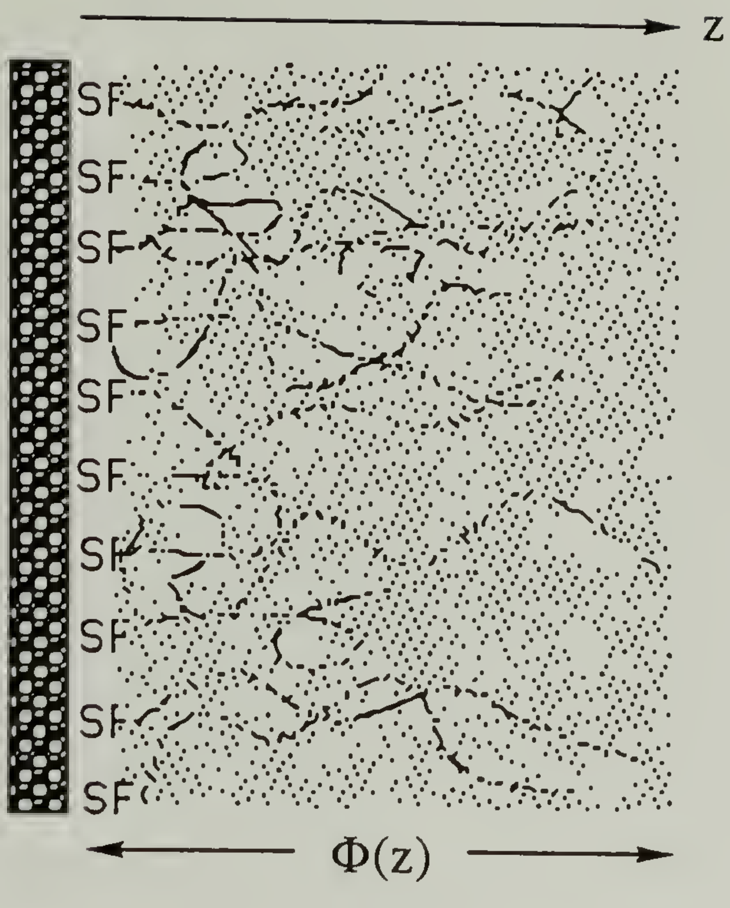
Polymer adsorption literature from the 50's and 60's suggests that flexible polymers of very high molecular weight adsorb to surfaces in a loop-train-tail fashion as shown in figure 1.1. The conformation of the chain at the interface is determined by that arrangement which minimizes the free energy of the chain as a unit, under the given solvent condition. Some parameters are considered to represent the adsorbed chain as shown in figure 1.2. Flexible and semi flexible homopolymers are now widely accepted to adsorb to a surface with their segments being present in trains, loops, and tails. In this case each and every segment is a potential adsorbate and the structure of the polymer at the surface is governed by such factors as the energy of interaction of the segment(s) with the surface, the interaction energy of the solvent molecules with the surface (the energy in kT units required to replace a solvent molecule on the surface by a polymer segment was first defined by Silberberg as χ_S), the polymer segment - solvent interaction energy (often described by the Flory interaction parameter χ), polymer molecular weight, and the concentration of the polymer in solution. All the existing theories recognize the importance of the above parameters and predict that large loops and tails contribute to greater adsorbance.

With the recognition of the ability of end-grafted polymers to stabilize colloidal dispersions, the polymer adsorption community has focussed its attention, in the last ten years, on the structure of polymer chains grafted by one end to a surface. The inherent temptation to idealize end-functionalized polymers as being attached to a surface just by one end with the rest of the segments extending away into the bulk solution bore the scaling analysis of end-functionalized polymers advanced by Alexander and de Gennes.[55,56] The main results of their arguments are that the extension of a polymer chain grafted by one end to a surface and its free energy should scale as its molecular weight. de Gennes suggested in his paper that this could be verified easily by adsorbing an A-B type block copolymer



Jenkel and Rumbach's hypothesis

Figure 1.1 Train - Loop - Tail Configurations in an Adsorbed Layer of Homopolymer



SF stands for sticky foot.

z stands for "z" direction.

F(z) is segment density distribution.

Parameter	Symbol	Method of determination
Adsorbance	A or Γ	Liquid scintillation counting or Ellipsometry
Thickness or extension	t_h	Force vs. distance of separation measurements Israelachvili apparatus
Root mean square thickness	t_{rms}	Ellipsometry or Neutron reflection.
Bound fraction	p	Infrared spectroscopy.
Segment density distribution	$\Phi(z)$	Neutron reflection.

Figure 1.2 Parameters Characteristic of the Configurations in an Adsorbed Layer

where one block will have a strong enthalpic interaction with the surface. This prediction has been verified by Taunton, et al.,[57] for the adsorption of zwitterion end-functionalized polystyrene to mica surface in toluene, by Parsonage, et al.,[58] for poly(styrene-b-2-vinylpyridine) adsorption to mica in toluene and Hair, et al.,[59] for poly(styrene-b-ethylene oxide) adsorption to mica in toluene using the force balance apparatus. However an adsorbed layer is hardly characterized fully by its extension in solution. There are other parameters of a grafted chain such as the segment density distribution away from the surface, end segment distribution in the adsorbed layer and the root mean square thickness of the layer as shown in figure 1.2. de Gennes's results are also applicable to those polymers that are adsorbed irreversibly by their end group (say the end groups in the case of diblock copolymers) alone. A more universal theory involving the prediction of the structure of adsorbed layers of end-functionalized (grafted) polymers is the self consistent - mean field approach advanced by Scheutjens and Fleer.[41] They arrange the polymer segments in a hypothetical lattice above the surface in question. No assumptions about the structure or the distribution of the segments in the adsorbed layer is made. Their theory is widely accepted for the case of the adsorption of homopolymers (particularly from from poor solvents) as their prediction of adsorbance (Γ; mass/area), the bound fraction (p; the number of segments in contact with the surface per chain/ the total number of segments per chain), the fractional surface coverage (θ), and the root mean square thickness (t_{rms}) agree well with experimental results. Their prediction about the parabolic density profile of segments away from the interface in the case of end-functionalized polymers was observed recently in neutron reflection experiments.[60, 61] However scaling arguments are simple to understand and do not involve the rigorous mathematical formalism of SCF and other theories, and their predictions are easy to verify. A detailed treatment of each of the theories is given in the following sections.

Another area of polymer adsorption in which theoretical analysis and experimental work are being published intensely is in block copolymers. The scaling analysis of

Marques and Joanny[43] and the SCF analysis of Scheutjens and Fleer[62] are again the two contending theories. Experimental work in this area is in progress, in many research groups around the world, to verify their predictions. In the next few years this area of research looks extremely promising.

1.2 Characteristics of Homopolymer Adsorption

Polymers in general and proteins in particular adsorb from solution onto a variety of substrates. In general a polymer adsorbs spontaneously to a surface if the loss of configurational entropy upon adsorption is surpassed by the gain in enthalpy owing to multiple points of segmental attachments at the surface, i.e the free energy change accompanying adsorption should be negative. A critical energy of interaction is recognized below which adsorption does not take place. The adsorption process is slow compared to a low molecular weight analog, say the repeat unit. This is attributed to the lower diffusion coefficient, the conformational changes of segments taking place in the adsorbed layer and the displacement of molecules of low molecular weight, which are adsorbed first, by molecules of higher molecular weight (polydispersity effect). The adsorption isotherms have a high-affinity character, i.e. the adsorbed amount increases steeply at very low increasing solution concentrations and reaches a plateau value at detectable concentrations. Adsorbance increases with molecular weight and decreasing solvent quality. The effect of temperature is small or significant on the adsorbance depending on how far it is from the theta condition, but affects the hydrodynamic thickness significantly. It is generally impossible to desorb polymers by dilution but they can be displaced by other polymers (higher segment - surface interaction enthalpy), by the same polymer of higher molecular weight (due to the gain of translational entropy for the same enthalpy of interaction) or by low molecular weight displacers (which interact with the surface with a higher enthalpy of interaction than the segments of the polymer). Cooperativity of attachment during adsorption and the low probability of simultaneous desorption of all the segments once adsorbed, are also recognized.

The adsorption of polymers is considerably different from the adsorption of small molecules. The entropy loss per molecule on adsorption is greater than that of small molecules (this difference is due to the large number of configurations that a macromolecule can assume in solution as well as at an interface). Therefore a minimum or a critical enthalpic gain per segment is necessary to offshoot the entropic loss per segment in the transition from a free coil to a bound or adsorbed coil. This critical enthalpic gain was introduced by Silberberg in 1968 and it is referred to by the symbol χ_{sc}. In general the adsorption enthalpies involved (χ_s) are greater than the critical adsorption enthalpy (few tenths of a kT) and therefore polymers adsorb to many surfaces. The adsorption enthalpy parameter χ_s is defined as the net enthalpy change in units of kT, of an exchange process, in which a segment on the surface having 1/2 (z - z') contacts with solvent molecules (z is the lattice coordination number and z' is the number of contacts that a segment has with the surface) and 1/2 (z - z') contacts with other segments, is exchanged with a solvent molecule in the solution having 1/2 z contacts with other solvent molecules and 1/2 z with segments. This definition enables segment - surface interaction to be defined independent of segment - solvent interaction, for which χ is a measure.[9] χ is the Flory - Huggins polymer segment - solvent interaction parameter and it is a measure of the quality of the solvent. χ is defined as the net enthalpy change in units of kT, per solvent molecule, per z solvent - segment contacts, where z is the coordination number of the lattice in which the polymer segments (1) and solvent molecules (2) are arranged [$\chi kT = z (\Delta H_{12} - 0.5 \Delta H_{11} - 0.5 \Delta H_{22})$].

The maximum amount of polymer adsorbed (adsorbance) is of the order of a few mg / m^2, and is equivalent to 1 to 10 monolayers depending on the solution conditions. However the adsorption isotherms do not reveal the multilayer pattern observed in the case of many small molecules. This led Jenkel and Rumbach to hypothesize that the segments in the adsorbed layer were present in three distinct sequences as in figure 1.1.[63] These are sequences of segments in contact with the surface called trains, stretches of segments in the solution whose ends are at the surface, called loops and sequences of segments of which one end is bound to the surface, called tails. Modern theories on the structure of adsorbed polymers are based on this hypothesis. There is experimental evidence based on the measurement of root-mean-square extension (t_{rms}) and the forces involved while bringing two surfaces containing adsorbed polymer layers together, at distances of the order of few radius of gyrations (R_g), which point to this end. The composition of trains, loops and tails in an adsorbed layer has been recognized to be affected by the solvent strength (χ), adsorption enthalpy per segment (χ_s), bulk polymer concentration (often represented by ϕ the volume fraction), and the molecular weight of the polymer.

The adsorbed layer is characterized by the the following parameters: adsorbance, Γ, the mass adsorbed per unit area, the total surface coverage, θ, defined as the ratio of the number of segments in the adsorbed layer divided by the number of segments if the surface were to be a monolayer of trains, the direct surface coverage, θ_1, defined as the number of segments of the adsorbed layer in trains divided by the number of segments if the surface were to be a monolayer of trains, the bound fraction, p, defined as the fraction of segments in the adsorbed layer that are in direct contact with the surface (by definition $p = \theta_1 / \theta$), the root-mean-square extension, t_{rms}, defined as an average thickness perpendicular to the surface from the contributions of trains, loops and tails in the adsorbed layer in the presence of the solvent and the segment density distribution, $\phi(z)$, away from the surface where the surface is defined as $z = 0$. Experimentally Γ, p, t_{rms}, and $\phi(z)$ can be determined and have been measured for a number of homopolymers. This enables critical comparison with theoretical predictions to be made as a better understanding of the structure of polymers in adsorbed layers is so crucial towards its application in several areas of vital technology.

The adsorption of homopolymers to surfaces has been treated theoretically by a number of researchers.[64-94] A large volume of this work concerns the adsorption of isolated macromolecules at interfaces and therefore their results are not amenable to experimental studies. The methods of Hoeve, Silberberg, Roe, Scheutjens and Fleer (SF), and de Gennes treat the adsorption of polymers from solution to surface under conditions in which a typical laboratory experiment would be conducted (the systems are comprised of a large number of macromolecules which interact with the surface, the solvent and among themselves) and as such their results can be verified. Among the above five theoretical approaches four of them are based on lattice models of the type used by Flory - Huggins to describe a polymer solution and the fifth by de Gennes uses scaling arguments (again uses Flory's arguments to describe the chemical potential of a polymer coil in a good solvent as a balance between swelling forces which expand the coil and elastic forces which contract the coil with two additional terms for confinement and adsorption energy).

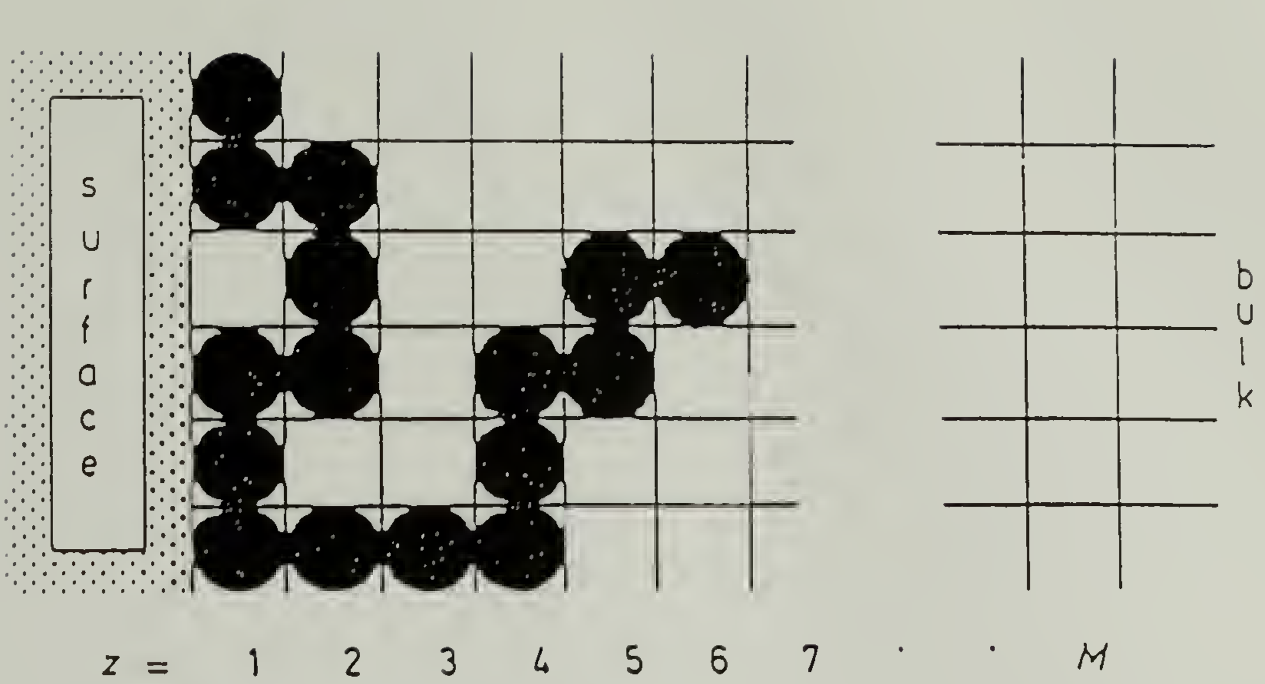
The theories of Hoeve and Silberberg start from the statistics of an isolated macromolecule. The partition function for the system consisting of many adsorbed molecules, free molecules and solvent molecules is evaluated using the Flory - Huggins χ parameter for segment - solvent interaction and Silberbergs adsorption enthalpy parameter χ_s (for segment - surface interaction). End-effects (tails) are neglected. The properties of the adsorbed macromolecules are evaluated from the partition function assuming an exponential (Hoeve) and step-function (Silberberg) segment density distribution profile. While the assumptions of the segment density distribution survived the experimental results of the 80's, the neglect of the role of tails in determining the properties of the adsorbed layer did not and therefore their theories are not widely accepted. However their efforts and the efforts of earlier researchers provided crucial insights, mathematical techniques and the recognition of an adsorption enthalpy parameter. The results of Silberberg and Hoeve are valid for systems which can be chemically designed to adsorb without tails. The Roe and SF theories do not assume any particular model for the state of the adsorbed chain and evaluate the properties of the adsorbed chains in an arbitrary concentration gradient near the surface. Roe neglects the role of tails and therefore his theory is not applicable to systems where tail effects are important (which is the case for homopolymer adsorption). Among the mean-field theories, the one that makes no assumption about the structure of the adsorbed layer (and therefore takes into account the role of tails) and predicts in detail the structure of the adsorbed layer (size distribution of trains, loops, and tails; the fraction of segments in trains, loops and tails) is the one by Scheutjens and Fleer. This theory is accepted widely by a number of research groups and is relevant to the results of this dissertation and therefore it is discussed in detail below. The scaling argument of de Gennes is also presented as it's predictions of some properties of homopolymers and grafted polymer brushes (where the grafting moieties are in a non-selective solvent) from good solvent conditions under which the coils overlap in the adsorbed layer have been verified. In addition this theory is mathematically simple, elegant and presents a physical picture, as well as predicts properties that can be measured experimentally.

1.3 Modern Theories of Homopolymer Adsorption

1.3.1 Scheutjens and Fleer theory (SF Theory)

Scheutjens and Fleer present a general theory of polymer adsorption using a quasi-crystalline lattice model.[88] They determine the partition function for a mixture of polymer chains and solvent molecules near an interface in an arbitrary but preassigned concentration gradient by adopting the Bragg-Willliams approximation (the mean-field approximation) of random mixing within each layer parallel to the surface. The interaction between segments and solvent molecules is taken in to account by use of the Flory-Huggins parameter χ, and that between segments and the interface is described in terms of the differential adsorption enthalpy parameter χ_s.

A typical SF lattice is shown in the next page.



The lattice is divided into M layers parallel to the surface, each containing L identical sites. The layers are numbered i = 1, 2, ...M, where i = 1 is the layer adjoining the surface and layer M is situated in the bulk solution. Each lattice site is occupied either by a polymer segment or a solvent molecule. The volumes of a segment and a solvent molecule are assumed to be the same. The degree of polymerization, r, is taken to be the number of segments per chain. If n_i and n_i^0 are the number of segments and solvent molecules in layer i, it follows immediately that, $n_i + n_i^0 = L$ and $rn + n^0 = ML$, where $n^0 = \Sigma\, n_i^0$ and $rn = \Sigma\, n_i$. The volume fraction ϕ_i for segments and ϕ_i^0 for solvent molecules in layer i are given by $\phi_i = n_i / L$ and $\phi_i^0 = n_i^0 / L$. The set of all volume fractions is indicated by $\{\phi_i\}$ where i = 1 to M. The coordination number of the lattice is z and therefore a lattice site has z neighbors, a fraction λ_0 of which are in the same layer and a fraction λ_1 in each of the adjacent layers (for a hexagonal lattice $\lambda_0 = 0.5$ and $\lambda_1 = 0.5$).

The ratio between the partition function for the polymer - solvent mixture in the adsorbed state and the reference state is given by the standard statistical mechanical expression given in equation 1.

$$Q = (\Omega / \Omega^+)\ \exp(-\Delta U/kT) \qquad \text{...............(1)}$$

where Ω is the number of ways of arranging the polymer and the solvent near the surface in accordance with the assigned concentration gradient, Ω^+ is the number of possible arrangements of n chains over rn lattice sites in pure disoriented (amorphous) polymer, and ΔU is the energy difference between the mixture and the reference state. Flory [95] has derived an expression for Ω^+. For n_1 segmental contacts with the surface and n_{12} segment - solvent contacts, $\Delta U = -n_1\chi kT + n_{12}\chi kT/z$ where the first term is from Silberberg[92] and the second from Flory - Huggins polymer solution theory.[95] Scheutjens and Fleer simplify n_{12} to be $zn^0\phi$ for a homogeneous system of n^0 solvent molecules and a segmental volume fraction ϕ (note that this is true only in dilute solution and it is an implicit assumption that is not mentioned). On applying the mean-field approximation of random mixing in each layer, each solvent molecule in layer i has $z\lambda_0\phi_i$ contacts with segments in layer i, $z\lambda_1\phi_{i+1}$ in layer i+1, and $z\lambda_1\phi_{i-1}$ in layer i-1. Therefore they replace the average volume fraction ϕ by a weighted average $<\phi_i>$ which leads to the expression for the energy change on adsorption as shown below (note: lattice theorists often mix the usage of energy and enthalpy though enthalpy is what they mean and define)

$$\Delta U = -n_1\chi kT + \chi kT \ \Sigma\, n_i^0 <\phi_i> \qquad \text{................(2)}$$

Scheutjens and Fleer evaluate Ω by taking into account all possible conformations as follows. An adsorbed chain can be placed in a lattice in many different conformations where the term conformation implies the location of its segments in the lattice sites. Thus a chain in a particular conformation n_c is represented by equation 3

$$(1,i)\ (2,j)\ (3,k)\ .....(r-1,l)\ (r,m) \qquad \text{................(3)}$$

where the first segment is in layer i, the second in layer j (j = i or i±1), etc. Many different conformations such as n_c are possible. The segments in turn can be placed in any of the L lattice sites in a given layer i. The number of arrangements in a specified conformation c is given by the expression $Lz^{r-1}\omega_c$ ($\omega_c = \lambda_0{}^x\,\lambda_1{}^{r-1-x}$ where x is the number of segments within one layer and r-1-x is the number of segments perpendicular to that layer). Thus SF theory arrives at the number of ways in which chains of conformation n_c, n_d, n_e, ...chains

($\Sigma n_c = n$) and n^0 solvent molecules can be arranged in the lattice and the expression is given in equation 4.

$$\Omega = (z/L)^{n(r-1)} \Pi \; (L!/(n_i^0)!) \; \Pi \; ((\omega_c)^n/n_c!) \qquad \text{..................(4)}$$

By differentiating the ratio of the partition functions (Q) with respect to the number of chains in each conformation, an expression is obtained that gives the number of chains in each conformation in equilibrium. Thus for a chain of conformation n_c mentioned in equation 3, the number of chains in the adsorbed layer in equilibrium with the bulk solution is given by equation 5.

$$n_c = L \; \omega_c \; (\phi/r) \; \Pi \; (p_i)^{r^*} \qquad \text{......................(5)}$$

where $r^* = r_{i,c}$ is the number of segments of conformation c in layer i and p_i is the free segment probability given by equation 6.

$$p_i = \{(\phi_i)^0/\phi^0\} \; \exp\{2\chi(<\phi_i> - \phi)\} \; \exp\{(\chi_s + \lambda_1 \chi) \; \delta_{i,j}\} \qquad \text{.........(6)}$$

p_i stands for the probability of a free segment (unattached) being in a site in layer i over a site in bulk solution.

Scheutjens and Fleer proceed to calculate the concentration profile $\{\phi_i\}$ as follows. The volume fraction of segments in layer i is given by $\phi_i = \Sigma \; \phi_i(s)$ where $\phi_i(s) = (\phi/rp_i)$ p(i,s) p(i,r-s+1). p(i,s) is the probability that a chain of s segments ends in layer i. If the end segment of an smer is in i the penultimate segment, s-1 can only be in layer i or i±1. Proceeding by similar arguments they arrive at a recurrent relationship for p(i,s) given in equation 7.

$$p(i,s) = p_i \; [\lambda_1 p(i-1,s-1) + \lambda_0 p(i,s-1) + \lambda_1 p(i+1,s-1)] \qquad \text{..............(7)}$$

The above equation can be expressed in a matrix format introduced by DiMarzio and Rubin.[69] Numerical calculations were performed using a computer. Computations for chains containing up to 5000 segments were performed. The total surface coverage (θ_1), direct surface coverage θ, the bound fraction p (θ / Γ) and the root-mean-square thickness were computed as well and given as a function of χ_S, the bulk solution volume fraction ϕ, and the chain length r for two χ values.

The best aspects of this theory are; i) the recognition and prediction of the role of tails in the structure of the adsorbed layer, ii) the prediction of a segment density profile away from the surface which will decay rapidly close to the surface and slowly at distances far away (30 to 40 lattice layers away) from the surface (again due to tails extending far away from the surface into the bulk solution; see figure 1.3), iii) that the root-mean-square thickness of the adsorbed layer will vary as the square root of the chain length (and hence the molecular weight at $\chi = 0.5$ and 0), iv) the determination of the average train, loop, and tail lengths and v) the train, loop and tail size distributions from the concentration of all the conformations contributing to the equilibrium set $\{n_c\}$, which in turn is determined from the M values of p_i (for example see figure 1.4). An example from SF prediction on the characteristics of pure polystyrene (number average molecular weight - 100000, $\chi_S = 1$ and $\phi = 1$) adsorbed to silica is given below.

	fraction of segments in	Number of segments in	average length of	Number of	% of total chain length
trains	0.05	50	3.5	~ 14	5
loops	0.3	300	21	~ 15	30
tails	0.65	650	344	~ 2	65

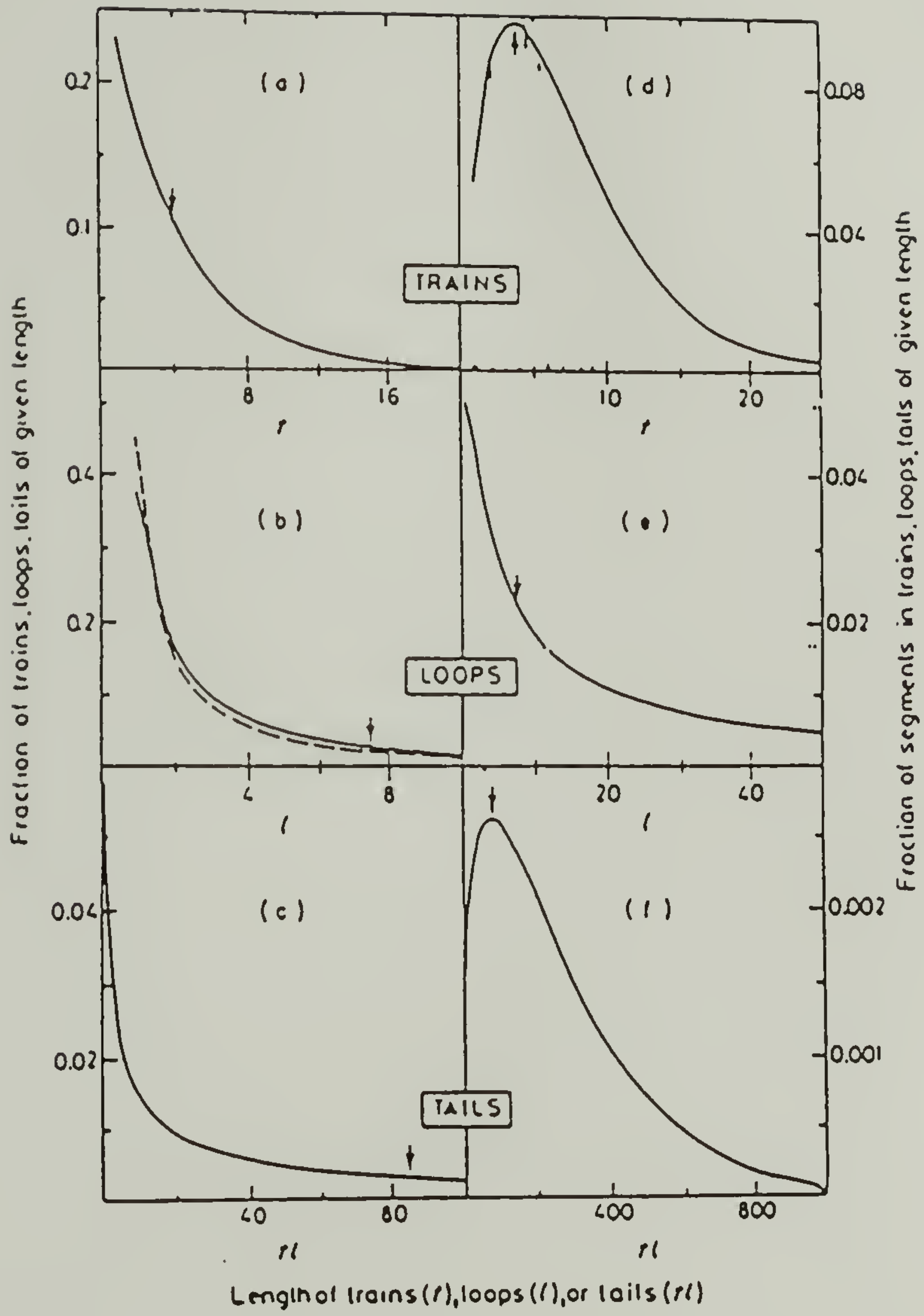


Figure 1.3 Examples of Size Distributions of Trains, Loops, and Tails from Scheutjens and Fleer Theory for r = 1000, ϕ = 0.001, χ = 0.5, χ_s = 1. Left: Fractions of Tails, Trains, and Loops of Given Length. Right: Fraction of Segments in Tails, Trains, and Loops of Given Length. The Average Train, Loop, and Tail Sizes are Indicated by the Arrows. The Dashed Curve Gives the Loop Size Distribution According to Hoeve. The Figure and Captions are Directly From Reference 9.

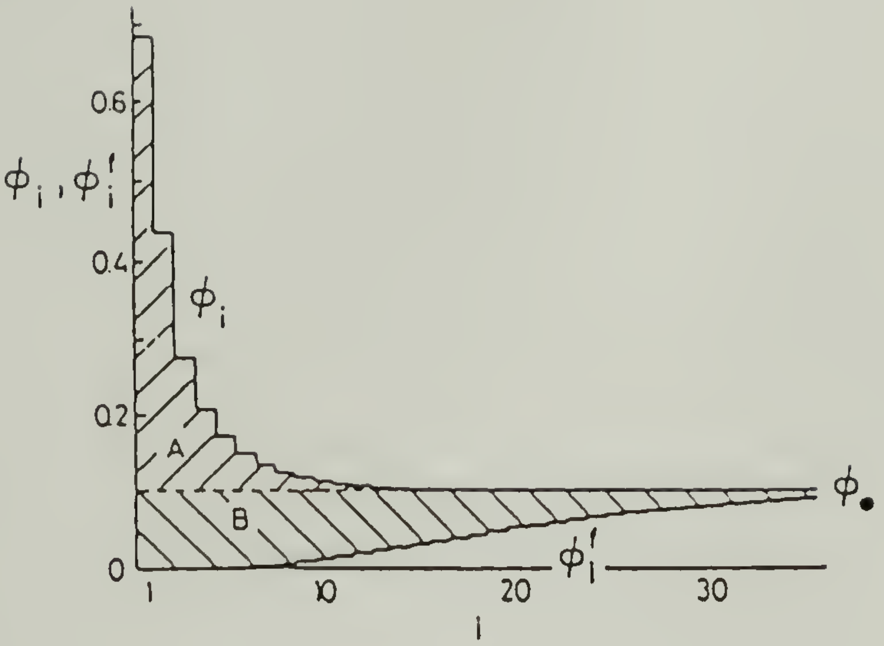


Figure 1.4 The Overall Concentration Profile ϕ_i and that due to Non-Adsorbed Chains $(\phi_i)^f$ near an Adsorbing Surface. The Sum of Area's A and B Equals θ. The Profiles are from Reference 9 obtained by the SF Calculations for $r = 1000$, $\phi = 0.001$, $\chi = 0.5$, $\chi_s = 1$, and $\lambda_0 = 0.5$.

Scheutjens and Fleer have also predicted similar characteristics for polymers adsorbed from dilute solution as a function of the molecular weight, the bulk volume fraction and the interaction parameters. Most of these predictions cannot be verified by the technology available in 1992. However the 0.5 power dependence of the root-mean-square thickness on the molecular weight of the polymer and the dynamics of the structure of the adsorbed layer (trains to tails and loops to tails) as a function of temperature confirmed SF predictions that tails cannot be ignored.[96, 97] The segment density distribution away from the surface determined in adsorbed homopolymer layers by neutron scattering[40] and spin - spin relaxation time measurements[98-100] confirm the trends predicted by this theory qualitatively and semi-quantitatively (minor shape differences between theory and experiments) i.e. close to the surface the segment density was found to decay exponentially (roughly) with increasing distance from the surface, but at larger distances the decay was found to be much slower. This was explained as due to the fact that a considerable fraction of the adsorbed segments were present in the form of long dangling tails. The other theories neglect the effect of tails.

The SF theory has minor discrepancies. The excluded volume effect is not treated explicitly and is accounted for by the use of Bragg - Williams approximation, which is a pair-wise potential between nearest neighbors and does not take into account next neighbor interactions. As a result its predictions fall apart for polymer coils adsorbed from a good solvent when they just start to overlap (2D semi-dilute solution). The entire range of polymer, solvent and surface interactions are dealt with using two enthalpy parameters while solvent orientation at the surface and around the segments and the resultant entropy effects are ignored. One among the other criticisms is that SF theory does not predict correctly the forces involved in bringing together two mica surfaces containing an adsorbed homopolymer in a good solvent at full coverage (F(D) vs D profiles).[101-104] An alternate explanation of the F(D) vs D profiles using the scaling laws of end-grafted polymers, which fits the experimental data, assumes that the homopolymer is grafted to the surface by a thin layer comprising of trains and loops (explicitly acknowledges the importance of tails). The very nature of the assumption indicates that it is a special case but the results suggest that a universal theory of polymer adsorption should be able to predict these special cases as well.[105]

1.3.2 Scaling Theory of Homopolymer Adsorption

The scaling theory of polymer adsorption from good solvents was proposed by de Gennes.[65] The reasoning behind his argument is that the mean-field approach of Flory is not adequate to describe polymer solutions in a good solvent, in the semi-dilute regime and as the segments in the adsorbed layer are likely to be in the semi-dilute region, the theory based on Flory's argument (SF) is not likely to predict the properties of the adsorbed layer. The mean-field argument in a good solvent neglects certain correlations between adjacent segments as well as with distant segments (self-avoidancy of segments is not effectively accounted) and assumes a self-consistent potential which is uniform in space. Such a potential cannot account for the swelling of the chains in good solvents and this led de Gennes to propose a scaling argument, which assumes that a self-similarity exists in semi-dilute solutions of polymers, i.e the solution can be adequately described by a network with an average mesh size ξ (correlation length). A chain is viewed as a succession of blobs of size ξ (see figure 1.5). Inside a blob the segments do not interact with segments of other chains and therefore correlations of the excluded volume type are applicable. Each blob consists of g_d monomers and this leads to N / g_d blobs per chain of length N. Inside each blob $\xi = a\,(g_d)^{0.6}$ holds good. Including correlations (excluded volume effects) de Gennes derives an expression for $\xi\,(\phi) \sim a\,\phi^{-3/4}$ and osmotic pressure $\Pi \sim \phi^{2.25}$ (mean-field predicts a $\phi^{2.0}$ dependence) where a is the monomer size and ϕ is volume fraction. The predictions of de Gennes have been verified by a number of experimentalists (Noda, et al., verified osmotic pressure dependence on concentration as 2.25 power[106]).

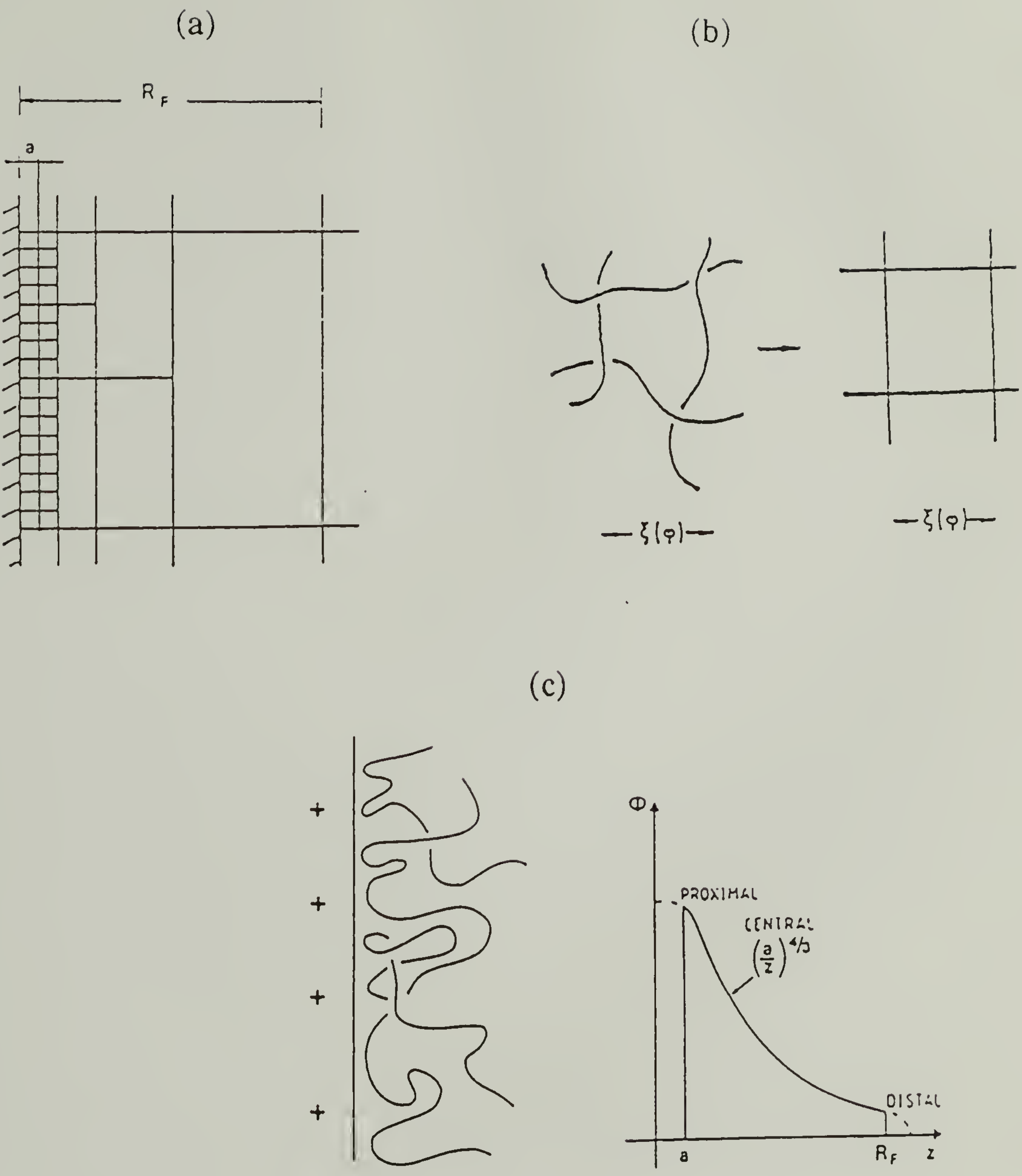


Figure 1.5 (a) An Adsorbed Polymer Layer Represented as a "Self-Similar Grid". At any Distance, z, from the Wall, the Local Mesh Size is Equal to z. (b) A Polymer Solution (Volume Fraction, ϕ) Idealized as a "Grid" with the Same Mesh Size, $\xi(\phi)$. (c) a Qualitative Aspect of the Diffuse Layer Adsorbed from a Good Solvent and the Concentration Profile Directly from de Gennes.

de Gennes's assumption about the self-similarity of the adsorbed layers allows its description in terms of the scaling laws of semi-dilute polymer solutions ($\xi(\phi) \sim a\,\phi^{-3/4}$; $g_d \sim \phi^{-5/4}$; and overlapping coils).

The other assumptions applied are i) the chain length is long ($N > 1000$ -10000), ii) adsorption is weak resulting in layer thicknesses of the order of hundreds to thousands of angstroms, iii) solvent is athermal i.e. $\chi = 0$, iv) polymer concentrations in the first and subsequent layers scale the same way.

An adsorbed layer is represented by a self-similar grid structure shown in figure 1.5a. At any distance, z, from the wall, the local mesh size is equal to z. This leads to an expression for the adsorbed layer profile (segment density distribution) as in equation 1.

$$\phi(z) = z / \xi \qquad \text{..................}(1)$$

Substituting the appropriate scaling law for ξ we find,

$$\phi(z) = (a/z)^{4/3} \qquad \text{..................}(2)$$

The segment density distribution is expected to decrease slowly with z as, $z^{-4/3}$. de Gennes also recognizes that the self-similar structure is not valid at $z \leq a$ and at $z \geq a\,N^{3/5}$ (the Flory radius). Therefore the segments in the adsorbed layer are predicted to be in three regions of space perpendicular to the surface, called proximal, central and distal as shown in figure 1.5c. de Gennes has predicted that the hydrodynamic thickness of the adsorbed layer based on the above picture should scale as $N^{3/5}$ and the ellipsometric thickness ($\{\phi(z)\, z.dz\}$ on integrating from 0 to z leads to $\sim N^{2/5}$) should scale as $N^{2/5}$. Experiments performed by Takahashi, et al.,[107] confirm the prediction about the scaling of the thickness obtained by ellipsometry while there is no consensus on the molecular weight dependence of the hydrodynamic thickness. The data of Takahashi, et al.,[108] obtained from the adsorption of poly(ethylene oxide) support de Gennes prediction while that of Cosgrove, et al.,[109] on the same system results in a different power law ($N^{0.8}$). That $\phi(z)$ follows a power law in z with an exponent close to de Gennes has been shown by neutron scattering experiments of Auvray, et al.,^{110} and in the absence of criticism from the proponents of the SF theory it can be taken as a sign of its validity.

Scaling theories are applicable to weakly overlapping chains of long lengths (large molecular weights) in good solvents ($\chi \approx 0$) where mean-field theories cannot and do not deal with some types of segment - segment correlations. It provides information about the global properties of the adsorbed layer and by its inherent simplicity of approach neglects the local properties (complete description of the structure of the adsorbed layer in terms of the contributions from trains, loops and tails). In its present form scaling theory is not capable of dealing with polydispersity effect, mixtures of different polymers, copolymers and polyelectrolytes and the versatility of SF theory in dealing with this aspects cannot be ignored.

1.4. Modern Theories of End-Grafted Polymer Adsorption

The theoretical description of polymers, one end of which is grafted to a surface, has been described by many workers. The first reported work is that of Hesselink^{111} who gave an analytical form for the segment density distribution without taking into account the segment - solvent or segment - surface interactions. Lal introduced the Monte Carlo (MC) approach for studying the conformations of macromolecules at interfaces and subsequently reported on the configurational states of a terminally anchored chain under good and bad solvent conditions.$^{112, 113}$ The results of the MC simulations were that, in a good solvent the molecule exists in an extended state. There was a strong tendency for the formation of a long train in the initial part of the molecule and a high proportion of the un-adsorbed segments existed in the tail. Formation of loops is less favoured and few configurations contained more than two loops. The long tail protrudes into the solution phase. The bad solvent destroys the tendency for the formation of the initial train and most of the time the molecule assumes train - loop conformation with a small or no tail. They explained their result taking into consideration all the relevant factors, as follows: "In good solvents segment - segment repulsions produce an extended rigid state in the chain. Such a state would induce cooperative effect among the segments leading to the formation of a train adjacent to the anchor. This effect can also produce a long array of un-adsorbed segments following the termination of the train. Long trains and tails are therefore the manifestation of cooperativity. Lack of loops in the configuration can be ascribed to the large energy required for bending the molecule. High probability states of the adsorbate molecule in the presence of the bad solvent would be those in which there are large numbers of segment - segment and segment - surface contacts. The molecule prefers to exist in the coiled state with a large number of segments attached to the surface. The presence of more loops in the configurations is an inevitable consequence of the coiled state of the molecule. In a bad solvent the molecules are coiled and large loops are formed". Clark and Lal have also reported on the configurational states of terminally attached chains, determined by the Monte Carlo approach, in good solvents for finite surface coverages.[114] The case of terminally adsorbed isolated chains has also been considered by Cosgrove (Monte Carlo approach) and Croxton (self-avoiding hard-sphere model not constrained by a lattice).[115, 116] In reality, the density of macromolecules at an interface, attached by an end, is high and therefore approaches involving interaction among chains emerged. Among those the theories of Dolan and Edwards[117, 118] and de Gennes [56] consider the case in which $\chi_s = 0$ and that of Levine, et al.,[119] considers many different values of χ_s.

A scaling description of the adsorption of macromolecules with a polar terminus was first presented by Alexander.[55] The lattice theory of Scheutjens and Fleer was extended by Cosgrove, et al.,[120] to describe the configurations of terminally attached chains at a solid-solution interface. Hirz working under the direction of Tirrell has also extended SF theory to terminally attached chains. She attempts to fit the force vs distance universal curve observed in experiments conducted in their laboratory, with a concentration dependent χ parameter.[121] Theories of grafted polymer brushes have also been described by Milner, et al.,[122-26] (provides an analytical solution to the self-consistent mean field equations of the Edward's type in the limit of strong stretching, high molecular weight and weak excluded volume interactions), Cosgrove (Monte Carlo),[127] Muthukumar and Ho[128] (numerical solutions to the self-consistent mean field equations of Edward's type; effective interactions are described by the excluded-volume parameter, space is discretized into grids and a van der Waals type interaction with the surface is considered for non adsorbing surfaces and good solvent conditions), Whitmore and Noolandi[129] (mean-field self-consistent theory of Edward's type), Murat and Grest[130] (molecular dynamics) and Chakrabarti and Toral[131] (Monte Carlo simulation study of a system of a large number of polymer chains end-grafted to a surface for several values of surface coverage and chain length).

Presently the mean field theories of Scheutjen and Fleer and the scaling arguments of de Gennes (explicit treatment of excluded volume interactions) are widely discussed in comparing experimental results and therefore a detailed account of those theories are presented below. It is also stressed that the research results described in this thesis concern the effect of end groups at the chain end(s) of polystyrene on adsorption and therefore a theory which describes explicitly the role of tails is more relevant for comparison.

1.4.1 Mean-Field Theory of Scheutjens and Fleer Type

Cosgrove, et al.,[120] and Hirz[121] have modified the Scheutjens and Fleer theory of homopolymer adsorption which in turn is an extension of Flory - Huggins theory (for a inhomogeneous solution; SF theory is described in detail in the section 1.3.1 of this chapter.) They constrained the first segment to layer 1, which in turn leads to the modification of the end segment probability. This modification enables the calculation of the segment density distribution away from the surface (also described as volume fraction profile), root-mean-square thickness, average length of trains, loops and tails and train, loop, and tail size distribution functions. Briefly, for $\chi_s < \chi_{sc}$ say 0, the segment density distribution is predicted to show a depletion layer between 0 and 2 lattice layers, followed by a maximum close to the surface (within 10 lattice layers) and gradual decrease to the bulk value, while for $\chi_s > \chi_{sc}$ say 0.6, a monotonically decreasing profile was predicted. In a good solvent the volume fraction of segments in tails was shown to go through a maximum as a function of increasing distance from the surface, the maximum being greater the smaller the surface - segment interaction (lower χ_s value). The volume fraction of loops in a good solvent dropped exponentially as a function of distance from the surface following the same trend with decreasing surface - segment interaction. Some of the results from Cosgrove, et al., are presented in figures 1.6 and 1.7.

The above theory does not treat excluded volume interactions completely and therefore like any other mean-field theory is limited to systems involving low and extremely high coverages in a good solvent. However its predictions of a parabolic segment density distribution of segments for $\chi_s < \chi_{sc}$, the monotonic decrease for $\chi_s > \chi_{sc}$ and the scaling of the brush height with molecular weight and surface coverage have been experimentally confirmed to be true for some specific cases.[127] All other mean-field theories predict a parabolic segment-density distribution profile, particularly for strongly stretched chains in a good solvent, but do not give a detailed picture of the structure of the adsorbed layer in terms of train, tail and loop size and distribution.

1.4.2 Scaling Theories

An excellent physical picture of end-functionalized polymers is given by de Gennes [56] (while the SF theory reduces this problem to that of a homopolymer in a lattice with one end being bound to the surface). Again de Gennes concerns himself with grafted chains of large lengths in a good solvent ($\chi = 0$). It is also assumed that the segments do not adsorb to the surface ($\chi_s = 0$ in lattice theory notation and $\delta < kT$ in scaling notation) as this considerably simplifies the scaling arguments to follow. Alexander has earlier presented a complicated set of scaling laws for the adsorption of a macromolecule with a polar head

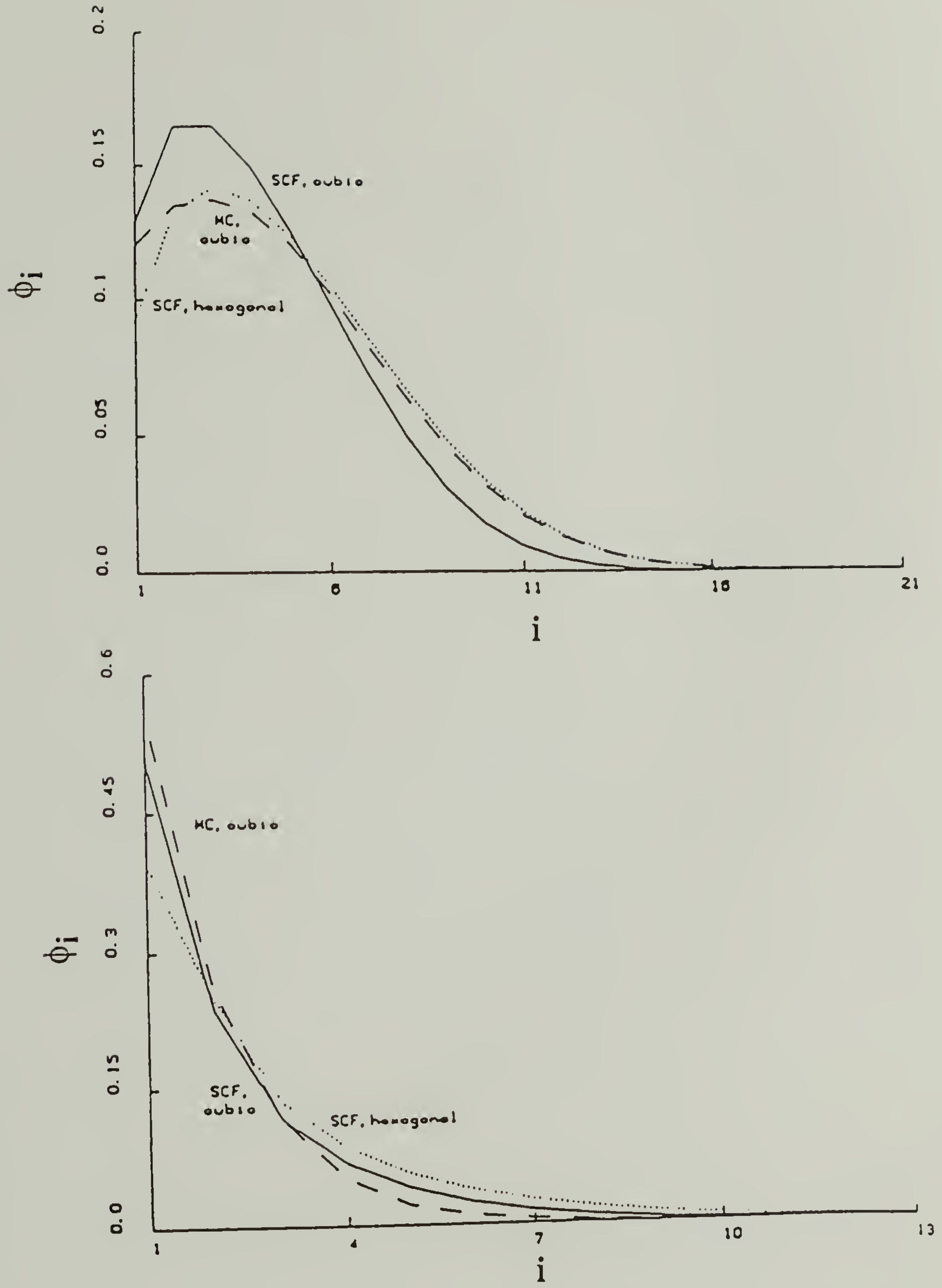


Figure 1.6 (top) Volume Fraction ϕ_i as a Function of Layer Number i for a Constant Value of θ (1.02). The MC Calculations (--) are for a Cubic Lattice, $\lambda_0 = 2/3$, while the SF Calculations are for a Cubic (--) and Hexagonal Lattice (...), $\lambda_0 = 1/2$. Data are Shown for $r = 50$, $\chi_s = 0$, and $\chi = 0.4$. (bottom) Analogous Data for $\chi_s = 0.6$. Data, Directly From Reference 120.

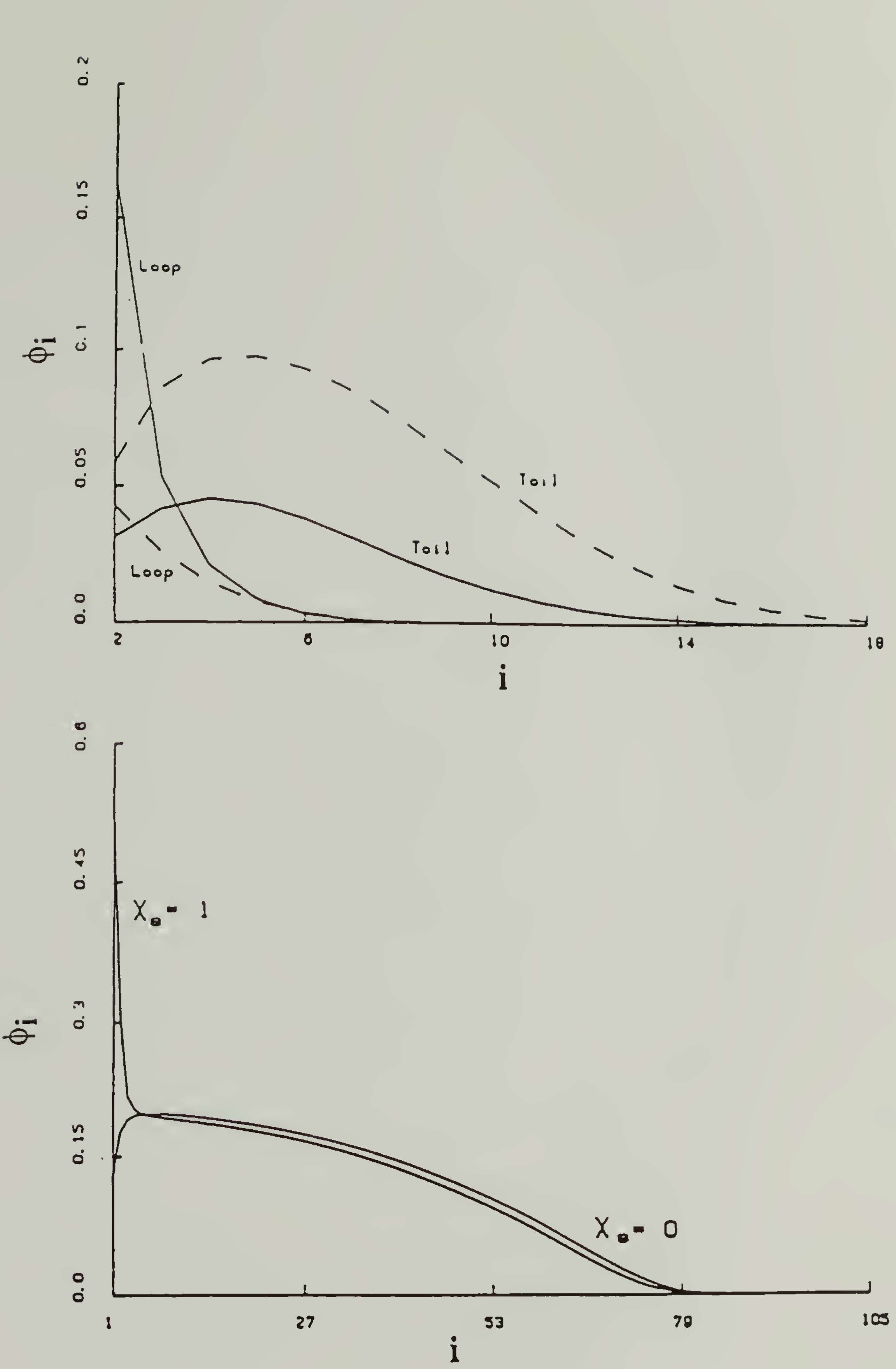


Figure 1.7 (top) Volume Fraction of Loops and Tails as a Function of Layer Number i for Two Different Values of χ_s in a Good Solvent Obtained Using SF Theory, $\chi_s = 0$ (--) and $\chi_s = 1$ (--); $\chi = 0$; $r = 50$; $\theta = 1$; $\lambda_0 = 1/2$. (bottom) Volume Fraction ϕ_i as a Function of Layer Number i. $\chi_s = 0$ and $\chi_s = 1$. Grafted amount $\theta = 10$; $r = 250$. Data, Directly From Reference 120.

group, the complication being the result of considering a finite surface - segment interaction energy, $\delta \approx kT$.[55] Therefore the scaling arguments presented by de Gennes alone is considered.[56] In passing, an interesting feature of Alexander's treatment that a first-order transition from a high grafting density (extended layer, chains confined in a cylindrical geometry) to a low grafting density (two dimensional regime) in the presence of uniform surface - segment attraction at equilibrium is noted (conjecture).

For the purposes of this thesis two special cases concerning grafted chains plus good solvent are presented. A chain grafted to a surface from a good solvent is recognized to exist in two distinct states, "mushrooms" and "brushes". At low graft densities, σ (fraction of surface sites grafted), the chains are assumed to occupy the surface as separate coils of half spheres, of dimension R_F (Flory radius = a $N^{3/5}$). The chains in this state of grafting are referred to as "mushrooms". The chain could also exist in a "brush" state at high grafting density. The chains in the two grafting states are shown in figure 1.8.

In the "mushroom" state the coils do not overlap and therefore $(\sigma/a^2)(R_F)^2 < 1$, where a is the monomer size (alternatively the mesh size). This inequality leads to a condition under which the chains do not overlap, i.e. $\sigma < N^{-6/5}$. The average concentration (segment density distribution) profile $\phi(z)$ for a random distribution of grafting sites as a function of z (z is the normal distance away from the surface, which is defined as z = 0) for $a \leq z \leq R_F$ is derived by scaling arguments. At $z = R_F$, de Gennes argues that the concentration is equal to the concentration inside a single coil $\{N/(R_F)^3\}$ times the fraction of the surface area occupied by coils $\{(\sigma / a^2)(R_F)^2\}$. Therefore,

$$\phi(z = R_F) \approx N\, \sigma\, a / R_F = \sigma\, N^{2/5} \qquad \text{..........................(1)}$$

At z = a, it follows that $\phi(z = a) = \sigma$ (definition). de Gennes assumes that in the region between z = a and $z = R_F$ a power law should hold true, i.e $\phi(z) = \sigma\,(z/a)^m$. Applying the boundary condition (equation 1) one obtains m = 2/3. The resulting profile is shown in figure 1.9. This profile has not been verified by experiments and it is a difficult

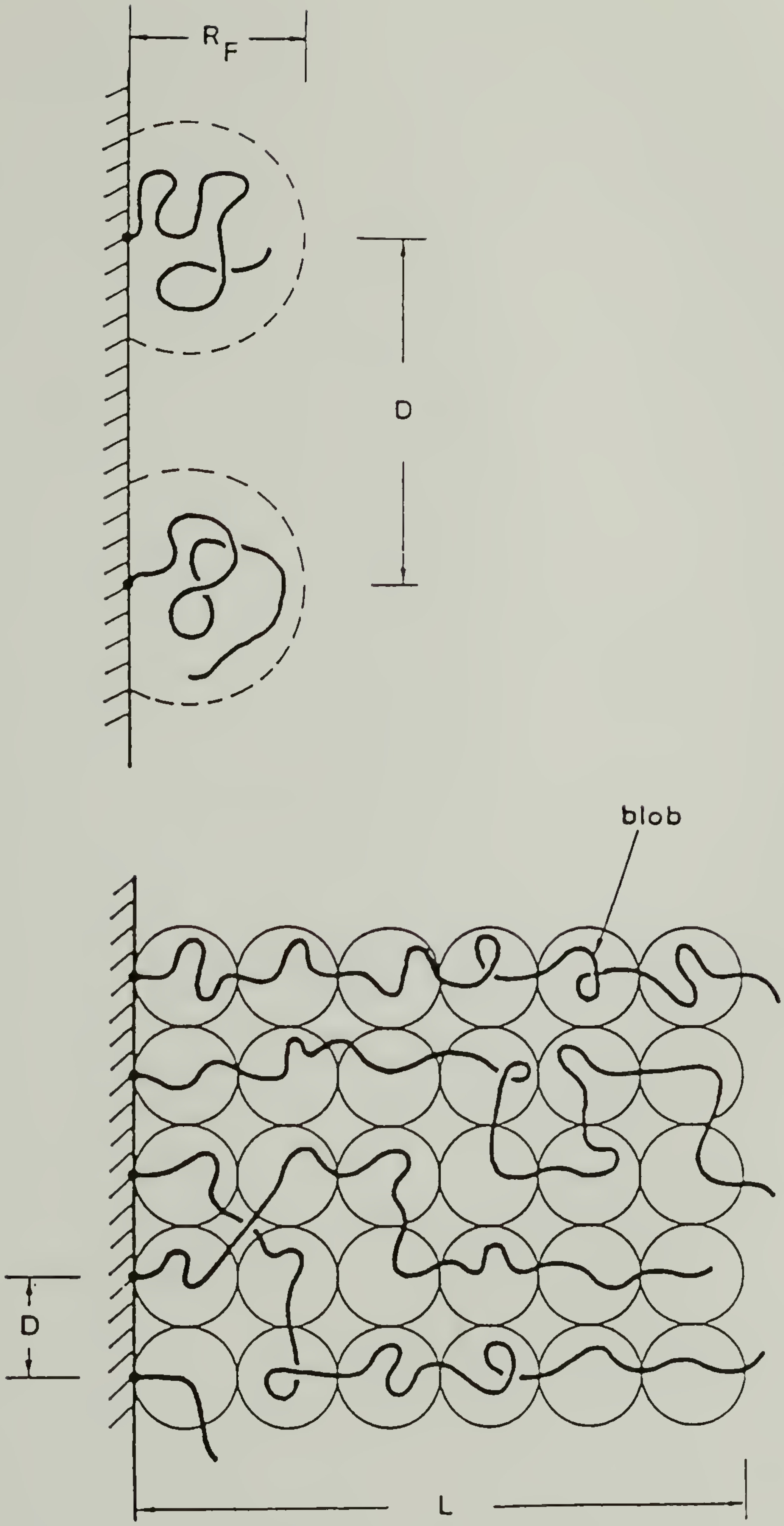


Figure 1.8 (top) Low Density of Grafted Polymers Referred to as "Mushrooms" and (bottom) High Density of Grafted Polymers Referred to as "Brushes". Directly from Reference 56.

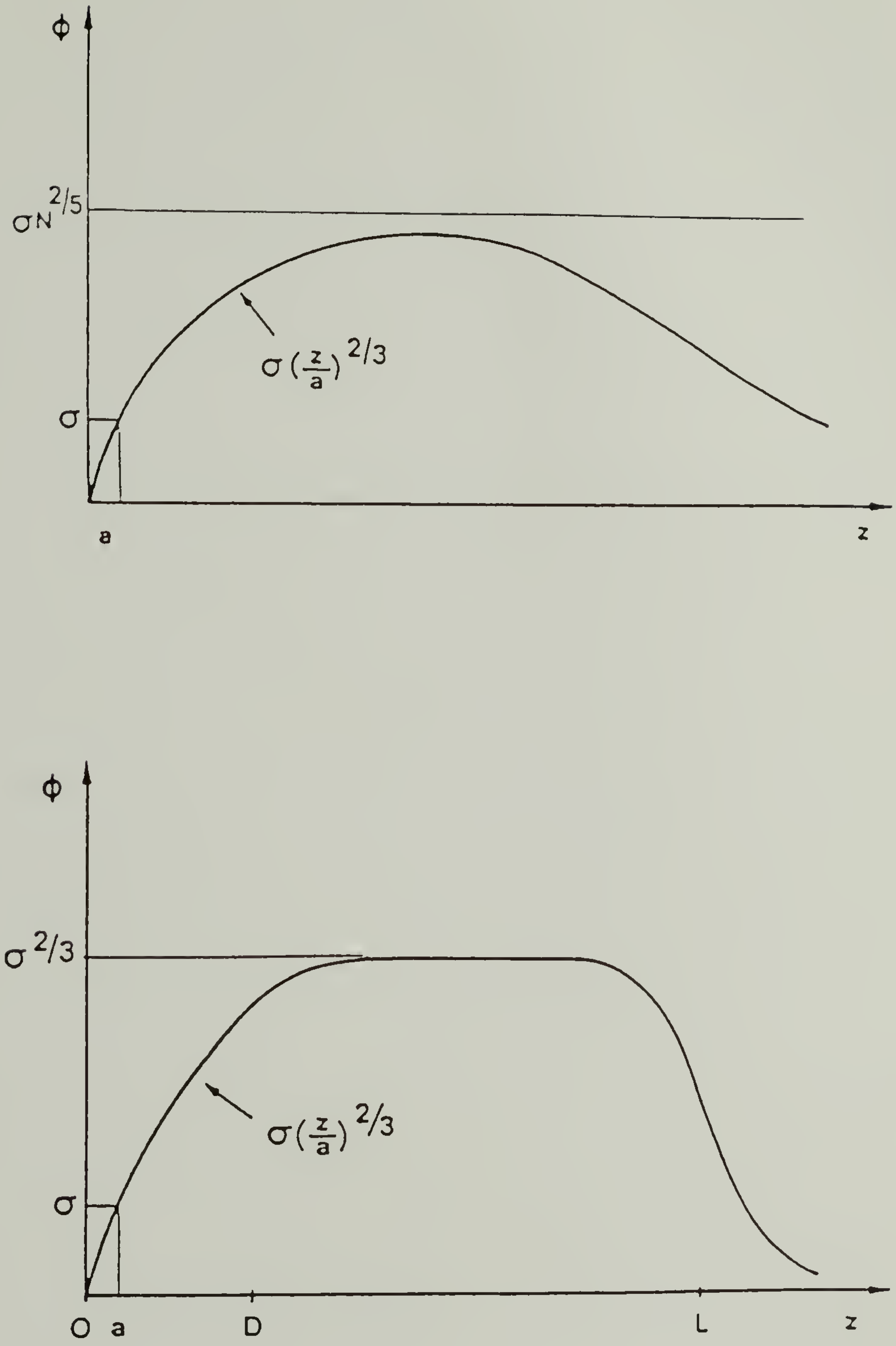


Figure 1.9 (top) Average Concentration Profile for Polymers Grafted as "Mushrooms" and (bottom) for Polymers Grafted as "Brushes". Directly from Reference 56.

prediction to verify, as the techniques available today are not sensitive to low grafting densities.

The "brush" state is obtained when the distance between grafting sites (D) is less than the radius of the coil is solution ($D < R_F$ or $\sigma > N^{-6/5}$). In terms of grafting density σ this distance is defined by the relationship, $\sigma = (a / D)^2$. The brush is assumed to build up a region of uniform concentration, ϕ, and the mesh size in the brush is assumed to be equal to D. The grafted chain is then divided into blobs of size D (note: $D = \xi(\phi)$), each of them containing g_d monomers. At small scales of the order $r < D$ the correlations are dominated by excluded-volume effects and therefore $a(g_d)^{3/5} = D$. At $D << R_F$, $g_d << N$ and therefore the blobs act as hard spheres and fill space densely. Thus, the polymer concentration in this region follows, $\phi(z=D) / a^3 \approx g_d / D^3$. Substituting the scaling behavior of D and g_d, $\phi(z = D) = \sigma^{2/3}$ and using the arguments and boundary conditions mentioned in the previous paragraph one can obtain for the the region between z = a to D, $\phi(z) = \sigma(z/a)^{2/3}$. The thickness of the adsorbed layer (L) can be calculated from the scaling relationship between the volume of a chain and $\phi(z = D)/a^3$, as follows: $\phi(z=D)/a^3 = N/(LD^2) = Na\sigma/L$ and since $\phi(z=D) = \sigma^{2/3}$, $L \approx Na\sigma^{1/3}$ (also $L \approx Na^{5/3} D^{-2/3}$). This is the central result of the scaling argument and many experimentalists claimed to have verified it.[57-59] (However Klein has pointed out that the end-group surface interaction is constant and D cannot be assumed to be high and constant, in an experiment. He assumes that the above interaction energy is equal to the overall excess repulsive energy per chain. This leads to the number of blobs per chain to be a constant and leads to $D \approx N^{3/5}$ and therefore $L \approx N^{3/5}$ which fits his experimental data well). However the flat concentration profile (see figure 1.9b) predicted for $D \leq z \leq L$ has been found to be incorrect and instead a parabolic concentration profile has been observed by neutron scattering[40] and neutron reflection experiments[60, 61]. de Gennes has extended the above scaling argument for brushes in between two plates and has predicted the forces that would be involved in bringing two such plates. The experiments of Taunton, et al.,[57] and Patel, et al.,[132] have shown that his predictions are true at very short distances of separation ($F(r) \approx r^{-1.25}$).

The scaling arguments are simple (mathematically) and provide a good physical picture. They predict global properties and are limited to the case where the chains start to overlap in a good solvent. It can be seen from the above two paragraphs that the argument treats mushrooms and brushes but does not treat the overlap regime explicitly. In this region a scaling of properties between the mushroom and brush has to be assumed by the reader. An adsorbed layer has other finer configurational features like trains, tails, and loops which in turn have some average lengths and distribution. The occurrence of tails is important for many practical applications.[133-35] Colloidal systems are stabilized or destabilized by polymeric additives. The adsorbed amount as well as the way the segments are distributed in the vicinity of a surface are important in its stability. High molecular weight flocculants rapidly remove the last submicroscopic particles in one of the last stages of water treatment. In that case uncovered particles are caught by tails and loops extending from covered ones, so that polymer bridges are formed. Particle separation by flotation involves the same mechanism. Steric stabilization plays an important role in paint industry and food technology.[133-35] An intricate picture of the stabilized or destabilized colloid in terms of its structure is not discussed by the scaling argument and it is not capable of doing that either.

A self consistent mean-field argument of the SF type which will effectively take into account excluded volume effect in good solvents and retain the finer details of SF theory will be the best one that theorists can contribute towards a better understanding of the structure of polymers attached to a surface by one functional group or by several functional groups and this is something to look forward with interest in future.

1.5 Research Objective

The Alexander and de Gennes theory predicts the properties of end-grafted polymer structures such as mushrooms and brushes and recognize the importance of grafted layer structure on its properties (globally). The theories of Scheutjens and Fleer predict the properties of end-grafted polymers and recognize that the structure of the adsorbed layer in terms of the size of trains, loops and tails and their distribution is crucial in determining its uses, say the stabilization of colloidal dispersions or packing of magnetic particles in information storage systems. Scheutjens and Fleer stress that long tails dangling into the bulk solution, in particular, determine the stability of dispersions and the hydrodynamic properties of grafted polymer layers. A consequence of the acceptance of the above argument means that the presence of weakly adsorbing groups at chain ends (and other selected locations on the backbone) should result in greatly reduced tail lengths, less adsorbed amount and therefore vastly different adsorbed layer properties. Therefore it should be possible to control the amount of polymer adsorbed and hence its architecture at a given interface by suitable organic modification of its backbone structure. This in turn will determine the properties of the adsorbed layer. Our research group is interested in studying the effect of location and density of functional groups (sticky feet or groups which interact exothermically with a surface) in a polymer backbone on the structure and properties of adsorbed polymer layers. A cartoon of our research group objective is shown in figure 1.10. Ideally we prefer conditions under which the segments from the backbone will not adsorb ($\chi_s = 0$) so that polymer structures can be tailored at an interface just by the specific interactions of appropriately located functional groups. Based on the known ability of polymers to form trains, loops and tails (for $\chi_s > 0$) and other grafted structures such as mushrooms and brushes we would also like to manipulate the structure of the adsorbed layer by the incorporation of functional groups at suitable locations, characterize and study its properties as well.

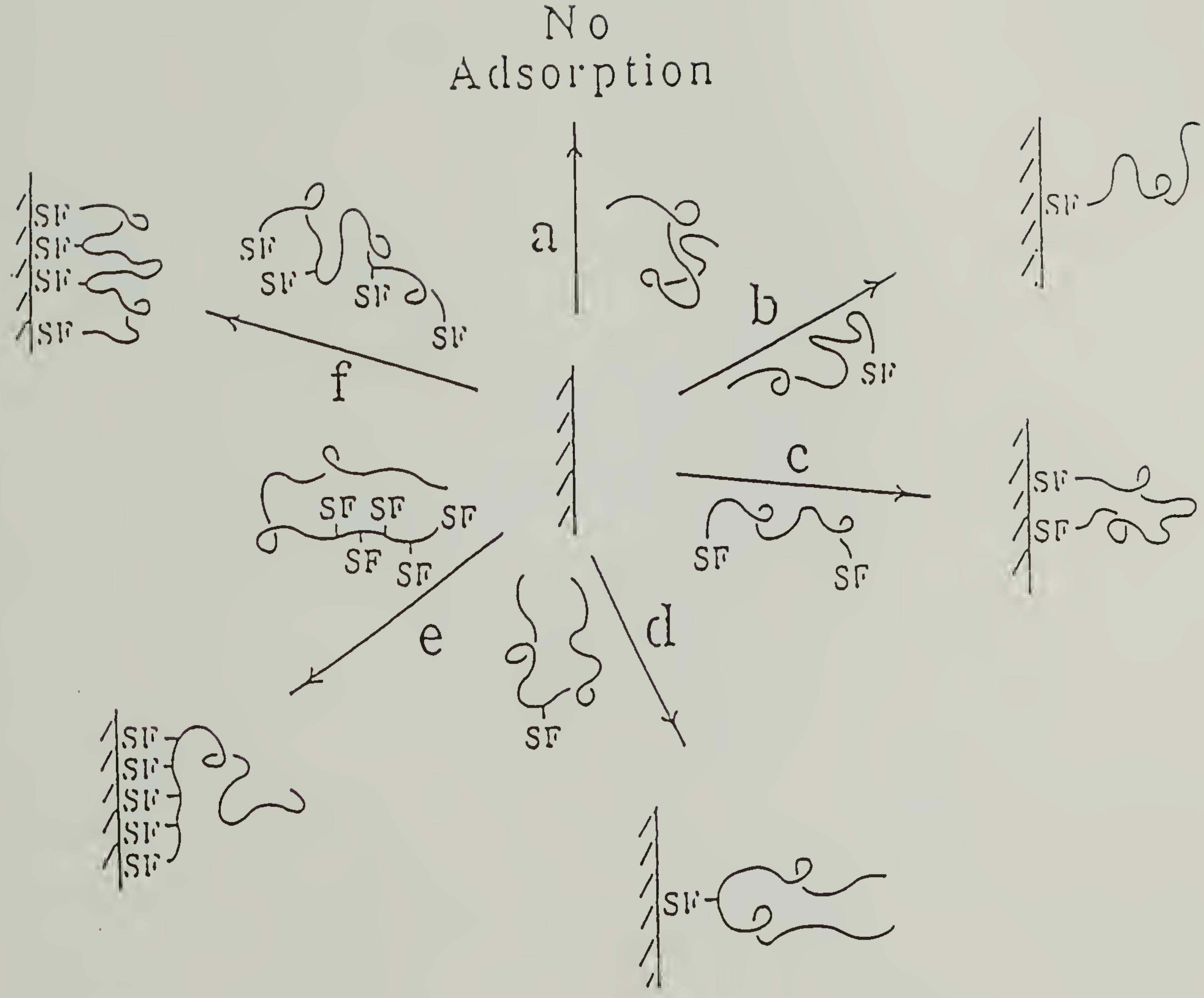


Figure 1.10 Pictorial Representation of Adsorption of Polymers to a Surface from a Solution which the Un-Functionalized Polymer will not Adsorb from (SF = Sticky Foot).

The objective of the research described in this thesis is a part of figure 1.10. We synthesize polystyrenes of narrow molecular weight distribution with a hydroxyl or carboxylic acid sticky foot at one chain end (PS-OH, PS-COOH) and both the chain ends (HO-PS-OH and HOOC-PS-COOH) by anionic polymerization. The presence of weakly adsorbing groups such as -OH and -COOH should in all probability result in adsorbed layers whose structure is devoid of tails. The absence of tails in the adsorbed layer structure should be more pronounced for polymers with functional groups at both the chain ends. This in turn should result in the adsorbed amounts being lower than that of un-functionalized polystyrene. Towards the above objective, the amount of polymer adsorbed (Γ μg/ sq. cm) to glass surface, as a function of time (kinetics), concentration, molecular weight, solvent conditions, nature and location of sticky foot were evaluated. The segment density distribution away from the interface and the distribution of the un-functionalized ends (free end) of the polystyrenes with a carboxylic acid sticky-end, grafted to polished silicon wafer, was determined by neutron reflection experiments in collaborative work performed with Professor Stein's research group and other researchers at the National Institute of Standards and Technology. These experiments were performed in order to verify the earlier theoretical predictions for grafted polymers.

1.6 Organization of the Thesis

Briefly, there are five chapters. The second chapter describes the anionic synthesis of polystyrenes with one sticky end and two sticky ends. It describes the successful synthetic methods and the various unsuccessful attempts in brief. The third chapter is about the thin layer chromatographic (TLC) characterization of the functionalized polystyrenes in various solvent conditions and the prediction of trends in adsorption by TLC. The fourth chapter discusses the kinetics of adsorption to glass determined by liquid scintillation counting (LSC). The adsorption isotherms, adsorbed amount, and graft density obtained from the LSC data as a function of molecular weight, solvent strength, location and type of sticky end are discussed as well. The fifth chapter is about the characterization of the dry adsorbed layer by x-ray photoelectron spectroscopy (XPS) and water contact angle analysis. It also discusses the segment density distribution away from the surface, for some specific cases, determined by neutron reflection experiments and compares the results with different theoretical predictions.

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CHAPTER 2

SYNTHESIS OF END-FUNCTIONALIZED POLYSTYRENES BY ANIONIC POLYMERIZATION

2.1 Introduction

Anionic polymerization involves an anion as the initiating and propagating species. Zeigler was the first to report that the polymerization of dienes to gums and resins could be initiated by organometallics such as alkyllithiums, involving the alkyllithium as the initiating species, a process which was believed to be initiated only by alkali metal ions such as lithium or sodium before 1920 by an unknown mechanism.[1,2] Zeigler and his co-workers also suggested that such a polymerization could take place without a termination reaction, a phenomenon which was later labelled as the living nature of the anionic polymerization.[3-5] Zeigler's dreams were not realized because of the termination of polymerizations by trace impurities present in the system, a fact which was recognized by Szwarc and demonstrated aptly by the polymerization of vinyl monomers initiated by sodium naphthalide.[6,7] Szwarc also demonstrated that the polymer chain ends maintain their reactivity over a long period of time by preparing 1) longer chains of the same polymer by the addition of the same monomer, 2) longer chains of a different polymer by the addition of a different monomer (block copolymer) and 3) by terminating the reactive chain ends with electrophiles. Szwarc coined the term "living polymerization" for polymerization reactions which retain the nucleophilic character of their chain end throughout the polymerization and after (in the absence of electrophilic impurities). A general description of an ideal living anionic polymerization reaction, assumed by Szwarc, is described in the next page.

$$I^-C^+ + M \xrightarrow{k_i} IM^-C^+$$

$$IM^-C^+ + n(M) \xrightarrow{k_p} I(M)_{n-1}M^-C^+$$

I^-C^+ is the initiator, M is the monomer, k_i is the rate constant for initiation and k_p is the rate constant for propagation

The degree of polymerization (DP) for a reaction as described above for the condition that $k_i \geq k_p$ is given by the ratio of the molar concentrations of the monomer and the initiator as [M]/[I]. At the end of the propagation reaction, ideally, an anion is assumed to retain its reactivity (entirely) and during the initiation and propagation reaction it is further assumed to be involved only in nucleophilic addition reactions that lead to chain propagation.

Szwarc's first report about the narrow molecular weight distributions of polymers and the absence of side reactions in polymerizations initiated by sodium naphthalide has been questioned by a number of authors of whom Wenger's reports are noteworthy.[8-12] The use of sodium naphthalide is also restricted to polar solvents such as tetrahydrofuran in which many vinyl polymers are insoluble and the polydispersity of the samples obtained is usually greater than 1.20. Presently alkyllithium initiators are used widely because of their solubility, the solubility of many vinyl polymers in hydrocarbon solvents, their stability, the polymer microstructural control that they allow if used with the appropriate amine and the narrow polydispersities that are obtained (less than 1.10).[13]

The objective of the research work presented in this chapter was to synthesize polystyrenes with carboxylic acid and hydroxyl end groups at one chain end (PS-COOH and PS-OH) and both the chain ends (HOOC-PS-COOH and HO-PS-OH) in narrow molecular weight distribution (less than 1.10) towards their use in subsequent adsorption studies.

This chapter outlines all the attempts that were made to synthesize end functionalized polystyrenes. It also describes what in the author's opinion is the best method to synthesize functionalized polystyrenes anionically without resorting to high vacuum techniques.[13-15] Every other system would demand some modifications of the procedures reported here and this is left to the discretion of the synthetic chemist in question. The work reported in this chapter and all the synthetic procedures followed in the thesis work are from "synthesis alone" lab-notebooks labelled as NB #n (n = 1 to 4), "synthesis of protected initiators and polymers from protected initiators" and "synthesis and polymerization of radioactive styrene" lab-notebooks. The organization of the rest of the chapter is as follows: section 2.2 is about materials and 2.3 about the methods. This is followed by the results and discussion section 2.4 and a summary of the chapter in 2.5.

2.2 Materials

The following chemicals were used after appropriate purification procedure as discussed in the methods section: styrene, perdeuteriostyrene, phenylacetylene, benzene, toluene, tetrahydrofuran (THF), pyridine, tetramethylethylenediamine (TMEDA), hexamethylenediamine, naphthalene, succinic anhydride (SA), carbonyldiimidazole (CDI), terephthaloyl chloride (TPC) (all purchased from Aldrich), pentane, hexane, cyclohexane, chloroform, methylene chloride, carbon tetrachloride, dioxane (all purchased from Fisher), ethylene oxide (Kodak). The following chemicals were used as received: benzophenone, 4-biphenylmethanol, sodium, lithium, Lindlar's catalyst, thionyl chloride, calcium hydride, pentane, ketene dimer, tetraethylene glycol dimethylether, 1,1,1-trimethoxy-4-bromobutane (all from Aldrich), ethyl acetate, diethyl ether, methanol, isopropanol, hydrochloric acid, sodium chloride, magnesium sulfate, ammonium chloride (all from Fisher). Dibutylmagnesium was purchased from Alfa.

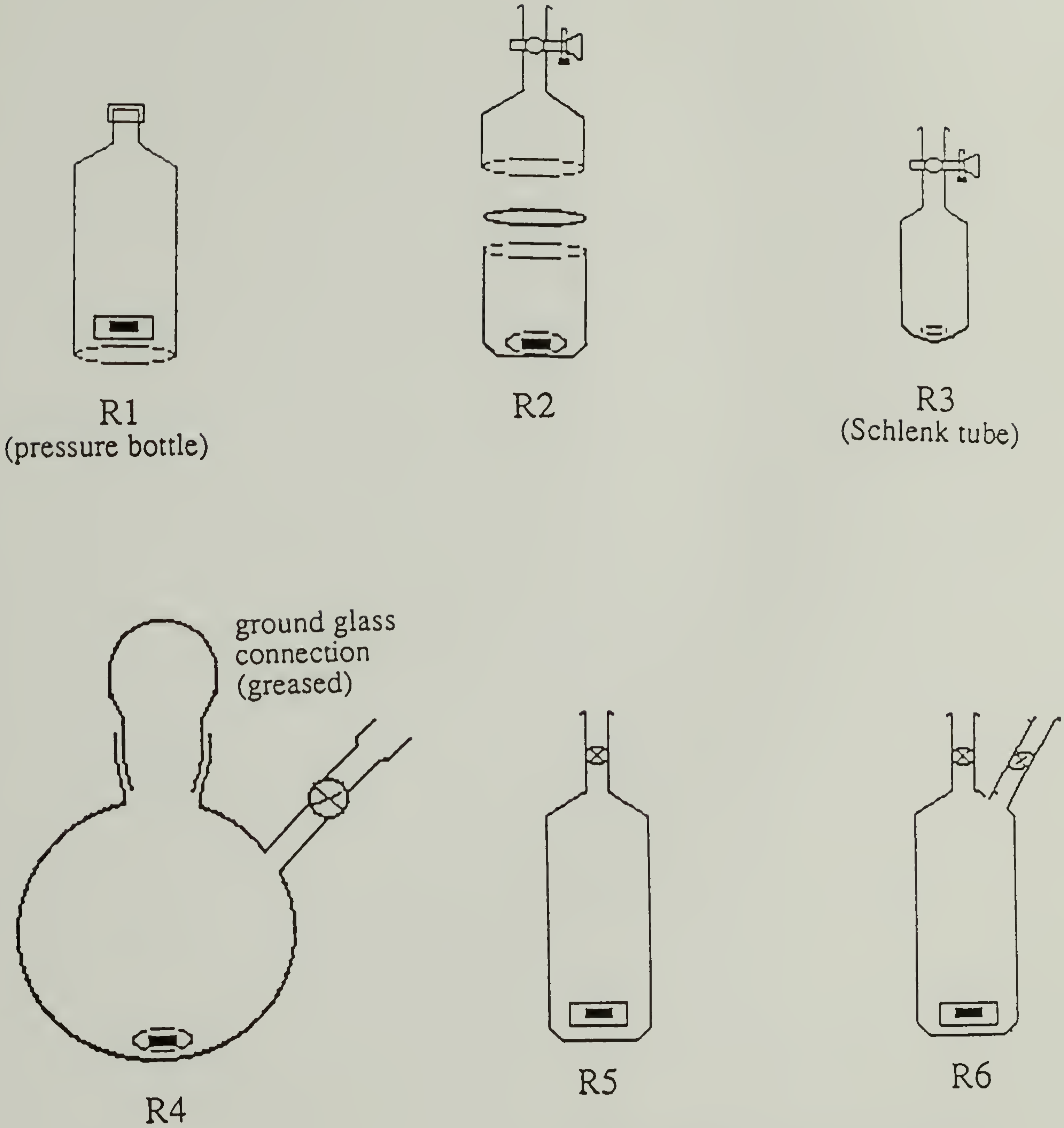
sec-butyllithium, *tert*-butyllithium and *n*-butyllithium (Aldrich) were used as received. They were periodically titrated using known amounts of 4-biphenylmethanol in THF to determine their concentration. 1,3-Bis(1-phenylethenyl) benzene and Acetaldehyde 6-lithiohexyl ethyl acetal were donated, respectively, by Dr. Tung of Dow Chemical Company and Ms. Pyati of the Chemistry Department at the University of Massachusetts.

Pure hydrogen, nitrogen, and argon (> 99.99%) and bone dry CO_2 (99.98% pure) supplied by Matheson were used as received. Tritiated water (100 mCi/g specific activity) was purchased from New England Nuclear.

2.3. Methods

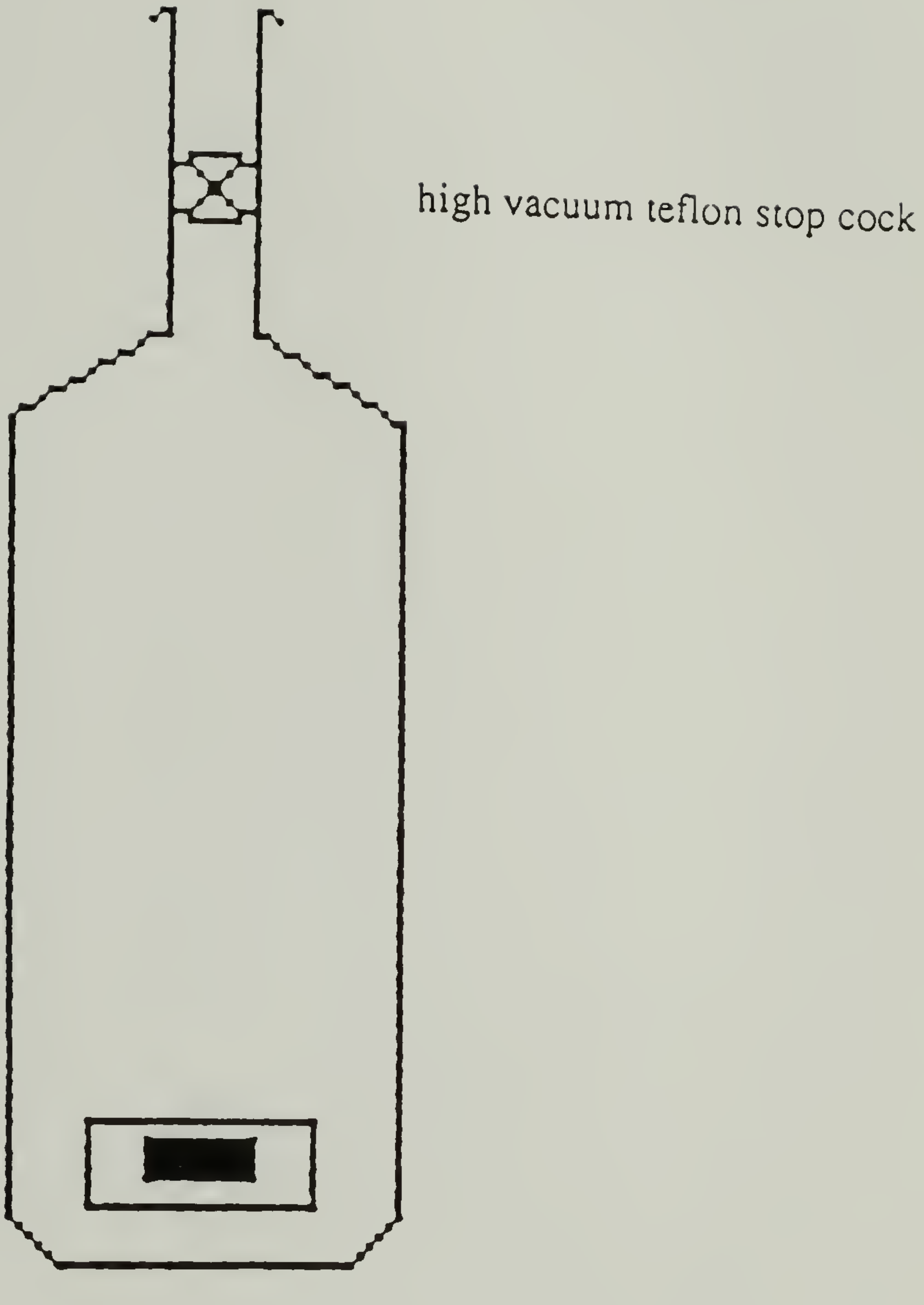
2.3.1 Choice of Reactors for Polymerization Reactions

Several types of reaction vessel were used in the syntheses depending on the type of the terminating step and subsequent work up procedure. These are shown in figures 2.1 and 2.2 and are labelled from R1 to R8. For the preparation of un-functionalized polystyrene (PS-H) reactor 1 (R1) was used as it is the most convenient one. This reactor is suitable for polystyrene syntheses in benzene and cyclohexane. However in THF, the minute rubber particles from the liner (used to obtain a tight seal from the atmosphere) react with polystyrllithium rapidly and terminate a fraction of the growing chains (rubber liner is often pierced during the introduction of syringe needles and cannulas) . The problems encountered with R1 are eliminated on using R2. R2 is suitable for most of the anionic syntheses except those reactions that are to be carried out for more than two hours. After two hours of reaction time the rubber "O" ring used in the reactor gets swollen by solvent (particularly with THF) and this allows the diffusion of reactive molecules from the ambient into the reactor. In addition THF extracts reactive small molecular weight additives from the components of the "O" ring (moreover the mangled "O" ring can not be used again on drying, as it loses shape). If the polymerization or modification time is less than 2 h, this would be the reactor of my choice as it is easy to assemble.



diameter of R5 and R6 = 2 inches
diameter of R3 = 1 inch

Figure 2.1 Type of Reactors Used in the Polymerization Reactions



R8

Figure 2.2 Reactor Suggested for Future Polymerization Reactions

R3 has a very narrow opening and it is relatively easy to seal this narrow opening with a teflon stopcock and thus minimize leaks. Small quantities of polymer were prepared using this reactor. In principle this design does not have any drawback. It was not used to make more than two polymers, primarily because the diameter of the reactor was too narrow for efficient stirring even with small quantities of solution and in addition teflon coated magnetic stir bar was sealed in. At that time we had difficulty using teflon stir bars in tetrahydrofuran (THF) as the polystyrllithium reacted with them killing a small fraction of the propagating chain ends. This troublesome reaction was not observed in benzene or cyclohexane as confirmed by the limits of detection of our GPC. However in view of the observed problem in THF, the use of R3 was abandoned. R4 was the type of reactor that was being used successfully for preparing poly(styrene-b-propylene sulfide) in the group. A few reactions were performed in it. Though it worked better, a modified version of R3 was used to perform most of the syntheses reported as it did not involve the use of grease (common belief in anionic polymerization literature is that grease is harmful to the synthesis). This is shown as R5. In my opinion this design is the best one if one is to avoid the complexity of high vacuum synthetic techniques. R5 worked best with all the solvents tried and could be used anywhere from -78 °C to 70 °C. However if the syntheses involve an additional step like freeze drying, R6 would be the reactor of choice. This has an additional greased ground glass stopcock, which can be used to expose the reactor to vacuum directly after freezing, avoiding an intermediate step involving the exposure of the neck of R5 to ambient. Polymerizations involving cyclohexane were not performed in this reactor as grease is soluble in cyclohexane vapors and is believed to terminate chains prematurely during the propagation step resulting in broad molecular weight distribution.

R7 is a modification of R4 with a male/female (24/40) ground glass connections swapped. This enables the application of grease on the outer part of the ground glass joint providing minimum exposure to grease. R7 is most ideal for polymerizations in THF as large quantities of solvent can be used and excellent stirring can be maintained throughout the reaction. R8 is a modification of R5 with a high vacuum teflon stop cock replacing the regular teflon stop cock that seals by cold flow. Based on the experience of this author the use of R8 is suggested, with appropriate user discretion. This is the kind of reactor used currently by most of the members of our research group involved in anionic polymerization of styrene and related monomers.

2.3.2 Purification of Solvents[16-18]

2.3.2.1 Pre "Roderick Quirk's Paper"

Benzene (400 ml) was dried over sodium (250 mg) overnight. Ten to twelve mg of benzophenone dissolved in 2 ml of benzene containing 3 to 4 drops of tetraglyme (tetraethylene glycol dimethylether) was added the next morning. Tetraglyme facilitates the breakdown of Na pieces. The benzophenone solution on contact with the benzene turns it light blue and within an hour it turns purple due to the formation of sodium benzophenone dianion. At this point the benzene was set to reflux for 2h after which it was collected in a nitrogen-purged storage flask (b. p. - 80 °C, 1atm. synthesis alone NB#1, p1) and was stored under a positive pressure of nitrogen. Much discussion has revolved around the use of sodium benzophenone for drying benzene and other solvents used in the anionic polymerization. From my experience it has been a problem only when the benzophenone is used in excess (more than 1g/800 ml) or when the benzene (in general the solvent) is distilled from a solvent still more than a month old. To make sure that the benzene distilled is good for polymerization two simple experiments were performed. Thin layer chromatography (TLC) on silica gel was carried out using benzene as the eluent. This detects benzophenone concentrations as low as 1μg per 100 μl of solvent. Gas chromatography was used to detect much smaller quantities of benzophenone. The following GC conditions were used; Analabs Superpak II column of dimensions 15 feet x 1/8 inch on a Hewlett Packard 5790A gas chromatograph equipped with an FID detector.

oven temp = 105 °C, heating rate = 28 °C/min, injection temp = 255 °C, detector temp = 300 °C, Analabs 10 ft x 1/8 in. 15% AN 600 column. Benzophenone can be detected 6.4 minutes after injection (see synthesis alone NB # 2, p78). This enables the detection of benzophenone in concentrations three to four orders of magnitude lower than the TLC technique. The benzene whose purity is verified by the above two techniques is good enough for making polymers up to a molecular weight of 100K with a polydispersity ≤ 1.07. Some of the end functional polymers made in this research were prepared in benzene distilled as in above.

Cyclohexane was distilled from CaH_2 and was stored in storage flasks under a positive pressure of N_2. Tetrahydrofuran was distilled from sodium benzophenone dianion and used directly in polymerization reactions. Dibutylmagnesium (1 ml, 1 mmole) in heptane was added to the THF (50 ml), before cooling it to -78 °C and before the addition of the monomer. This takes care of traces of impurity (the reaction of polystyrllithium with styrene is several orders of magnitude faster than the reaction of dibutylmagnesium with styrene and/or polystyrllithium as is evident from the data on "synthesis alone" lab-notebook #3, p16. This saves a lot of time otherwise consumed during the second stage involved in the purification of THF).

2.3.2.2 Post "Roderick Quirk's Paper"

After Quirk's paper appeared in the 1989 January issue of Macromolecules,[16] claiming 100% carboxylic acid end-termination from the reaction of carbon dioxide with a known molar concentration of polystyrllithium, polymerization and end-functionalization reactions were performed in solvents purified by even more rigorous conditions. This meant one more purification stage for all the reagents involved. Benzene (100 ml) distilled from sodium benzophenone dianion was stirred for an hour over a small amount of *n*-butyllithium (1 ml of 2.5 M solution in hexane) and a drop of styrene. The orange solution was distilled using a trap-to-trap distillation set up as shown in figure 2.3 and a known

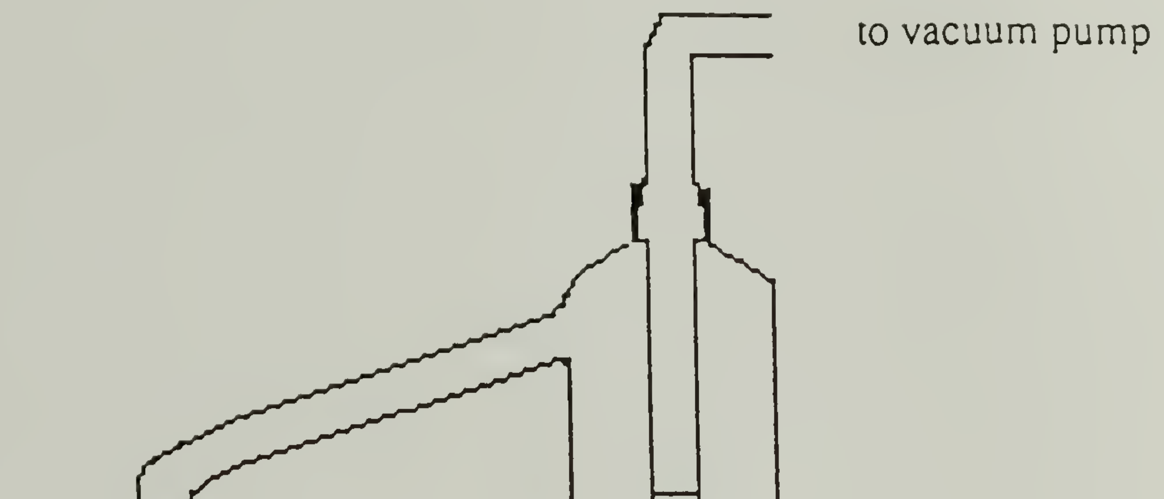


Figure 2.3 A Trap-to-Trap Distillation Setup

volume (50 to 60 ml) was used immediately for polymerization. Benzene, trap-to-trap distilled from dibutylmagnesium in heptane, was also used for some polymerization reactions though the former procedure was used for almost all the reactions carried out after Jan 89.

Cyclohexane was distilled from CaH_2 and was stored in storage flasks under a positive pressure of N_2. Just before polymerization it was stirred over *n*-butyllithium (a drop of styrene was added to serve as an indicator) and was trap-to-trap distilled for immediate use. Tetrahydrofuran was distilled from sodium benzophenone anion by a procedure similar to the one used with benzene and was stored in storage flasks over a positive pressure of nitrogen. Just before the polymerization (or the end-termination reaction or any other reaction in this solvent) it was trap-to-trap distilled from a weakly greenish mixture of THF (75 to 80 ml) and four to five drops of 2.5 M *n*-butyllithium.

2.3.3 Purification of Other Chemicals[17,18]

Sodium metal was cut into small pieces under mineral oil and was rinsed several times with pentane under nitrogen before use. Lithium wire in mineral oil was scraped with a knife under mineral oil to obtain a shiny surface. It was washed several times with pentane, thrice with benzene and twice with THF under argon and was weighed before use. Carbon tetrachloride, chloroform and methylene chloride were distilled from phosphorus pentoxide under nitrogen and were stored under a positive pressure of nitrogen in the dark. Hexane was distilled from calcium hydride. Phenylacetylene stirred overnight with calcium hydride was distilled under vacuum (at 20 mm Hg, b. p. = 52 °C) and was stored at -20 °C under positive nitrogen pressure. Naphthalene was recrystallized from methanol and was purified further by sublimation before use. Methanol, isopropanol and water used in the termination of the living polystyryl anion were used after extensive degassing (isopropanol seems to work the best as the dimer peak observed in the GPC chromatogram of polystyrenes is not observed in most of its usage).

2.3.4 Purification of the Monomer

Styrene (unlabelled, perdeuterio, and β-tritiated) is the only monomer that was used in the research work. It was stirred over calcium hydride for 24 h, distilled under vacuum (25-27 mm of Hg, b. p. = 52-54°C; synthesis alone NB#1, p2)) and was stored under a positive pressure of nitrogen at -20 °C. Just before polymerization an excess amount of styrene was stirred over dibutylmagnesium until it turned dark yellow and was trap-to-trap distilled. It was introduced to a graduated centrifuge tube, previously evacuated and purged of atmospheric contaminants, using a steel cannula under nitrogen and a known amount (1 to 3 ml) was used immediately.

2.3.5 Purification of the Additives[17,18]

Succinic anhydride (SA) was recrystallized from chloroform first and then from benzene. The crystals were washed with ether and were dried under vacuum (synthesis alone NB#1 p44, p46 and p67). Its purity was checked by proton NMR in $CDCl_3$ before use (one and only peak at $\delta= 3.0$ ppm). Carbonyldiimidazole (CDI) as supplied was stored in a nitrogen filled glove-box. Required amounts were taken out in a nitrogen-filled Schlenk tube and were dissolved in minimum amount of benzene or THF (depending on the solvent in which the end capping reaction was to be performed). The solution was cooled to 10 °C (in benzene) and to 0 °C (in THF). The crystals thus formed were retained by transferring the mother liquor (using a cannula). This procedure was repeated thrice and the crystals obtained were dissolved in required amounts of freshly distilled benzene or THF as the case may be and were used in the end capping reactions. Terephthaloyl chloride (TPC) was recrystallized from dry hexane. All transfers, dissolutions, filtrations, and recrystallizations were performed in nitrogen atmosphere.

Tetramethylethylenediamine (TMEDA) was stirred over calcium hydride for 24 hr, and was distilled under vacuum (25 mm of Hg, b.p - 45 °C). It was stored under a positive pressure of nitrogen at -20 °C. Just before its addition to living polystyrllithium it was stirred over *n*-butyllithium (for 5 ml of TMEDA, 0.5 ml of 2.5 M *n*-butyllithium was used) and was trap-to-trap distilled. Ethylene oxide (EO) was stirred over calcium hydride at the melting temperature of ice for 2 h, distilled under nitrogen and was stored under a positive pressure of nitrogen at -20 °C. It was stirred over dibutylmagnesium for 0.5 h to 1 h at 0 °C and was trap-to-trap distilled just before its use in end termination reactions. Pyridine was distilled from calcium hydride.

2.3.6 Preparation of Naphthalide Initiator Solutions

Di-functional initiators of Szwarc's type such as sodium naphthalide and lithium naphthalide were prepared in the same general fashion as reported by Cheng,[19a] Kanga,[19b] and Nakahama,[20] independently. The preparation of a lithium naphthalide solution is discussed below (a typical preparation is discussed in synthesis alone lab-notebook #4 , p 72-76). Lithium metal along with the mineral oil was weighed in a round bottomed flask (0.2845 g). The mineral oil was repeatedly extracted in hexane in an argon atmosphere (weight after oil extraction = 0.2436 g). The surface of the lithium thus obtained was black and therefore it was scraped in an argon filled glove bag till a metallic lustre was visible throughout the surface of the sample (weight of lithium after scrapping = 0.2133 g or 0.0307 gramatoms). The lithium metal was introduced to reactor R7 with a small amount of benzene to protect its surface while transferring. 3.737 g (0.0292 moles; 5% less than lithium as suggested by Nakahama, et al.) of naphthalene was weighed into a round-bottomed flask. R7 and the round-bottomed flask were purged with argon overnight. In the morning the lithium metal was washed twice with freshly distilled THF (25 ml each) and was submerged in 60 ml of freshly distilled THF. The naphthalene crystals were dissolved in 40 ml of freshly distilled THF and the solution was introduced to the lithium metal in THF. The mixture turned light green on contact and dark green a few hours after. It was allowed to stir overnight and was filtered through a glass frit (10µ) into an argon-purged graduated cylinder (Schlenk type), and was stored at -20 °C. The preparations with a 5% excess of naphthalene as suggested by Cheng (and Kanga), was performed as well and this lead to the same result in terms of polymer molecular weight and distribution as that obtained by Nakahama, et al.'s method (see lab-notebook #4, p 58-69).

2.3.7 Synthesis of Tritium-Labelled Styrene

Tritiated styrene was prepared by the hydrogenation of phenylacetylene labelled previously with tritium (in an acid-base exchange reaction using *n*-butyllithium) using Lindlar's catalyst. The procedure followed was the same as the one previously used in this laboratory except that an additional component (carboxylic acid-terminated polystyrene) was added to the mixture to be reduced. This component inhibits the subsequent reduction of styrene to ethylbenzene by competing with styrene for surface sites. To a nitrogen-purged reactor, R5, was added 34 ml of *n*-butyllithium in hexane (1.6 M solution; 0.054 moles). It was cooled to -12 to -15 °C using an ammonium chloride/ice bath following which six ml of phenylacetylene (0.054 moles) was added over a period of thirty minutes in drops. The white precipitate formed was allowed to warm to room temperature overnight as it was being stirred in hexane. One ml of tritiated water (100 mCi specific activity; 0.055 moles) diluted to 5 ml using benzene was added gradually to the white slurry at -80 °C, the next morning. After the addition the mixture was trap-to-trap distilled and 41.0 ml of the mixture was recovered as a clear solution (the other 4 ml lost is probably hexane as it is the most volatile component in the mixture; synthesis of radioactive styrene and polystyrene lab-notebook #1, p 33). It was divided into three portions each of which was added to a nitrogen-purged mixture of Lindlar catalyst (0.0812 g), carboxylic acid-terminated polystyrene (0.38 g obtained from Szwarc's reaction, $M_n = 20000$) and 0.9 g of calcium hydride. Benzene (35 ml) was added to the above mixture and the hydrogenation was performed with pure hydrogen at 15 psig for 10 min following which the reaction mixture was stirred for 3.5 h and a gas chromatographic analysis was performed to calculate the yield of styrene (synthesis of radioactive styrene and polystyrene lab-notebook

#1, p 38-39). This condition usually leads to > 99.98% yield of styrene. If the yield were less than 99.98%, a small amount of hydrogen was allowed into the reactor followed by stirring for 15 min. As soon as a yield of 99.98% was obtained from the GC analysis of an aliquot the contents of the reaction were purged with nitrogen and were trap-to-trap distilled after extensive freeze-thaw degassing cycles. Unless otherwise stated all radioisotope labelled reactions were preceded by mock reactions using nonradioactive components under exact experimental conditions used for the radioisotope containing mixture.

2.3.8 Synthetic Technique[13, 21-23, 58]

All syntheses were performed under nitrogen or argon atmosphere after appropriate precautions to remove (or at least minimize) air, water and other reactive gases in air. Two approaches were followed for the removal of air and other reactive molecules. In the initial stages of this work the reactive gases were purged out by inserting a source from which a high flow of nitrogen is maintained and allowing the contents of the pressurized reactor to flow through a mineral oil filled bubbler. Typical purging times range from 1 h to 6 h depending on the volume of the reactor. In the latter stages of this work the air and reactive contents of the atmosphere present in the reactor taken from an oven (at 200 °C), and assembled hot, were pumped out using a vacuum pump till a pressure of 50 mTorr was achieved. The reactor was then filled back with pure (99.999%) and dry nitrogen and the contents were pumped out again but this time the reactor was heated uniformly using a heat gun. The whole procedure of evacuating the reactor and filling it back with nitrogen was carried out several times. All transfers were carried out using steel cannula (20 - 22 gauge) under nitrogen. Graduated Schlenk type cylinders were used for transferring known volumes of solvent while graduated centrifuge tubes were used for transferring known volumes of the monomer and the initiator (as purchased and after dilution with cyclohexane). The reaction flasks, graduated cylinders and centrifuge tubes used were purged of the reactive contents of atmosphere by repeated evacuation and back-filling with nitrogen or argon as the case may be.

2.3.9 Synthesis of Polystyrllithium Using *sec*-butyllithium as the Initiator

Styrene was anionically polymerized to the desired molecular weights in benzene at room temp, in cyclohexane at room temperature and in THF at -78 °C, using *sec*-butyllithium as the initiator and the appropriate amount of styrene. Most of the polymerizations were carried out in benzene in a dry nitrogen atmosphere. A typical reaction was conducted as follows: a hot beverage bottle straight from the oven (200 °C) was taken along with a teflon coated magnetic stirrer in it. Its mouth was sealed using a rubber liner (it was pierced several times before sealing to get rid of any fine particles that may fall into the reaction vessel) and a soda cap with two holes using a soda bottle sealer. It was purged with dry nitrogen for approximately 2 to 2.5 h. Dry benzene (50 to 60 ml) was introduced using a steel cannula. The desired amount of *sec*-butyllithium of known concentration was introduced in to the bottle from a graduated centrifuge tube under nitrogen. The appropriate amount of styrene monomer (for the desired number average molecular weight) was introduced via cannula under nitrogen. The reaction was allowed to proceed under uniform stirring for 1.5 to 2h based on the molecular weight desired. At the end of the desired time a small fraction of the living polystyrllithium solution was terminated using degassed isopropanol. The polymer was isolated by precipitating the reaction mixture in an excess of methanol. The precipitate was filtered, redissolved in tetrahydrofuran and reprecipitated using an excess of methanol. It was filtered again and was dried and stored under vacuum. The major fraction of polystyrllithium was used for end-termination reactions.

2.3.9.1 Reaction of Polystyrllithium with Succinic Anhydride

Polystyrllithiums of desired chain length were synthesized in reactor R1 under nitrogen atmosphere, by reacting appropriate amounts of *sec*-butyllithium with styrene monomer in ≈50ml of benzene as discussed in section 2.3.9. The reaction was allowed to proceed for 90 minutes at the end of which 90% (v/v) of the red-orange anion was introduced to a stoichiometric excess of succinic anhydride in ≈50ml of benzene (degassed by several freeze-pump-thaw cycles) in a sealed glass bottle under nitrogen atmosphere using a cannula. Upon transfer the red-orange color disappears instantaneously. After 30 minutes a 5% (v/v) solution of HCl in methanol was introduced, the volume of which was varied depending on the chain length of the product expected (synthesis alone NB#1 p 45-72). The rest of the polystyrl anion was killed using degassed methanol and polystyrene was precipitated using excess methanol. For DP < 15 both polystyrene and end-capped polystyrene thus prepared were first subjected to benzene/water extract. The benzene layer thus separated was dried over magnesium sulfate. It was distilled under vacuum to isolate the polymer which was subsequently dissolved in methylene chloride. This solution was extracted again with water and the methylene chloride layer was subjected to the same procedure as in above for the benzene layer. In the case of chains with DP > 15 the polymer precipitates out upon adding an excess of acidic methanol. This was filtered through a Buchner funnel, was repeatedly washed with methanol and dried under vacuum. A typical end-capped oligomer (DP=4) looks like motor oil. This shall be called crude product as it may still contain non-acidic chains of comparable length.

2.3.9.1.1 Separation of the Pure Acid

A weighed quantity of the end capped oligomer (DP = 4) was introduced to a 5% aqueous solution of $NaHCO_3$. After 24 hours the oligomer which remained undissolved was extracted into ether. The ether layer was repeatedly extracted with water to free it from any base. It was dried over anhydrous $MgSO_4$ and was distilled to dryness. The product thus obtained was dried under vacuum at room temperature. This was called the non-acid part. The aqueous layer was acidified with HCl to a pH of 2. It was extracted into ether and was repeatedly washed with water to remove the hydrochloric acid. The ether solution was subjected to the same procedure as in for the non-acid part, to obtain a product which was called the acid part. The separations were performed for the oligomer of DP=4, extensive characterization of which will be reported. Oligomer of DP= 9 was partly soluble in aqueous bicarbonate solution, and above this chain length onwards polymeric behavior takes over and water insoluble products were obtained.

2.3.9.1.2 Derivative Preparation

A weighed quantity (460 mg) of the oligomer of DP=4 was dissolved in 30 ml of methylene chloride. Thionyl chloride (5 ml) was added and the mixture was refluxed overnight at 20 °C under nitrogen. The mixture was evaporated to dryness and an IR spectrum of the product was taken. Carbon tetrachloride (30 ml) was added to this product mixture followed by the addition of 2 ml of pyridine. Hexamethylenediamine (0.03 g) in 20 ml of water was added subsequently and the mixture was stirred for 24 hr at room temperature. At the end of this time the aqueous layer was discarded and the organic layer was evaporated to dryness. A resinous mass was obtained a portion of which was soluble in toluene. The toluene insoluble portion had a fibrous texture and was insoluble in most of the conventional organic solvents.

2.3.9.2 Reactions of Polystyrllithium with Carbonyldiimidazole and Terephthaloyl Chloride

Polystyrllithium of required degree of polymerization was prepared by reacting appropriate amounts of *sec*-butyllithium and styrene. In benzene, the polymerizations were carried out at room temperature for 75 min and in THF at -78 °C for 15 min. At the end of polymerization the living polystyrllithium was introduced to a well stirred dilute solution of the end-capping agent usually present in a large stoichiometric excess. After the transfer, the reaction mixture was stirred for an hour at the end of which 10-15 ml of acidic methanol (3-5 ml 1 N HCl and 10-12 ml of methanol) was syringed in and the acid hydrolysis was allowed to proceed for a few hours. This was followed by filtration to remove any insolubles. In the case of the CDI end capping reaction, filtration was followed by the precipitation of the polymer, using excess methanol. The filtered polymer was washed repeatedly with water and methanol and dried by evacuation. With the TPC end capping reaction, the filtration was followed by distillation of the solvent. The polymer recovered was dissolved in toluene and a bicarbonate extract was performed to remove any terephthalic acid impurity. This was followed by few aqueous HCl extractions and subsequent acidification of the organic layer by acidic methanol and precipitation of the polymer using excess methanol.

2.3.9.3 Reaction of Polystyrllithium with Carbon Dioxide

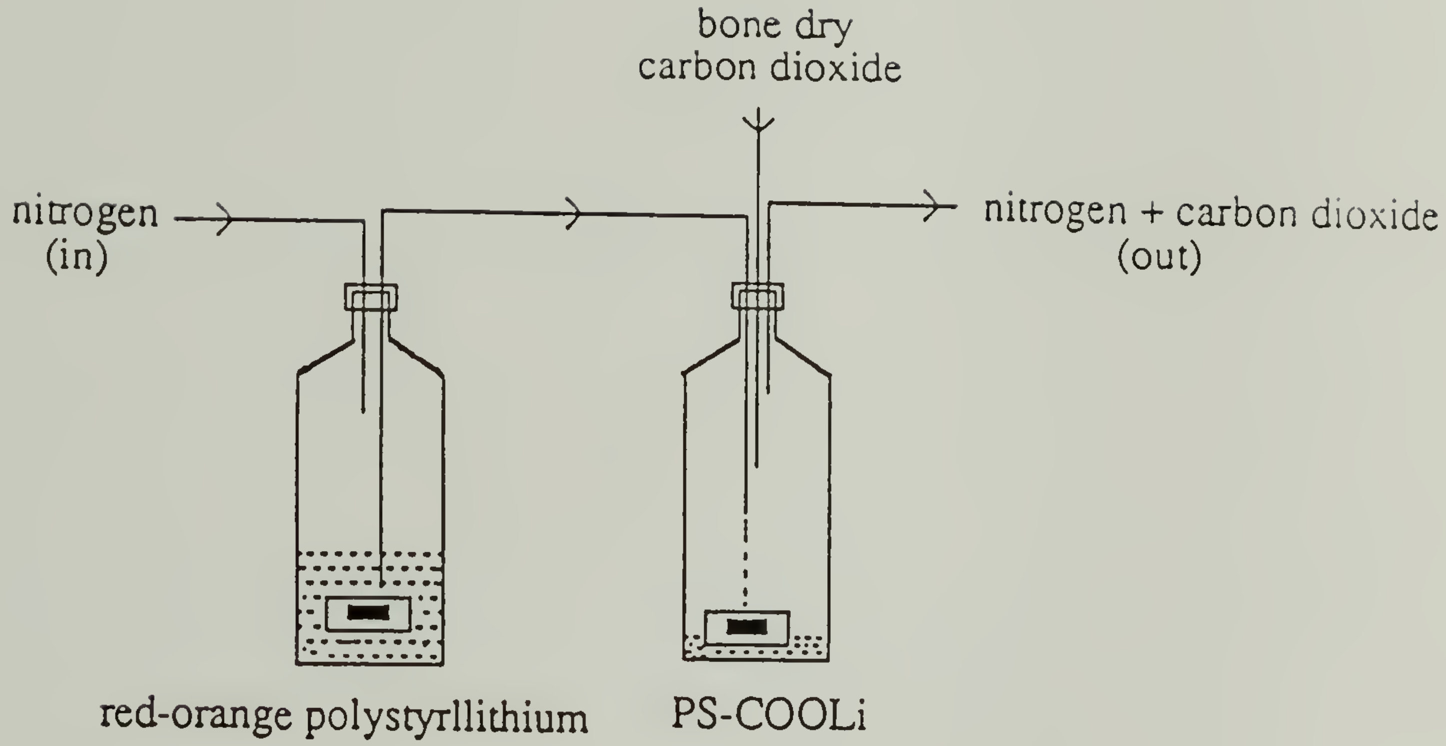
2.3.9.3.1 Roderick Quirk's Reaction[16, 24]

Polystyrllithium of required degree of Polymerization (DP) was prepared by reacting appropriate amounts of *sec*-butyllithium with a 10% v/v solution of styrene in dry benzene in a moisture-free reaction flask under nitrogen atmosphere for 75 minutes. At the end of this time dry TMEDA (10 equivalents based on *sec*-butyllithium) was introduced to the reaction flask. The red/orange/yellow polystyrllithium changes to a cranberry red color after the addition. A small portion of this polystyrllithium was killed using degassed isopropanol and the rest of the contents of the reaction was subsequently frozen using liquid nitrogen. A trap-to-trap distillation apparatus was attached to the reaction flask and benzene was sublimed into a liquid nitrogen filled trap at a pressure of ≈ 50 to 70 mTorr over a period of 12 h. The reaction flask was further pumped for an additional 12 hr to ensure that traces of benzene were removed. After this procedure the reaction flask was filled back with nitrogen and the trap-to-trap setup was removed. Carbon dioxide was let in at 1 atm pressure till the red color of polystyrllithium turned colorless. The colorless sample was left in a blanket of carbon dioxide for 12 h after which it was stirred with 50 to 100 ml of acidic THF (10 ml 1 N HCl and 90 ml THF) for 12 hr. After hydrolysis the end-capped polymer was precipitated using a large excess of methanol. The polymer was filtered at the pump and was dried in a vacuum oven. It was characterized by GPC, TLC, IR (for DP ≤ 20) and acid-base titration against an alcoholic solution of KOH of known strength (KOH standardized by titration against a standard solution of benzoic acid in methanol). Most carbonations were performed according to Quirk's procedure (addition of TMEDA to polystyrllithium in benzene followed by freeze-drying and carbonylation). Some reactions were performed in cyclohexane as per Quirk's procedure and worked as effectively as in benzene.

An important procedural change that was very different from Quirk's reaction was the way hydrolysis were carried out. It was discovered that hydrolysis by acidic methanol was incomplete (NB#2 p 15-16) in contrary to Quirk's observation. It was also observed that hydrolysis by acidic THF (HCl, 1 N/THF; 1:10, v/v) was complete after 12hr. The GPC eluent used was toluene up to sample RPQ Rn10 (and refractive index detector). It was changed to THF after RPQ Rn10 (after 7/10/88) to permit the analysis of other polymer samples. Therefore all samples starting with RPQ Rn1 to 23 were rerun in THF using a UV detector (see synthesis alone NB#2 p 69 -151 and NB#3 p 1-11 for the chromatograms and molecular weights reported in this dissertation).

2.3.9.3.2 Present Suggestion for Simple Carbonylation Reactions

Some carbonylation reactions were performed by transferring a fine jet of polystyrllithium to a reaction flask (R1) purged continuously with carbon dioxide at high pressure as shown in figure 2.4.



Reaction of a large excess of carbon dioxide with fine droplets of polystyrllithium

Figure 2.4 A Simple Carbonylation Procedure

Here, a typical reaction which is a very quick way of synthesizing carboxylic acid-terminated polystyrene quantitatively (synthesis alone NB#3 p 55-57), is described. A dry pressure bottle (R1) with a gasket (this should be pierced several times outside before using it as a sealant so that rubber particles do not fall into the reactor during the course of adding and removing substances; these particles can terminate growing chains) was sealed using a rubber liner and a double-holed crown cap. The glass-metal joint was wrapped around with teflon tape, as extra security against leaks. After purging the reactor with nitrogen, a regular anionic polymerization was performed. Following the polymerization the living anion was cannulated slowly into another pressure bottle (in a fine jet) through which a constant flux of CO_2 was maintained. This was followed by hydrolysis and workup as described in the previous sections.

2.3.9.4 Reaction of Polystyrllithium with Ethylene Oxide[25]

Polystyrllithiums of required DP was prepared by reacting appropriate amounts of *sec*-butyllithium and styrene in benzene for 75 minutes. After the polymerization, dry ethylene oxide was introduced into the reaction flask using a steel cannula from a reservoir at 0 °C till the color of the solution changed from red to colorless. The solutions were stirred further in a blanket of ethylene oxide for 12 h and subsequently hydrolyzed using acidic THF (10 ml of 1 N HCl and 90 ml THF) for 12 hr. The polymers were precipitated using a large excess of methanol, were filtered at the pump and dried in a vacuum oven. They were characterized by GPC, TLC and IR (for DP $\leq$ 20).

2.3.9.5 Synthesis of Acetoacetyl-Terminated Polystyrenes[26]

1g of PS-OH (M_n = 2000) synthesized as above was taken in a jacketed schlenk tube with 50 mg of sodium acetate. It was purged with nitrogen for 1 h and then 25ml of THF from a continuously distilling still was introduced. Ketene dimer (0.5 ml) was introduced by cannula and the mixture was stirred in an oil bath at 55 °C for 24 hr. The color of the reaction mixture was yellow at the beginning of the reaction and was red at the end of 24 h. The polymer was precipitated using a large excess of methanol, was filtered at the pump, dried under vacuum and was characterized by GPC, IR , and TLC for acetoacetyl end-group.

2.3.10 Synthesis of Di-Functionally-Terminated Polystyrenes

2.3.10.1 Using Sodium Naphthalide as the Initiator[27-29]

The polymerizations were conducted in reactors R5 or R7. Typically 1-5 ml of freshly prepared sodium naphthalide (0.004 to 0.005 M) in THF prepared according to references 11, 30 and 31 was added to 60 to 70 ml of freshly distilled THF (trap-to-trap distilled from *sec*-butyllithium just before use) in R5. For reactions initiated or propagated at low temperatures, the temperature of the "spinach green" mixture at room temperature was reduced to -78 °C using a mixture of ethyl acetate and liquid nitrogen upon which the color of the mixture turns brown and a slurry is formed. The desired amount of styrene (0.0087 to 0.0435 moles) distilled from dibutylmagnesium, just before use, was transferred to the initiator solution. The usual procedure followed for adding styrene was to introduce the entire amount in a single transfer. However for room temperature initiation reactions and propagation reactions it was added in drops with the contents of the reactor being stirred uniformly. After 30 min at -78 °C and 15 min at room temperature, a small amount of the contents of the reactions were killed using degassed methanol. The polystyrenes formed were characterized by gel permeation chromatography. The major portion of the reaction contents were reacted with carbon dioxide without stirring. Subsequently they were hydrolyzed using a mixture of HCl/ THF and some of the carboxylic acid-terminated polystyrenes were analyzed by GPC as well.

2.3.10.2 Using Organolithiums Containing a Protected Functional Group

Two organolithium initiators containing protected functional groups were used: a protected carboxylic acid group namely 1,1,1-trimethoxy-4-lithiobutane prepared from 1,1,1-trimethoxy-4-bromobutane and a protected hydroxyl group namely acetaldehyde 6-lithiohexyl ethyl acetal prepared from 6-iodo-1-hexanol. The synthesis and recrystallization of the former is discussed. The latter was donated by Meera Pyati. 1,1,1-trimethoxy-4-bromobutane (1 ml, ≈ 4.41 moles) was introduced to a nitrogen-purged reactor (R5). 15 ml of dry heptane was introduced using a cannula under nitrogen. The temperature of the solution was reduced in increments of 5 °C to observe the solubility changes in heptane. 1,1,1-trimethoxy-4-bromobutane forms a precipitate at -85 °C which refuses to dissolve on diluting it two-fold. At -70 °C it forms a cloudy solution suggesting that it is still insoluble in heptane. However at -50 °C it dissolves completely to form a transparent solution. To this solution 4 ml of *tert*-butyllithium (6.84 millimoles, 1.71 M) in 10 ml of heptane was added in increments of 1ml per every 15 min using a cannula. 2 min after the addition of *tert*-butyllithium a white precipitate was formed at the surface of the solution which spread to the bulk with time. After completing the addition of *tert*-butyllithium, the mixture was left to stir overnight at -50 °C. The next day the supernatent solution was removed using a cannula and 25 ml of dry heptane was introduced. The solution was allowed to warm to 0 °C and the supernatent was removed again. This procedure was repeated thrice after which 10 ml of dry heptane was introduced and the mixture was cooled to -50 °C and the supernatent at this temperature was discarded as well. The lithium salt was recrystallized using 30 ml of benzene at 0 °C (as it crystallizes out from a benzene solution at 0 °C). The salt was dried under nitrogen, freeze-dried from benzene and was stored in a dry box (synthesis of protected initiators NB#1 p 1-5). A typical polymerization was conducted by the transfer of the appropriate amount of the initiator (weighed in a glove box and appropriate amount of dry benzene was added in a Schlenk tube) in the case of 1,1,1-trimethoxy-4-lithiobutane or by transferring a solution of acetaldehyde 6-lithio-hexyl ethyl acetal in benzene (2 ml, 0.07 M) to 50 ml of benzene in reactor R5. One to two ml of dry styrene was added and the polymerizations were run for 90 to 120 min after which a small portion of the solution was killed using degassed isopropanol. The polymer was precipitated using excess methanol, was filtered, dried and characterized by GPC. The major portion was killed using carbon dioxide (ethylene oxide for the polymerization conducted using acetaldehyde 6-lithio-hexyl ethyl acetal) without stirring the solution. It was hydrolyzed using a HCl/THF mixture, precipitated using excess methanol, filtered, dried and characterized by GPC as well.

2.3.10.3 Using Tung's Initiator

Tung's initiator was prepared by the reaction of 0.2 g (0.00071 moles) of 1,3-bis(phenylethenyl)benzene (PEB) with two equivalents of *sec*-butyllithium (0.001418 moles) in benzene as well as cyclohexane. The exact strength of *sec*-butyllithium was determined by titration against 4-biphenylmethanol just before the preparation. A typical reaction was performed as follows: to 50 ml of dry benzene in a nitrogen-purged pressure bottle was added 0.1 ml of isopropanol (0.00134 moles) and 3 ml of *sec*-butyllithium (0.001404 moles). After 10 min, 1 ml of *sec*-butyllithium was added to ensure dryness and a 25 ml benzene solution of PEB (0.2 g or 0.00071 moles) was added. Two min after the addition, the color of the solution turned yellow and within 5 min the entire solution turned deep yellow and eventually grape red in color. An aliquot of the solution was killed using methanol and a gas chromatographic (GC) analysis was performed. The GC was performed under the following conditions: Supelco SPB-1 fused silica capillary column of length 15 m and ID = 0.53 mm on a Hewlett Packard 5790A gas chromatograph equipped with an FID detector. injection temperature = 200 °C; T1 = 75 °C; t1 = 0.5 min; rate = 10 °C /min; T2 = 250 °C; t2 = 0 min; and detection temperature = 200 °C. Under these conditions cyclohexane, benzene, methanol, isopropanol, PEB and the adducts elute at 1.32, 1.76, 1.21, 1.48, 15.52, 17.09, 18.39 min respectively. *sec*-butyllithium addition was continued in small increments after the addition of 1.8 equivalents and the reaction was followed by GC. The reaction was taken to be complete with the disappearance of PEB and the mono-adduct peaks at 15.52 and 17.09 min, respectively. At this point 2 ml of styrene was added to the solution (0.0174 moles) and the color of the solution turned cranberry red. The polymerization was allowed to proceed overnight in benzene and a small portion was killed using methanol the next morning. The polymer was precipitated using excess methanol, filtered, dried and was analyzed by GPC. The rest of the cranberry red polystyrllithium solution was divided into two portions, a portion of which was treated with bone dry carbon dioxide and the other was treated with ethylene oxide. The end-functionalized polymer samples thus prepared were hydrolyzed using a mixture of HCl/THF, precipitated using excess methanol, dried and were analyzed by GPC and TLC. The initiator preparation, characterization and polymerization in cyclohexane were conducted in an analogous fashion as in benzene (synthesis alone NB#4 p 3-23).

2.3.10.4 Using Lithium Naphthalide as the Initiator

The polymerizations were conducted in reactors R5 or R7. 50 ml of dry benzene was added to the reactor (after evacuation and argon purge). 1 to 10 ml of the initiator solution was added to the benzene depending on the molecular weight desired. The benzene solution turned chocolate brown on contact with the dark green initiator solution. 2 to 5 ml of styrene was then added while vigorously stirring the initiator-solvent mixture. The solution turned rust red to orange (depending on the concentration of initiator used) on contact with styrene. After 90 min to 2h, a portion of the solution was killed by transferring it to degassed isopropanol. The major portion of the living polystyrllithium was divided into two portions. One portion was treated with ethylene oxide while the other portion was treated with bone-dry carbon dioxide gas without stirring the contents. The lithium salts thus obtained were hydrolyzed using a HCl/THF (1/10) mixture to obtain the dihydroxyl (HO-PS-OH) and dicarboxylic acid-terminated polystyrenes (HOOC-PS-

COOH). The polystyrenes thus obtained were characterized by GPC and TLC (synthesis alone NB#4 p 24-78).

2.3.11 Isolation of Di-Functionally-Terminated Polystyrenes of Narrow Molecular Weight Distribution by Fractional Precipitation

The di-functionally-terminated polystyrenes prepared according to the procedure discussed in section 2.3.10.4 invariably exhibited a tail in their GPC chromatogram suggesting the presence of a low molecular weight species in addition to the desired high molecular weight species. The concentration of the low molecular weight species ranged from 10 to 15% of the high molecular weight species. Therefore the high molecular weight species was isolated from the mixture by fractional precipitation. A typical fractional precipitation was performed as follows. 50 ml of a 5 mg/ml solution of the polymer to be separated in toluene (in THF 10 mg/ml) was titrated with methanol till turbidity is maintained by the solution. A 5 % excess of methanol was added to ensure complete separation and the turbid solution was centrifuged for 5 min. The supernatent was removed with a pastuer pipette and the fractional precipitation was continued. All the fractions were characterized by GPC and TLC. The precipitate obtained in the first step was most often the desired molecular weight species and was obtained in ≈ 50% yield.

2.3.12 Characterization Techniques

Molecular weights (number average - M_n and weight average - M_w) and poly dispersity index (PDI) were determined using gel permeation chromatography (GPC) technique. Commercial narrow molecular weight standards were used earlier to calibrate the instrument. A dilute solution of the oligomer/polymer (1 mg/ml) prepared in toluene / methylene chloride / THF was injected through a series of Polymer Laboratories PL gel columns (mean pore diameter 10^4, 10^3, 10^2 Å respectively), through which a constant flow of the eluent (toluene / methylene chloride / THF, 1ml / min) was maintained using a Rainin

Rabbit diaphragm pump. The eluted sample was detected by a differential refractometer (Knauer 98) or a UV detector (IBM). GPC data accumulation and analysis were performed initially by using Interactive Microware GPC software, an Apple IIe computer while Polymer Laboratories software and an IBM PC/AT were used at later dates. A previously determined calibration curve for polystyrene commercial standards was used to obtain the molecular weights. Infrared spectra were obtained using an IBM 38 FTIR by casting the oligomer/polymer onto a NaCl window from a dilute solution in toluene. Thin layer chromatograms for individual samples were obtained using thin layers of silica (Kodak) on polyester support and alumina on glass support (Baker). Thin layer chromatography of a series of a particular end-functionalized polymers were performed using silica gel thin layers (250 μm thick, 60-Å pore diameter) supported on 20 X 20 cm glass (Aldrich) and preparative alumina thin layers (250 μm thick) supported on 20 X 20 cm glass (Analtech, Inc.). ^{1}H and ^{13}C NMR spectra of the oligomers were obtained using Varian XL200 and 300 spectrometers, respectively. Gas chromatography (GC) was performed using a Hewlett-Packard 5790A gas chromatograph equipped with an FID detector using Analabs 10 ft x 1/8 in. 15% AN 600 column, 15 ft. x 1/8 in. Superpak II column and Supelco's SPB-1 fused silica capillary column of length 15 m and ID = 0.53 mm.

The number of carboxylic acid end-groups and therefore the number averaged molecular weight was also calculated by titrating a weighed amount of the oligomer / polymer in 25 ml of toluene against 0.01 M KOH in methanol, using phenophthalein as indicator. The KOH used was standardized by titrating against a known quantity of benzoic acid in methanol using the same indicator.

2.4. Results and Discussion

Anionic polymerization of styrene enables the synthesis of polystyrenes of desired molecular weight and narrow molecular weight distribution.[13] The anionic polymerization of vinyl monomers such as styrene, butadiene and isoprene initiated by alkyllithiums and alkali metal naphthalides involves a rapid initiation step compared to the propagation. This in theory should give a polymer of narrow molecular weight distribution, as it involves simultaneous growth of chains.[13] In the absence of chain termination, a chain of desired molecular weight can be obtained by using the desired concentration of the monomer for a given concentration of the initiator. Further the living anionic ends can be suitably terminated using an electrophile to quantitative yields as well.[35] An anionic polymerization of styrene initiated by *sec*-butyllithium in benzene is described in figure 2.5. For the polymerization to proceed ideally as desired, large number of conditions have to be met. These are stressed in the order of decreasing importance. 1) the reactivity of the initiating anion towards the monomer should be greater than that of the propagating anion, i.e $k_i > k_p$; 2) Monomer and solvent chemical structure should be so selected such that during the desired time period of polymerization, no other side reaction will take place. For example, proton abstraction by the initiator results in lesser number of moles of the initiator and therefore a number average molecular weight higher than theoretical; proton abstraction by the propagating anion would result in a broader molecular weight distribution (MWD) depending on the rate of that reaction; Halogen-cation exchange or any other chemical reaction can convert the living initiator or propagating species to something less reactive or dead;[33,34] 3) Monomer and solvent should be free of impurities. The preceding statement does not define tolerance. Concentration of impurities should be reduced to an order (or two) of magnitude lower than the initiator concentration. The higher the molecular weight that one wishes to prepare, the more careful one should be about purifying the monomer, solvent and other additives as a small amount of initiator is involved; 4) An inert gas environment should be maintained till the end of the polymerization, as the anion

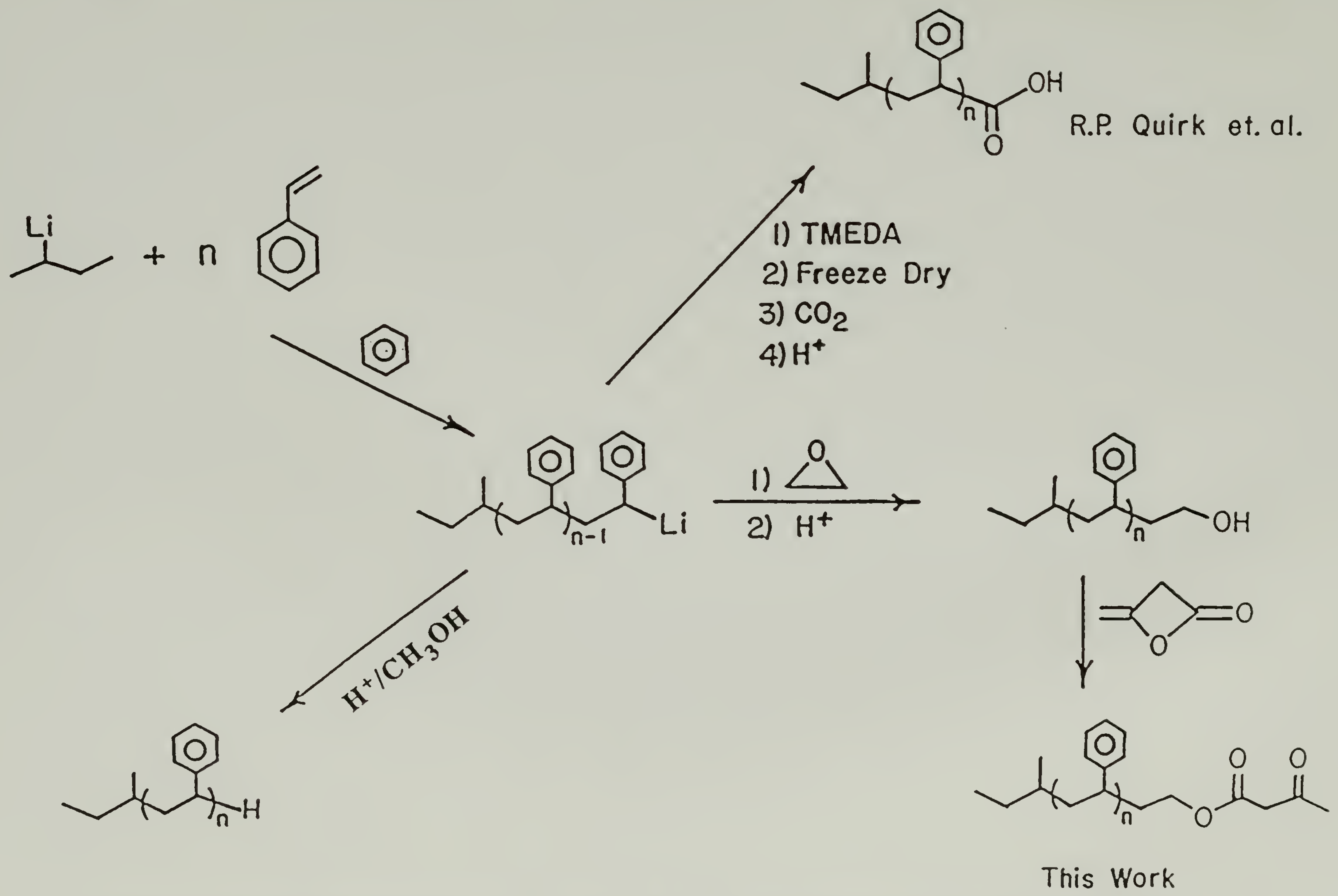


Figure 2.5 Anionic Polymerization of Styrene Initiated by *sec*-butyllithium and Subsequent End-Functionalization Reactions

(initiating/propagating) is capable of reacting with air or moisture or other gases present depending on its reactivity; 5) Reaction flask, syringes, cannula and transfer vessels (like centrifuge tube, Schlenk type graduated cylinder, etc.,) must be perfectly dry and free of impurities.

The first two of the conditions were met by the appropriate choice of initiator (*sec*-butyllithium), monomer (styrene), solvent (benzene and cyclohexane at room temperature and THF at -78 °C) and carefully selected polymerization conditions.[29, 33-35] The rest of the conditions were met by adherence to stringent purification steps. The GPC results of polystyrenes prepared by terminating (killing) living polystyrllithium prepared according to the conditions stated above are shown in Table 2.1.

Table 2.1 GPC Characteristics of Polystyrenes (PS-H)

Sample code	M_n	MWD	Lab. Note-Book reference
PS-H #1 in CH	1500	1.06	synthesis alone NB #3 p 19
PS-H enroute PSEO0	2000	1.06	synthesis alone NB #2 p 32
PS-H #1 in CH	2821	1.05	synthesis alone NB #3 p 20
PS-H enroute PSOH2	4300	1.05	synthesis alone NB #3 p 32
PS-H syn with DBuMg	6500	1.05	synthesis alone NB #3 p16
PS-H enroute PSEO1	9000	1.05	synthesis alone NB #1 p 32
PS-H enroute RPQ Rn 4	10000	1.04	synthesis alone NB #2 p 53
PS-H enroute RPQ Rn 5	12000	1.04	synthesis alone NB #1 p 11
PS-H enroute PSCOOHPB2	17500	1.05	synthesis alone NB #3 p 87
PS-H enroute PSOH3	20000	1.04	synthesis alone NB #3 p 36

Continued, next page

Table 2.1 Continued

Sample code	M_n	MWD	Lab. Note-Book reference
PS-H enroute RPQ Rn 21	30000	1.04	synthesis alone NB #2 p 142
PS-H enroute PSCOOHPB4	50000	1.04	synthesis alone NB #3 p 93
PS-H enroute PSOH6	58000	1.03	synthesis alone NB #3 p 68
PS-H enroute PSCOOH4	60000	1.04	synthesis alone NB #3 p 96
PS-H enroute PSEO5	70500	1.05	synthesis alone NB #2 p 32
PS-H enroute RPQ Rn 22	100000	1.03	synthesis alone NB #2 p 151
PS-H 02/27/89	280000	1.07	synthesis alone NB #3 p 75
PS-H enroute RPQ Rn 17	300000	1.05	synthesis alone NB #2 p 137
PS-H enroute PSOH7	320000	1.03	synthesis alone NB #3 p 71
PS-H enroute PSCOOH8 (f)	600000	1.10	synthesis alone NB #3 p 101
PS-H enroute PSCOOH7 (f)	825000	1.10	synthesis alone NB #3 p 99

Note: Some polystyrenes of molecular weight greater than 100,000 and narrow molecular weight distribution (< 1.10) were purchased from Polysciences, Inc. The molecular weight of the purchased samples are 150K, 200K, 250K, 290K, 400K, 450K, 600K, 860K, 980K, 1860K, 3000K, 7000K, 10000K, 15000K and 20000K. Samples marked (f) were fractionally separated.

2.4.1 Synthesis of Carboxylic Acid-Terminated Polystyrenes (PS-COOH)

As the first step towards the objective, the synthesis of a mono carboxylic acid-terminated polystyrene was undertaken. Several researchers have reported the synthesis of polystyrenes terminated by a carboxylic acid-end group.[38-40] Most of these syntheses involve the reaction of polystyrl anion with gaseous or solid carbon dioxide a reaction involving a liquid-gas interface. These reactions generally result in the formation of a significant amount of a ketone and a tertiary-alcohol.[38] Based on the simplicity of addition reactions that take place within a liquid phase and the desire to get pure carboxylic acid-terminated polymer (this would make the interpretation of adsorption results easier) the reactions of the carboxylic acid precursor molecules succinic anhydride (SA), carbonyldiimidazole (CDI) and terephthaloyl chloride (TPC) with polystyrllithium were studied as alternate routes for the synthesis of carboxylic acid-terminated polystyrene. It was hoped that polystyrl anion would react with succinic anhydride to form the γ-keto acid in 100% yield as reported earlier.[41] The reactions with carbonyldiimidazole and terephthaloyl chloride[41] were also expected to give pure carboxylic acid-terminated polymers as one might expect from conventional organic chemistry. The reactions and the expected products are described in figure 2.6. Long chain molecules with carboxylic acid end groups can be synthesized in principle by this method. The reactions of polystyrllithium with carboxylic acid precursor molecules are discussed in the next few sub-sections.

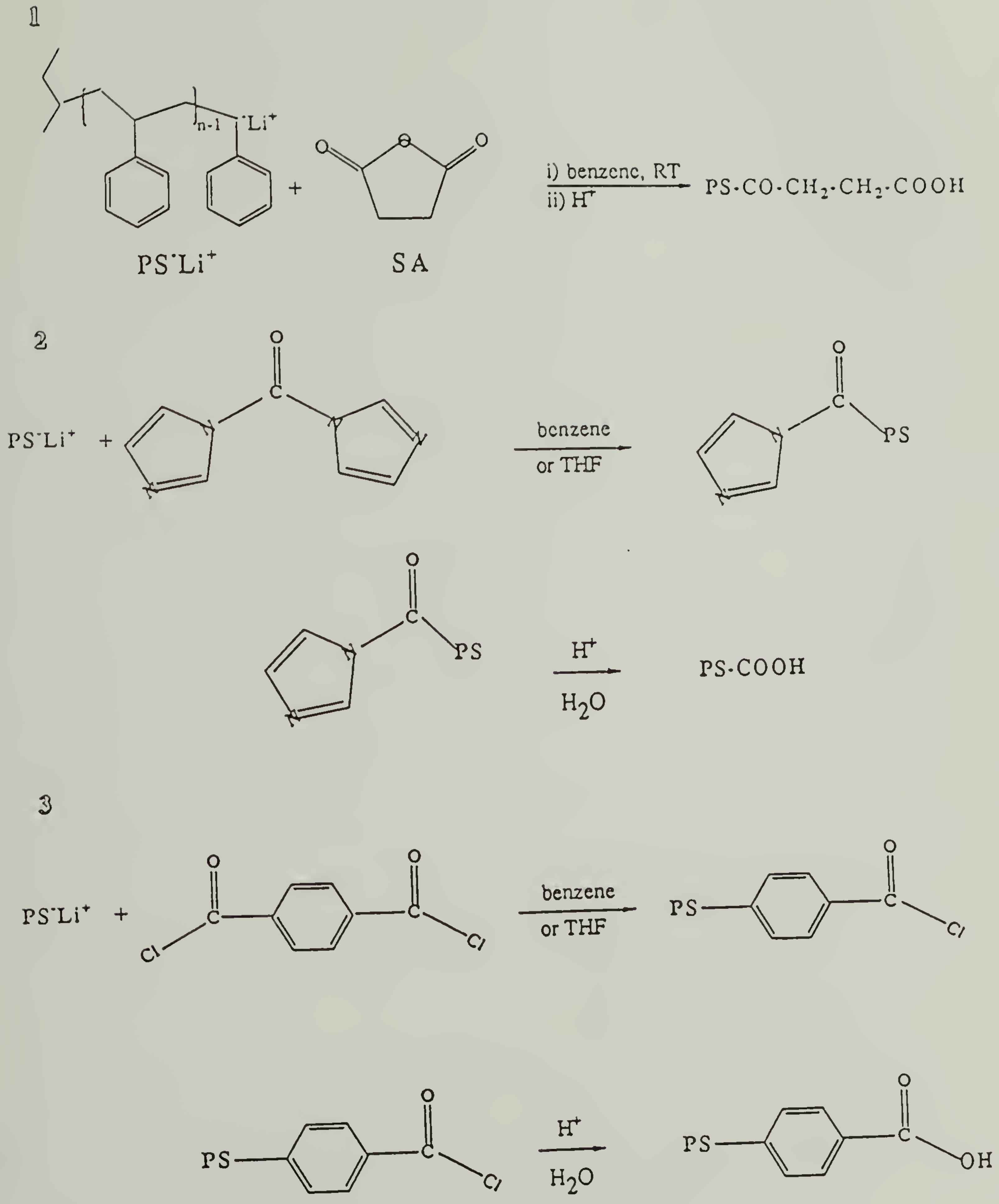


Figure 2.6 Reactions of Polystyrllithium with Carboxylic Acid Precursor Molecules and Expected Products

2.4.1.1 Reactions of Polystyrllithium with Succinic Anhydride

The reactions of polystyrllithium with succinic anhydride were carried out according to the procedure in section 2.3.9.1. The GPC results of the syntheses are summarized in Table 2.2. An increase in molecular weight of 100 is expected upon the reaction of polystyrllithium of any given degree of polymerization (DP) with succinic anhydride. However the increase in the number average molecular weights of the carboxylic acid end-terminated polystyrenes are much greater than 100. This is possible if polystyrene and carboxylic acid end-terminated polystyrene coils exhibit different radii of gyration in toluene. If that is the case, the use of a calibration curve based on polystyrene coil dimensions in toluene is unlikely to give the correct molecular weight increase on reaction with succinic anhydride.

Some of the carboxylic acid end-terminated polystyrenes (oligomers) were characterized for their number average molecular weight by volumetric titration of their acid end-group with alcoholic KOH in addition to GPC. The results are summarized in Table 2.3. The data point to the presence of a considerable amount of non-titratable (non-acidic) component(s) in the end-capped product. In the case of the oligomer of DP=4, the increased molecular weight obtained by the titration of the crude product points to the presence of 52% non-acidic component(s) in any given weight of the crude product. Separation of the crude product into acidic and non-acidic component(s) by base extraction, followed by weighing also yielded 52% (w/w) of the non-acidic component(s). The end group titration of the pure acid component(s) obtained from the crude product (see section 2.3.9.1.) leads to a number averaged molecular weight greater than the one obtained from the crude product. This result suggests that the non-acid component(s) might be formed from the acid itself by an isomerization as shown on page 80.

Table 2.2 GPC Characteristics of Polystyrllithiums End-Terminated with Succinic Anhydride

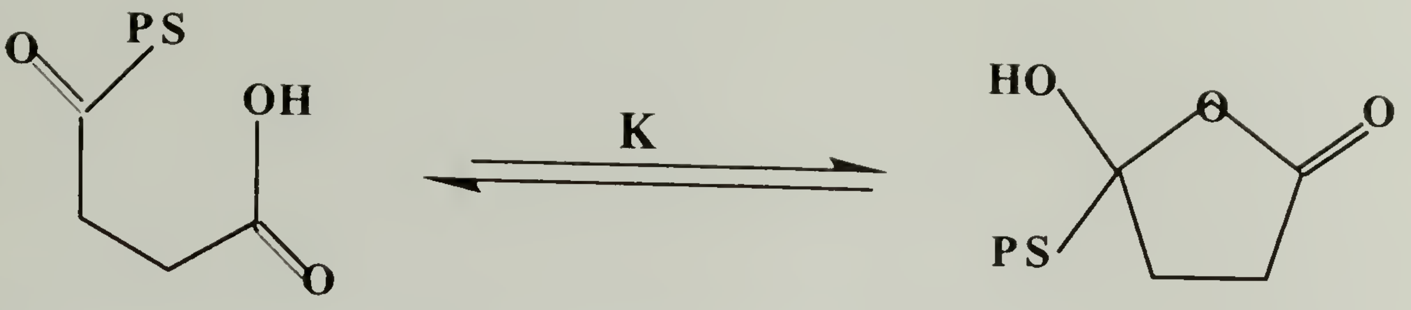
Sample	moles of s-buLi [I]	moles of styrene [M]	moles of SA	Expected DP [M] / [I]	M_n PS-H	PDI	M_n PSSA	PDI	Lab-notebook reference
PSSA00	0.0013	0.0087	0.00142	6.7	836	1.06	1018	1.14	synthesis alone NB#1 p 44-48
PSSA01	0.013	0.0435	0.0145	3.4	546	1.07	776	1.13	synthesis alone NB#1 p 54-61
PSSA02	0.0052	0.0435	0.0085	8.4	959	1.07	1347	1.15	synthesis alone NB#1 p 67-70
PSSA03	0.0195	0.0435	0.0210	2.3	481	1.20	715	1.22	synthesis alone NB#1 p 75-76
PSSA04	0.00221	0.0435	0.025	19.7	2089	1.23	2951	1.18	synthesis alone NB#1 p 91-94
PSSA05	0.00026	0.0087	0.025	33.5	6654	1.60	6256	1.59	synthesis alone NB#1 p 87-90

Note: s-buLi stands for *sec*-Butyllithium, SA for succinic anhydride, PSSA for succinic anhydride-terminated polystyrene, DP for degree of polymerization, PS-H for polystyrene, PDI for the polydispersity index and M_n for the number average molecular weight.

Table 2.3 Acid-Base Titration Results of Polystyrllithiums End-terminated with Succinic anhydride

Sample	DP	Expected M_n GPC M_n of PS-H+100	M_n from acid-base titration	M_n of acid component after separation
PSSA03	4	581	1104	1581
PSSA01	5	646	665®	-
PSSA02	9	1059	825	2959
PSSA04	20	2200	14598	-
PSSA05	66	6754	69000	-

Note: DP stands for degree of polymerization, PS-H for polystyrene and M_n for the number average molecular weight. ® indicates that the particular sample was titrated immediately after synthesis and purification steps. It is also to be noted that beyond a DP of 9 it was not possible to extract the acid component into the base.



Similar results were obtained for the oligomer of DP=9. Such an isomerization has been reported in the literature for small molecular weight γ-keto acids as well.[42] The volumetric titration of the non-acidic component(s) isolated from base extraction of the oligomer of DP=4 enabled us to calculate an equilibrium constant value of 9.79. The acid-base titration of the oligomer of DP = 5 immediately after the synthesis resulted in nearly 100% yield of the end-group while a slow increase in molecular weight was observed with time. This suggests that the equilibrium conversion to the lactone is slow.

The infrared spectrum of the crude oligomer of DP=4 displays the following prominent carbonyl stretches at 1713, 1740 and 1774 cm^{-1}, corresponding to carboxylic acid dimer, ketone and lactone carbonyl carbons. The IR spectra of the acidic and non-acidic components separated by base extraction display the same peaks in the carbonyl region as well. However the relative intensities of the different carbonyl stretches were different; the 1774 cm^{-1} peak (lactone carbonyl stretch) had a higher relative intensity for the non-acidic components while the 1713 cm^{-1} peak (carbonyl stretch in a carboxylic acid dimer) had a higher relative intensity for the acidic components (as well as for the crude oligomer).

The results of the thin layer chromatographic (TLC) characterization are summarized in Tables 2.4 and 2.5. These results indicate that the crude product is made up of 3 components; a high R_f component and two low R_f components, too close to be separated using silica gel or alumina. An attempt was made to separate the high R_f fraction by column chromatography using silica gel as the adsorbent and ethyl acetate as the eluent. The IR spectrum of this fraction exhibits a predominant lactone carbonyl stretch. This implied that a major component of the high R_f fraction was the lactone. A quantitative separation using a thin layer of silica gel and ethyl acetate as the mobile phase showed that the high R_f fraction constituted 92% of the crude product, suggesting that silica gel could be assisting the transformation of the γ-keto acid to the lactone.

To conclude this sub-section, the above results indicate that polystyrllithium reacts with succinic anhydride to form the γ-keto acid which subsequently isomerizes to the lactone slowly. The isolation of the non-acidic component and the presence of a small amount of acid (10%) as evidenced by acid-base titration conducted a few days after the synthesis indicates that the lactone is in equilibrium with a small amount of the acid. This result disproves the earlier claims by Rempp, et al.,[41] that carboxylic acid-terminated polystyrenes could be synthesized in good yield by reacting polystyrllithium with succinic anhydride. The conversion of the γ-keto acid to a mixture predominant in the lactone (with time or in contact with silica gel) and the observation that these lactones exhibit a high R_f value suggested that the lactones may not adsorb well in the subsequent adsorption experiments to be performed. Therefore alternate routes were explored for the synthesis of carboxylic acid-terminated polystyrenes as discussed in the sub-sections following this one.

Table 2.4 Thin Layer Chromatographic Characterization of Succinic Anhydride-Terminated Polystyrllithium on Silica, DP ≈ 4.

Eluent			R_f values	
	#1	#2	#3	PS-H of M_n = 500
benzene	0.00®	0.85		0.82
benzene/chloroform, 50/50 (v/v)	0.00®	0.86		0.89
chloroform	0.00®	0.80		0.88
tetrahydrofuran	0.00	0.82®	0.07	0.85
ethyl acetate	0.00	0.86®	0.14	0.91
benzene/ethyl acetate, 1/1 (v/v)	0.0®	0.86	0.04®	0.93
chloroform/methanol, 9/1 (v/v)	0.00®	0.88		0.89
chloroform/methanol, 3/1 (v/v)	0.00	0.89®		0.89
chloroform/methanol, 6/4 (v/v)	0.95	0.92®		0.92
chloroform/methanol, 1/1 (v/v)	0.89	0.88®		0.90
Methanol		0.86®		0.90

Note: The above data was recorded for the end-capped polymer PSSA03 spotted on a silica gel thin layer from a dilute solution in toluene (3 mg/ml) (see synthesis alone NB#1 p 77-83). An R_f value of zero was recorded in pentane, pentane/methylene chloride (4/5 and 3/7 volume/volume) mixtures, cyclohexane and CCl_4 on silica gel and alumina thin layers. Polystyrene standard of M_n = 500 and PDI=1.10 had an R_f value of 0.98 in cyclohexane and 0 in CCl_4. PSSA03 samples did not elute on alumina (R_f value of 0.00) from cyclohexane, THF, pentane, pentane/methylene chloride mixtures and methylene chloride.

Table 2.5 Thin Layer Chromatographic Characterization of Succinic Anhydride-Terminated Polystyrllithium (DP = 5) on silica.

Eluent	R_f values			
	#1	#2	#3	PS-H of M_n = 500
chloroform	0.00®	0.92		0.88
chloroform/methanol, 90/10 (v/v)	0.00®	0.93		0.89
chloroform/methanol, 80/20 (v/v)	0.00®	0.95		0.88
chloroform/methanol, 75/25 (v/v)	0.00	0.91®		0.89
chloroform/methanol, 72.7/27.3 (v/v)		0.92®		0.89
chloroform/methanol, 70/30 (v/v)		0.92®		0.89
chloroform/methanol, 50/50 (v/v)		0.893		0.90
ethyl acetate	0.00	0.86®	0.08	0.88
tetrahydrofuran	0.00	0.88®		0.77
Methanol		0.86®		0.90

Note: The above data was recorded for the end-capped polymer PSSA01 spotted on a silica gel thin layer from a dilute solution in toluene (3 mg/ml) (see synthesis alone NB#1 p 71-74). An R_f value of zero was recorded in pentane, pentane/methylene chloride(4/5 and 3/7) mixtures, cyclohexane and CCl_4 on silica gel and alumina thin layers. Polystyrene standard of M_n = 500 and PDI=1.10 had an R_f value of 0.98 in cyclohexane and 0 in CCl_4. PSSA01 samples did not elute on alumina (R_f value of 0.00) from pentane, cyclohexane, pentane/methylene chloride mixtures, methylene chloride, chloroform, THF, and methanol. The end-capped polymer of DP ≈ 66 and polystyrene of DP ≈ 66 have an R_f value of zero in cyclohexane and an R_f value between 0.84 and 0.86 in ethyl acetate and THF (synthesis alone NB#1, p 89).

2.4.1.2 Reactions of Polystyrllithium with Carbonyldiimidazole and Terephthaloyl chloride

The reactions of polystyrllithium with carbonyldiimidazole[43, 45] and terephthaloyl chloride were carried out for preparing a predominantly or fully monocarboxylic acid-terminated polystyrene. The reaction conditions and the characterization of the products by GPC and acid-base titration are summarized in Tables 2.6 and 2.7. The synthetic procedures are described in section 2.3.9.2. Though the chemistry involved was interesting the discussions shall be biased towards the goal. The reaction of polystyrllithium with CDI and TPC did not work out as shown in equations 2 and 3 of figure 2.6. From the results in Tables 2.6 and 2.7 it appears that polystyrllithium in benzene in the absence of any coordinating lewis base reacts to form the ketone with CDI and the diketone with TPC. In the presence of a small amount of coordinating lewis base such as TMEDA (10 times stoichiometric excess) in benzene, polystyrllithium still forms the simple ketone and an addition product across the C=N bond in CDI.[34, 46] However if the end-capping reaction or the polymerization and the end-capping reaction were performed in a basic solvent such as THF, 30-70% of acid-terminated polystyrene was obtained as the yield (determined by the acid-base titration) along with side products such as the ketone (and the addition product across the C=N bond in the case of addition to CDI). The reactions with terephthaloyl chloride in THF were not reproducible as shown in Table 2.7. All the adsorption experiments require pure monocarboxylic acid-terminated polystyrene of narrow molecular weight distribution so that the physical effects of adsorption could be attributed as only due to the effect of the end-group and not to other extraneous factors. Therefore no further end-termination reactions were performed with CDI and TPC.

The characterization of a single end group in a long chain polymer is difficult if not impossible by any conventional technique and so the results pertain to the characterization

Table 2.6 GPC and Acid-Base Titration Characteristics of Carbonyldiimidazole-Terminated Polystyrenes

No	[s-buLi] moles	[styrene] moles	S/T S/°C	[CDI]/S/T moles/S/°C	M_n (GPC) PS-H	PDI	M_n (GPC) PS-CDI	PDI	M_n (titration) PS-CDI	lab-notebook reference
1	0.0024	0.026	B/25	0.019/B/25	1086	1.07	2600	1.11	100000	synthesis alone NB#1 p95-98
2	0.0024	0.026	B/25	0.028/T/-78	1086	1.07	1909	1.17	20351	synthesis alone NB#1 p95-99
3	0.0039	0.052	B/25	0.0074/B/45	1362	1.06	3508	1.08		synthesis alone NB#1 p109-11
							1504	1.04		
4	.00034	0.0087	B/25@	0.0067/B/25	2800	1.05	2810	1.03	9706	synthesis alone NB#1 p 127-32
5	0.0016	0.0087	T/-78	0.009/T/-78	484	1.21	710	1.27	5104®	synthesis alone NB#1 p114-16
6	.00032	0.0087	T/-78	0.0086/T/-78	1545	1.17	2193	1.18	3333	synthesis alone NB#1 p118
7	.00035	0.0087	T/-78	0.0324/T/25	2096	1.10	2232	1.12	11167	synthesis alone NB#1 p119-41
8	.00016	0.0174	T/-78	0.0136/T/-78	10324	1.05	11000	1.06	59444	synthesis alone NB#1 p123-39

Note: B stands for benzene, T for tetrahydrofuran and @ for tetramethylethylenediamine. TMEDA was added just before the end-capping reaction. ® Bicarbonate extraction indicated the presence of 2.7% acid and 97.3% non-acidic components. Elemental analysis of the non-acidic component gave the following composition, %C = 84.91, %H = 8.89, %N = 1.57.

Table 2.7 GPC and Acid-Base Titration Characteristics of Terephthaloyl Chloride-Terminated Polystyrenes

No	[s-buLi]	[styrene]	S/T	[TPC]/S/T	M_n (GPC)	PDI	M_n (GPC)	PDI	M_n (titration)	lab-notebook reference
	moles	moles	S/°C	moles/S/°C	PS-H		PS-TPC		PS-TPC	
1	0.0024	0.026	B/25	0.0049/T/-78	1362	1.07	1391	1.04	9078	synthesis alone NB#1 p109-11
2	0.0039	0.052	B/25	0.0059/B/25	1362	1.06	3178	1.15	-	synthesis alone NB#1 p109-12
3	.00034	0.0087	B/25@	0.0065/B/25	2800	1.05	2683	1.10	9861	synthesis alone NB#1 p 127-32
4	0.0016	0.0087	T/-78	0.020/T/-78	1545	1.17	2158	1.25	1603	synthesis alone NB#1 p114-43
5	.00032	0.0087	T/-78	0.033/T/-78	2100@	1.13			2200	synthesis alone NB#1 p119-21
6	.00035	0.0087	T/-78	0.013/T/25	10324	1.30	11595	1.10	24762	synthesis alone NB#1 p123-36
							27898	1.06		
7	.0008	0.0174	T/-78	0.013/T/-78	2849	1.11	3690	1.17	10520	synthesis alone NB#1 p125-34
8	.00033	0.0174	T/-78	0.013/T/-78	14472	1.28	15219	1.12	53480	synthesis alone NB#2 p1-8
							37150	1.05		
9	.00065	0.0174	T/-78	0.0032/T/-78	3092	1.09	2109	1.09	17485	synthesis alone NB#1 p9-12
							6279	1.20		

Note: B stands for benzene, T for tetrahydrofuran and @ for TMEDA. TMEDA was added just before the end-capping reaction.

of end groups in the oligomeric cases alone. It is assumed that the end-termination reaction of polystyrl anion proceeds independent of it's chain length.

Subsequently, the reaction of freeze dried mixture of polystyrllithium and a ten molar excess of TMEDA, with carbon dioxide was carried out as reported by Quirk, et al.

2.4.1.3 Reactions of Polystyrllithiums with Carbon Dioxide

2.4.1.3.1 Synthesis of Carboxylic Acid-terminated Polystyrenes; Rod Quirk's Method

The gas phase reaction of CO_2 with freeze-dried polystyrllithium was reported by Quirk and Yin at the American Chemical Society meeting held at New Orleans in the Fall of 1987.[24] They claimed in that report that they obtained 100% acid end-group yield. The results of carbonylation reactions performed according to the procedures in the preprint were discussed subsequently in detail as well.[25] The reactions reported in this sub-section were performed according to the later version of Quirk, et al and their details are presented in section 2.3.9.3. The molecular weight characteristics of the reactions performed according to Quirk are summarized in Table 2.8. A detailed account of these reactions are described in "synthesis alone NB#2 p 13-151 and NB#3 p 1-11. These reactions were labelled RPQ Rn 1-23 after Roderick P. Quirk.

The IR spectrum of the sample obtained in reaction RPQ Rn1 is shown in figure 2.7. The carbonyl stretch at 1707 cm^{-1} indicates that it is probably from carboxylic acid groups present as dimers. The GPC chromatograms indicated the formation of a small amount of ketone (1-5%) in these reactions (synthesis alone NB#2 p 13-151). The number average molecular weights obtained by acid-base titration (for molecular weights less than 15000) also indicated that at least 5 to 10% of the end-capped product was not an acid. Subsequent TLC experiments (see Table 2.8 for TLC results using benzene as the eluent) confirmed the

Table 2.8 GPC Characteristics of Carboxylic Acid End-Terminated Polystyrenes (PS-COOH)

Sample code	reactor	M_n GPC/titration	MWD	TLC R_f's	Lab. Note-Book reference
RPQ Rn 1	R3	2000/2879	1.09	0.0, 0.82	synthesis alone NB #2 p 13-17 and p 41-42
RPQ Rn 2 @	R3	3100/6098	1.09	0.0, 0.80	synthesis alone NB #2 p 18-21
RPQ Rn 3	R5	3000/3200	1.08	0.0, 0.80	synthesis alone NB #2 p 48-53
RPQ Rn 4	R5	9700/10400	1.04	.04, 0.85	synthesis alone NB #2 p 48-53
RPQ Rn 5	R5	12300/13000	1.03	.04, 0.92	synthesis alone NB #2 p 55-57
RPQ Rn 10	R5	33600	1.19	.17, 0.93	synthesis alone NB #2 p 64-69
RPQ Rn 13	R5	12000	1.07	.04, 0.92	synthesis alone NB #2 p 96-148
RPQ Rn 14	R5	19100/20400	1.06	.05, 0.92	synthesis alone NB #2 p 147
RPQ Rn 15	R5	78000	1.04	.58, 0.92	synthesis alone NB #3 p 6
RPQ Rn 17	R5	326000	1.04	.58, 0.70	synthesis alone NB #3 p 2
RPQ Rn 18	R5	93000	1.03	-	synthesis alone NB #2 p 138
RPQ Rn 19	R5	133000	1.05	.74, 0.90	synthesis alone NB #3 p 4
RPQ Rn 20	R5	23400	1.04	.12, 0.94	synthesis alone NB #2 p 149
RPQ Rn 21	R5	37000	1.05	.17, 0.94	synthesis alone NB #2 p 150
RPQ Rn 22	R5	99000	1.03	0.85	synthesis alone NB #2 p 151
RPQ Rn 23	R5	7100	1.07	.04, 0.89	synthesis alone NB #2 p 146
PSCOOHPB1	R1	2500/2700	1.10	0.0, 0.79	synthesis alone NB #3 p 85-90
PSCOOH PB2	R1	16800	1.05	.05, 0.93	synthesis alone NB #3 p 87
PSCOOH PB3	R1	47000	1.03	.20, 0.92	synthesis alone NB #3 p 88

Continued, next page

Table 2.8 Continued

Sample code	reactor	M_n GPC/titration	MWD	TLC R_f's silica/benzene	Lab. Note-Book reference
PSCOOHPB4	R1	51400	1.05	-	synthesis alone NB #3 p 93
PSCOOH2	R4	4100/4300	1.05	0.0, 0.84	synthesis alone NB #3 p 76-84
PSCOOH4	R6	60000	1.04	.32, 0.92	synthesis alone NB #3 p 94-96
PSCOOH5	R6	100000	1.03	0.85	synthesis alone NB #3 p 94-97
PSCOOH6	R6	120000	1.04	0.78	synthesis alone NB #3 p 98
PSCOOH7 (f)	R4	825000	1.04	0.10	synthesis alone NB #3 p 100
PSCOOH8 (f)	R4	640000	1.07	0.36	synthesis alone NB #3 p 101
PSCOOH1(d8)	R7	6000	1.04	-	synthesis alone NB #3 p 103-08
PSCOOH2(d8)	R7	12528	1.06	-	synthesis alone NB #3 p 103-08
PSCOOH ®	R5	5000	1.04		syn. rad. mon. polym. #1 p 45
PSCOOH ®	R5	10000	1.03		"
PSCOOH ®	R5	30000	1.04		"
PSCOOH ®	R5	140000	1.06		"

Note: RPQ Rn stands for reactions performed according to Quirk, et al. The rest were performed according to the procedure developed in this thesis. @ implies carbonylation was performed without using TMEDA upon which 15 to 20% yield of ketone was detected by GPC. Since all the carboxylic acid-terminated polystyrenes exhibited a low molecular weight tail, the tail region was not included in the molecular weight distribution calculations. Inclusion of the tail increases the MWD; it was still ≤ 1.10. ® stands for cold polystyrenes prepared in parallel while synthesizing Tritium-Labelled polymers.

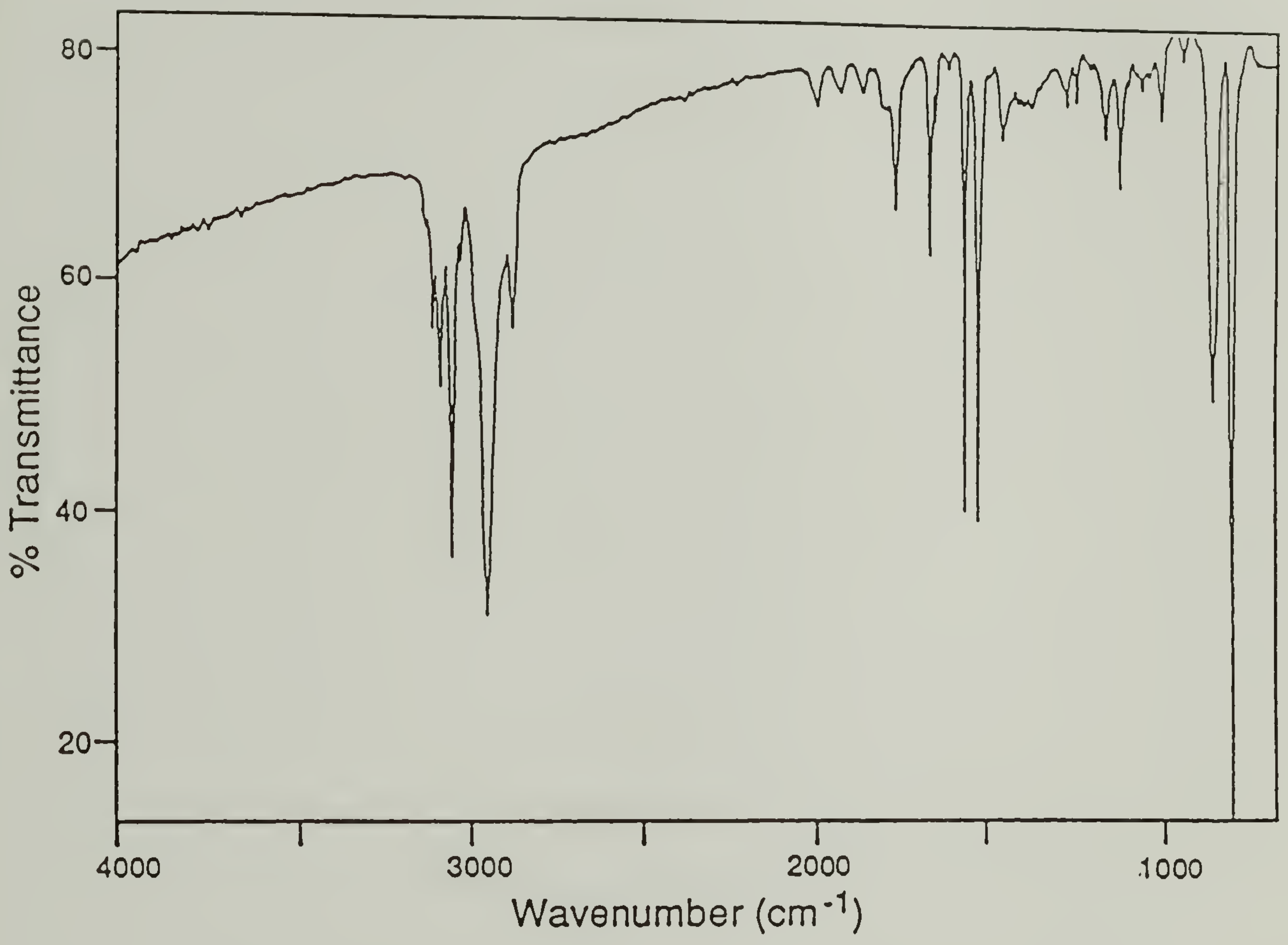
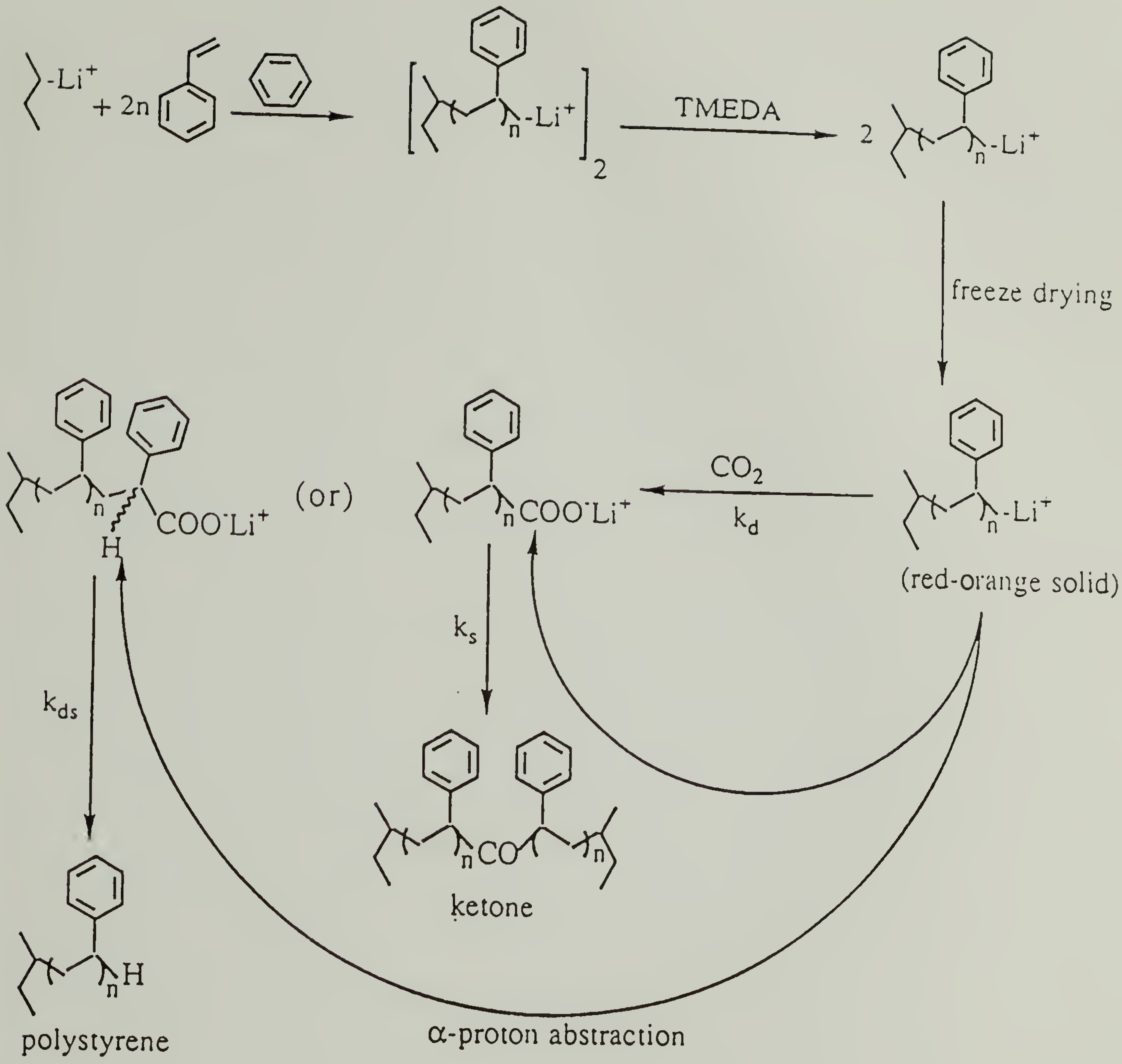


Figure 2.7 IR Spectrum Carboxylic Acid-Terminated Polystyrene Prepared in Reaction RPQ Rn1

formation of polystyrene even under the most rigorous conditions tried. The formation of the ketone and polystyrene are best explained by the mechanism of the carbonylation reaction as outlined in figure 2.8.[16, 38] This mechanism follows from the fact that a small amount of ketone and polystyrene are almost always formed in carbonylation reactions as evidenced by thin layer chromatography. At room temperature at which the carbonylation reactions were conducted, the end groups have sufficient mobility so that an unreacted polystyrllithium can abstract a proton α to a carbonylated chain-end. Further if the chain-ends were assumed to be close to each other (they are in hydrocarbon solvents in the absence of TMEDA) the reaction of a polystyrllithium with the carbonyl group of the functionalized polystyrene will result in the formation of the ketone. From the mechanism it is evident that, if the carbonylation reaction were to be conducted at temperatures at which nitrogen is a liquid (-196 °C), the temperature at which end-group segmental motion in polystyrene is frozen, 100% carbonylation is likely to result. An unpublished communication attributed to Fetters indeed claims such a result.[47] In spite of several attempts it was not practically possible to do carbonylation reactions at liquid nitrogen temperature conditions. At these temperatures the reaction was so slow (carbon dioxide is a solid and reaction is driven by the sublimation of carbon dioxide from the solid to vapor in order to replenish what will be consumed by the polystyrllithium) that the living anion had to be kept at very low temperatures for several days (7 days) at the end of which the polystyrllithium maintained its color indicating incomplete reaction. We do point out here that the possibility of this reaction going to 100% is hard to achieve practically. In order to minimize the time and energy consumed in Quirk's reaction a modified version was followed which resulted in quantitative yields of carboxylic acid-terminated polystyrenes. The results of this method are discussed in the next paragraph. Another method to get PSCOOH quantitatively is to let CO_2 into un-stirred PS^-Li^+. This has been reported in Quirk's paper. But this method gives >5% ketone and at least 10% PS-H.



Polystyrllithium possess translational, rotational and segmental motion in solution and mostly rotational and segmental motion in the solid state at room temperature. k_s and k_{ds} (in solution) depend on the mobility of polystyrllithium while k_d depends on the diffusion of carbon dioxide in to the solid (or the solution).

Figure 2.8 The Mechanism of the Reaction of Polystyrllithium and Carbon Dioxide

2.4.1.3.2 A Simpler Procedure for the Reaction of Polystyrllithium with Carbon Dioxide

A simpler carbonylation procedure leading to the production of "quantitative" yields of carboxylic acid-terminated polystyrenes was discovered in the process of understanding Quirk's reaction. The details of the procedure are discussed in section 2.3.9.1 and the samples obtained by this procedure are labelled as PSCOOHPB or PSCOOH. In brief, this process involves the slow transfer of polystyrllithium to a large excess of carbon dioxide. The word "quantitatively" is defined in detail below. The observations while performing the carbonylation reactions by Quirk's procedure (using even more rigorous drying procedure's like trap-to-trap distilling benzene from *n*-buLi, styrene from dibutylmagnesium, TMEDA from *n*-buLi) was that a small amount of ketone (<5%, by GPC) and polystyrene (<10%, by TLC) was always formed. A whole range of reactors (to enhance the surface area of the freeze dried polystyrllithium), freeze-drying temperatures from liquid nitrogen to melting ice, carbonylation temperatures from room-temperature to dry ice conditions and different amounts of TMEDA (from twice the initiator concentration to ten times) lead to similar results. Since a small amount of ketone was almost always formed independent of the synthesis or the workup condition, the definition of "quantitative" will be any synthetic product which on analysis shows the formation of greater than 90% PS-COOH. For example, the number average molecular weight of the sample PSCOOHPB1 obtained by chromatography is 2500 while that obtained by acid-base titration is 2700 following the present carbonylation procedure indicating quantitative conversion. Such a sample is sufficient for adsorption experiments as will be shown in the subsequent chapters.

Tritium-labelled polystyrene, hydroxyl and carboxylic acid-terminated polystyrene were prepared by Quirk's reaction. The synthesis of tritium-labelled styrene and polystyrenes are shown in figure 2.9. In the presence of polystyrene the reduction of phenylacetylene can be stopped at the styrene stage as polystyrene competes with styrene for catalytic sites.

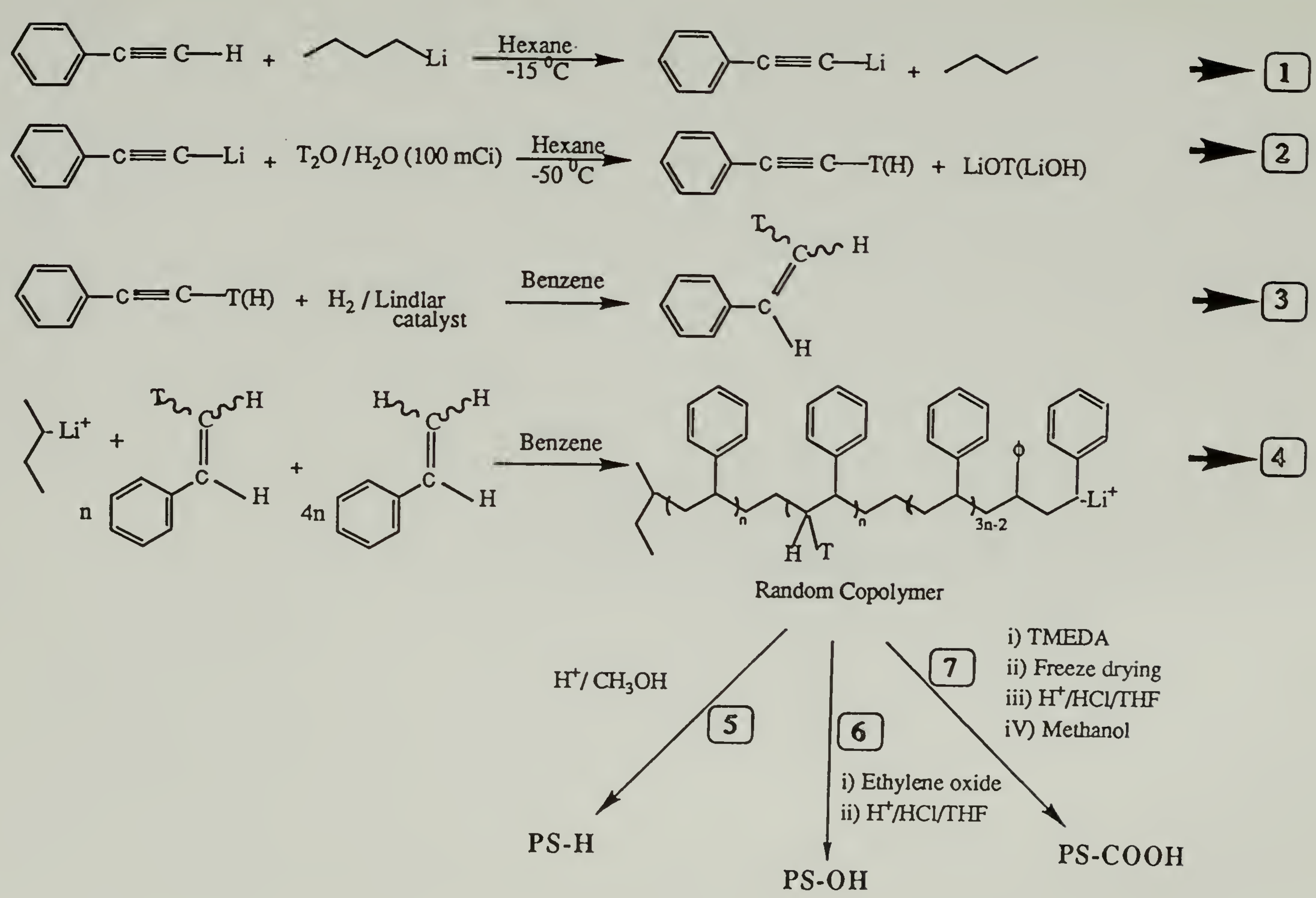


Figure 2.9 Synthesis of Tritium-Labelled Styrene and Polystyrenes

The GPC characteristics of non-radioactive polymers prepared in parallel, under identical experimental conditions, were assumed to represent the radioactive polymers.

To summarize this section, the reaction of freeze dried polystyrllithium in the presence of TMEDA with carbon dioxide at room temperature almost always yields >90% acid-terminated polystyrene but never 100% as claimed earlier.[16] The earlier workers do not mention any details about their freeze-drying conditions and carbonylation procedure. It is also possible that more rigorous conditions such as high vacuum and break-seal techniques as used by them could minimize the yield of the side products and since we were using Schlenk tubes and inert gas technique we refrain to compare their results with ours. It is assumed that polystyrene samples containing >90% carboxylic acid-end groups are sufficient at low molecular weights ($<10^5$) for adsorption studies. The thin layer chromatographic characterization of PS-COOH samples indicates that they adsorb in preference to un-functionalized polystyrene justifying the assumption at least at this stage.

2.4.2 Synthesis of Hydroxyl-Terminated Polystyrenes

Hydroxyl terminated polystyrenes were synthesized according to the procedures reported by Schulz and Milkovich.[25] The hydrolysis step was modified as reported in section 2.3.9.4 to ensure complete hydrolysis. The results of the syntheses are summarized in Table 2.9. Tritium-labelled polymers were prepared by the same procedure and non-radioactive polymers prepared in parallel under exact conditions were characterized to obtain the number average molecular weight and polydispersity index. The TLC results in particular indicate that hydroxyl-terminated polystyrenes could be synthesized in quantitative yields.

Table 2.9 GPC Characteristics of Hydroxyl End-Terminated Polystyrenes (PS-OH)

Sample code	reactor	M_n GPC/titration	MWD	TLC R_f's	Lab. Note-Book reference
PSOH1	R1	1500	1.07	0.05	synthesis alone NB #3 p 19
PSEO4	R1	1900	1.05	0.07	synthesis alone NB #2 p 29-39
PSEO0	R1	2000	1.06	0.08	synthesis alone NB #2 p 29-39
PSOH2	R1	4400	1.05	0.09	synthesis alone NB #3 p 37
PSEO1	R1	8200	1.05	0.19	synthesis alone NB #2 p 29-39
PSOH4	R1	12300	1.04	0.30	synthesis alone NB #2 p 45
PSOH3	R1	20200	1.04	0.47	synthesis alone NB #2 p 36
PSEO2	R1	24200	1.10		synthesis alone NB #2 p 29-39
PSEO3	R1	36300	1.05	0.81	synthesis alone NB #2 p 29-39
PSOH6	R5	58000	1.03	0.86	synthesis alone NB #2 p 68
PSEO5	R1	70500	1.05	0.86	synthesis alone NB #2 p 29-39
PSOH5	R4	100000	1.03	0.86	synthesis alone NB #2 p 64
PSOH7 (f)	R6	200000	1.06		synthesis alone NB #2 p 69-71
PSOH7 (f)	R6	320000	1.05	0.56	synthesis alone NB #2 p 69-71
PS-OH ®	R5	5000	1.04		syn. rad. mon. polym. #1 p 45
PS-OH ®	R5	10000	1.03		"
PS-OH ®	R5	30000	1.04		"
PS-OH ®	R5	140000	1.06		"

Note: Samples marked (f) were fractionally separated for TLC purposes. ® stands for cold polystyrenes prepared in parallel while synthesizing Tritium-Labelled hydroxyl-terminated polystyrenes.

2.4.3 Synthesis of Acetoacetyl-Terminated Polystyrene

The synthesis of acetoacetyl-terminated polystyrene was performed by the reaction of hydroxyl-terminated polystyrene with ketene dimer using a reaction analogous to that reported for *tert*-butanol and ketene dimer.[26] The details of the reaction procedures are discussed in section 2.3.9.5. One and only reaction involving PS-OH of number average molecular weight 2000 was performed. The starting material, PS-OH, elutes with an R_f of 0.08 on silica and 0.10 on alumina, benzene being the eluent. The product after the reaction exhibits an R_f of 0.48 on silica and 0.0 on alumina, under identical conditions. From the thin layer chromatographic evidence it was concluded that this reaction goes to completion under the prescribed experimental conditions.

2.4.4 Other Interesting Observations Concerned With Polystyrenes Terminated With a Single End-Group

1) Polymerizations can be performed in THF, distilled once from sodium benzophenone anion, in the presence of dibutylmagnesium. No additional purification of the solvent is necessary (for the reaction conditions and the GPC chromatogram of a polymer prepared this way see synthesis alone NB#3 p 16-17). 2) Polystyrenes of narrow molecular weight distribution can be prepared in presence of Dow Corning high vacuum grease (0.5g of grease was applied to the teflon magnetic stir bar before polymerization; for the chromatogram of a polymer synthesized this way see synthesis alone NB#3 p 89. The degree of polymerization expected from the ratio of monomer to initiator concentrations was 30 while the number obtained from GPC was 27).
3) Carboxylic acid-terminated polystyrene degrades upon storage under ambient atmosphere and light (The GPC of one such polymer, RPQ Rn 3, 6 months after storage is shown in synthesis alone NB#3 p 2-3. PS-H of similar molecular weight does not degrade this badly, but nevertheless reacts with oxygen as evidenced by the atomic composition obtained by x-ray photoelectron spectroscopy).

To summarize section 2.4.1 to 2.4.3, carboxylic acid-terminated polystyrenes in greater than 90% yield can be prepared by Quirk's reaction or solution carbonylation of polystyrl lithium, i.e by allowing small drops of living polystyrllithium to flow into a large stream of CO_2. The procedure reported by Quirk, et al., does not result in 100% acid end-group yield as claimed by the authors, unless their freeze-drying and carbonylation (at what temperature and how long it was done) procedures are drastically different than all the permutations that we have tried. However for adsorption experiments >90% carboxylic acid-terminated polystyrenes are sufficient as carboxylic acid-terminated polymers adsorb preferentially over un-functionalized polystyrenes as shown by the TLC results. Contrary to popular myth grease does not hamper anionic polymerization, particularly when one is trying to make a low molecular weight sample. **Carboxylic acid-terminated polystyrene and polystyrene degrade upon storage under ambient light and atmosphere.** Samples were (and should be) stored in a vacuum oven in the absence of light or in a nitrogen filled glove box, with aluminum foil wrapped around it. Hydroxyl-terminated polystyrenes were prepared by the solution reaction of polystyrllithium with ethylene oxide. Reaction of the hydrolyzed product with diketene in THF leads to the acetoacetyl terminated polystyrene. Synthesis of perdeuterated and tritiated polystyrenes and functionalized polystyrenes are also reported. For more details one is referred to Damo's "synthesis alone" notebooks #1 to #3, adsorption and phase separation in TLC notebook #1 and synthesis and characterization of tritium-labelled styrene and polystyrenes NB#1.

2.4.5 Synthesis of Di-Functionally-Terminated Polystyrenes[31,32,54-57]

This section summarizes all the reactions that were performed in order to prepare di-functionally-terminated polystyrenes of narrow molecular weight distribution (MWD < 1.10). In general three preparative schemes as shown in figure 2.10 are discussed in the literature.

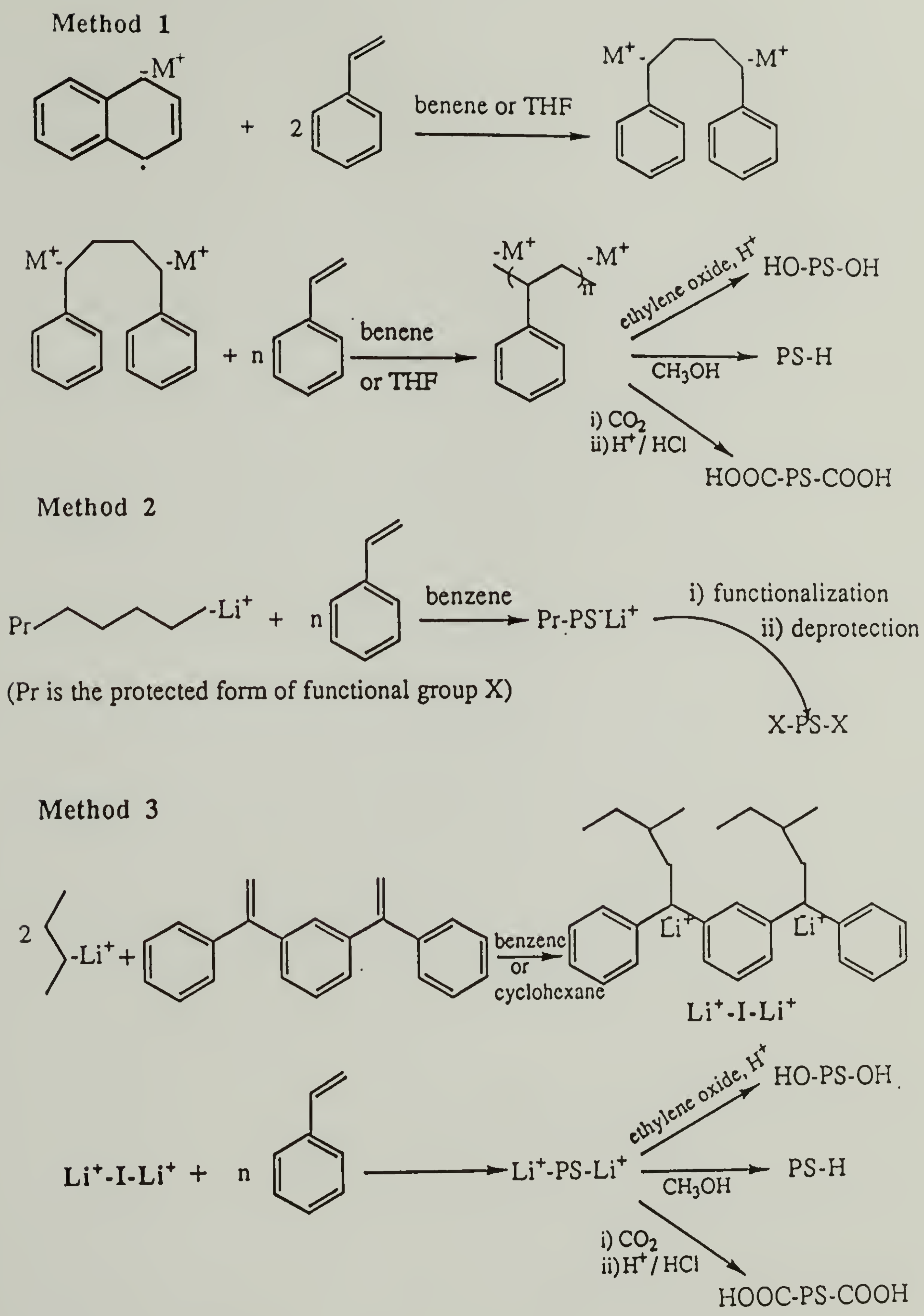
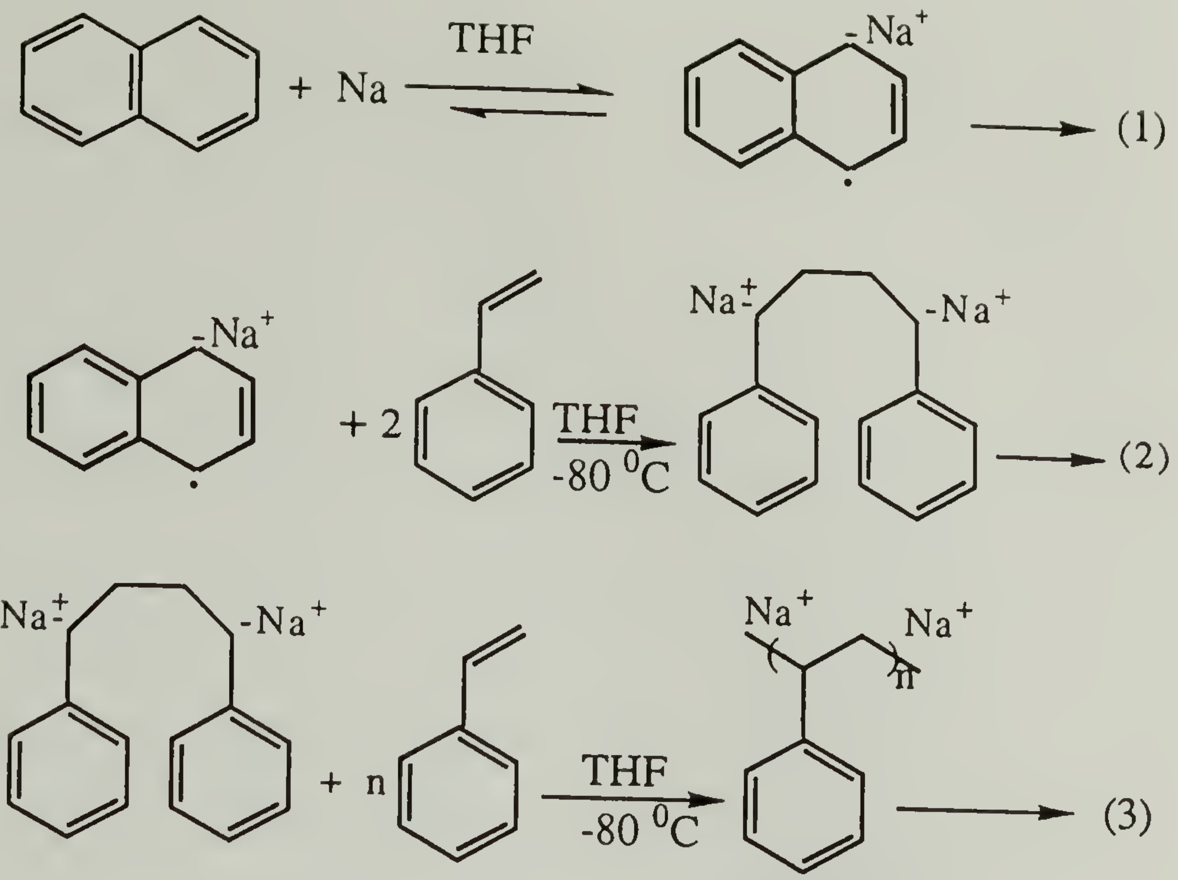


Figure 2.10 **Reported Methods for the Preparation of Di-Functionally-Terminated Polymers**

The first method involves the reaction of sodium/lithium naphthalide in THF (-78 to 25 °C) with styrene in THF (-78 to 25 °C) or in benzene at room temperature.[7, 11, 19, 20, 27, 30, 31] The second method involves the use of a organolithium initiator containing the desired functional group in the protected form.[48, 49] The third method is the one developed by Tung and involves the reaction of a hydrocarbon soluble organolithium di-initiator with styrene in a hydrocarbon solvent at room temperature.[32] The di-initiator in turn is prepared by the reaction of two molar equivalents of *sec*-butyllithium with a mole of 1,3-bis(phenylethenyl)benzene in a hydrocarbon solvent. Each one of the routes were tried and the results of the reactions are discussed in the following sections. It is to be noted here that the reactions were not performed in the same order as they are discussed.

2.4.5.1 Synthesis of Di-Functionally-Terminated Polystyrenes Using Naphthalide Anion as the Initiator

The first reaction performed along this line was the classical one reported by Szwarc.[27] It involves the reaction of sodium naphthalide and styrene in tetrahydrofuran at -80 °C. The reaction is shown in the next page. The reagents involved were prepared and purified as reported earlier.[30, 50] Few reactions were performed according to Szwarc's procedure. These resulted in polystyrenes of polydispersity greater than 2.0. The results were not surprising as sodium naphthalide was observed to form a brown slurry on cooling (insoluble in THF at -80 °C) even at very low concentrations (2.5×10^{-5} to 10^{-6} moles / 50 ml) suggesting that the initiation might be heterogeneous. Several authors [10, 11, 51, 52] have criticized Szwarc's results and suggest the use of dioxane as the solvent [10](to slow down propagation compared to initiation) or sodium biphenyl as the initiator [51, 52] in THF and various other alternatives such as performing the initiation at room temperature and propagation at -80 °C.[11, 31]



Na^+-PS-Na^+

$$Na^+\text{-PS-}Na^+ \xrightarrow[H^+/\ HCl]{CO_2} HOOC\text{-}(PS)_n\text{-}COOH$$

The best reported work, in our opinion that takes into account the viewpoints of different groups is that of McCormick, et al., working for Dow chemical company.[11] The reason for conducting the propagation reaction at low temperatures can be best understood from the following experiment. Upon adding freshly prepared sodium naphthalide solution (5ml of 0.25 M) to dry benzene (50 ml) the green color of the initiator turns flesh red color and stays that way for 15 min and then turns colorless indicating that sodium naphthalide reacts with benzene. This implies that sodium naphthalide will react with polystyrene as well. This has literature precedence as well.[11, 53] A summary of the reactions performed using sodium naphthalide as the initiator and their results are given in Table 2.10 This method did not result in samples with narrow molecular weight distribution under the conditions reported earlier. The polydispersity for most of the low molecular weight samples ($M_n <$ 80000) synthesized were greater than 1.5. Initiation at room temperature using freshly prepared sodium naphthalide and propagation by slow addition of monomer at room temperature however resulted in a polymer of desired molecular weight and marginally satisfactory molecular weight distribution of 1.21.

The draw backs of this reaction is the insolubility of sodium naphthalide at low temperatures in THF and the potential reaction of the propagating anion with the backbone at room temperature if allowed to proceed for a long time. For a detailed account of this reaction the reader is referred to experts.[9-14] Two reactions were performed using lithium naphthalide prepared in benzene as the initiator for the polymerizations in benzene. Both the reactions resulted in 70% of a polymer of number average molecular weight (M_n) twice that of the other 30% of the polymer. The best aspect of this reaction was that it did result in narrow molecular weight distribution (PDI < 1.10) for both the polymers from a given reaction. However in view of the high yield of the side product the method was abandoned.

Table 2.10 Reactions of Naphthalide Anion With Styrene

[initiator] moles/l	[styrene] moles/l	S	T_i °C	T_p °C	M_n GPC	PDI	reference
0.00025	0.04002	T	-78	-78	71043	2.07	synthesis alone NB#3 p 112
0.00005	0.0261	B	25	25	185908	1.54	synthesis alone NB#3 p 115
0.00005	0.0174	T	25	25	71139	1.21	synthesis alone NB#3 p 116
0.0005	0.0174	T	25	25	4193	1.57	synthesis alone NB#3 p 121
0.00034	0.0174	T	25	25	7097	1.58	synthesis alone NB#3 p 125
0.00015	0.02175	T	25	25	20027	1.61	synthesis alone NB#3 p 127
0.00025	0.0174	T	-78	-78	58000	1.74	synthesis alone NB#3 p 128
0.00391	0.0174	T	25	-78	19927	5.09	synthesis alone NB#3 p 130
0.00234	0.0261	T	25	-78	43230	3.80	synthesis alone NB#3 p 121
0.00391	0.0174	T	25	-78	12240	5.59	synthesis alone NB#3 p 133
0.000061	0.0261	B	25	25	51K-76%	1.04	synthesis alone NB#3 p 141
					22K-24%	1.08	
0.000096	0.0348	B	25	25	87K-77%	1.04	synthesis alone NB#3 p 145
					36K-23%	1.09	

Note: Reactions 1-10 were performed using sodium naphthalide as the initiator while 11 and 12 (†) were performed with lithium naphthalide. S stands for solvent, B for benzene, T for THF, T_i and T_p for temperatures of initiation and propagation, M_n for number average molecular weight and PDI for the polydispersity index. å implies that a drop of styrene was added first to initiate polymerization followed by the addition of the rest of the styrene.

2.4.5.2 Synthesis of Di-Functionally-Terminated Polystyrenes Using Initiators Containing a Protected Functional Group

This section discusses the result of the next set of reactions tried, i.e those based on organolithium initiators containing a protected functional group. 1,1,1-trimethoxy-4-bromobutane (contains a protected -COOH group), and the 6-iodohexyl-n-propyl acetal of acetaldehyde (contains a protected -OH group) were converted to the corresponding lithium salts by lithium-halogen exchange reaction as discussed in section 2.3.10.2. The recrystallized form of the former and the latter as synthesized by Pyati were used in benzene. Upon initiating the polymerization of 0.0435 moles of styrene with 0.0294 millimoles of the first initiator (50 ml benzene) it was observed that the solution turned yellow 6 min after the addition of styrene and turned red 18 min after. Typical time for completion of polymerization for the molecular weight which we attempted to prepare is 30-35 min if the initiator were *sec*-butyllithium. The number average molecular weight obtained from the above reaction was 110436 and the polydispersity index was 1.36. The result combined with the observation suggests that the initiation rate is smaller than the propagation rate. In the case of a polymerization reaction initiated by the second initiator it was not until 30 min after which the orange color of the polystyrllithium anion appeared in benzene. This also suggests that the initiation rate is smaller than the propagation rate. The details of polymerization reactions are presented in section 2.3.10.2. As these initiators did not result in polymers of narrow molecular weight distribution (PDI= 1.2-1.5) their utilization was abandoned.

2.4.5.3 Synthesis of Di-Functionally-Terminated Polystyrenes Using Tung's Initiator

The synthesis of dihydroxyl and dicarboxylic acid-terminated polystyrenes were performed with Tung's initiator as shown in figure 2.10 and the details are discussed in section 2.3.10.3. The number average molecular weight expected from the ratio of the monomer to initiator concentration for the reaction discussed in section 2.3.10.3 was 5000.

However the number average molecular weight obtained was 10549 (in benzene) and 13018 (in cyclohexane). The polydispersity indices were 1.38 and 1.35 respectively suggesting that the initiation rate is smaller than the propagation rate under the conditions in which Tung's initiator was used. Since the polydispersity of the samples synthesized were too high to be used in an adsorption experiment this method was abandoned.

2.4.5.4 Synthesis of Di-Functionally-Terminated Polystyrenes Using Lithium Naphthalide in Tetrahydrofuran as the Initiator with Styrene in Benzene

The synthesis of di-functionally-terminated polystyrenes of narrow molecular weight distribution was reported by Cheng, Kanga, and Nakahama, recently.[19a, 19b, 20] Cheng's method (Kanga's as well) involves the preparation of lithium naphthalide in THF using a small excess of naphthalene while Nakahama's method under the same condition uses a small excess of lithium. Lithium naphthalides were prepared by both the methods. A typical polymerization reaction is shown in figure 2.11. The gel permeation chromatogram of polystyrenes prepared by both the methods are shown in figure 2.12. From these results and the earlier results with lithium naphthalide prepared in benzene it was concluded that a small amount of low molecular weight polymer (10-15%) was a consequence of the reaction mechanism (unknown) and no attempts were made to improve it. Several di-functionally-terminated polystyrenes were synthesized and the low molecular weight polymer from the mixture was separated by fractional precipitation as discussed in section 2.3.11. The gel permeation chromatogram of polystyrenes as synthesized and after fractional precipitation are shown in figures 2.12 to 2.15. Although the yield of the desired polymer after fractional precipitation was $\leq 50\%$ the chromatograms show that its polydispersity is low enough to be used in adsorption experiments (PDI < 1.10). The polymers prepared and their GPC characteristics are shown in Table 2.11.

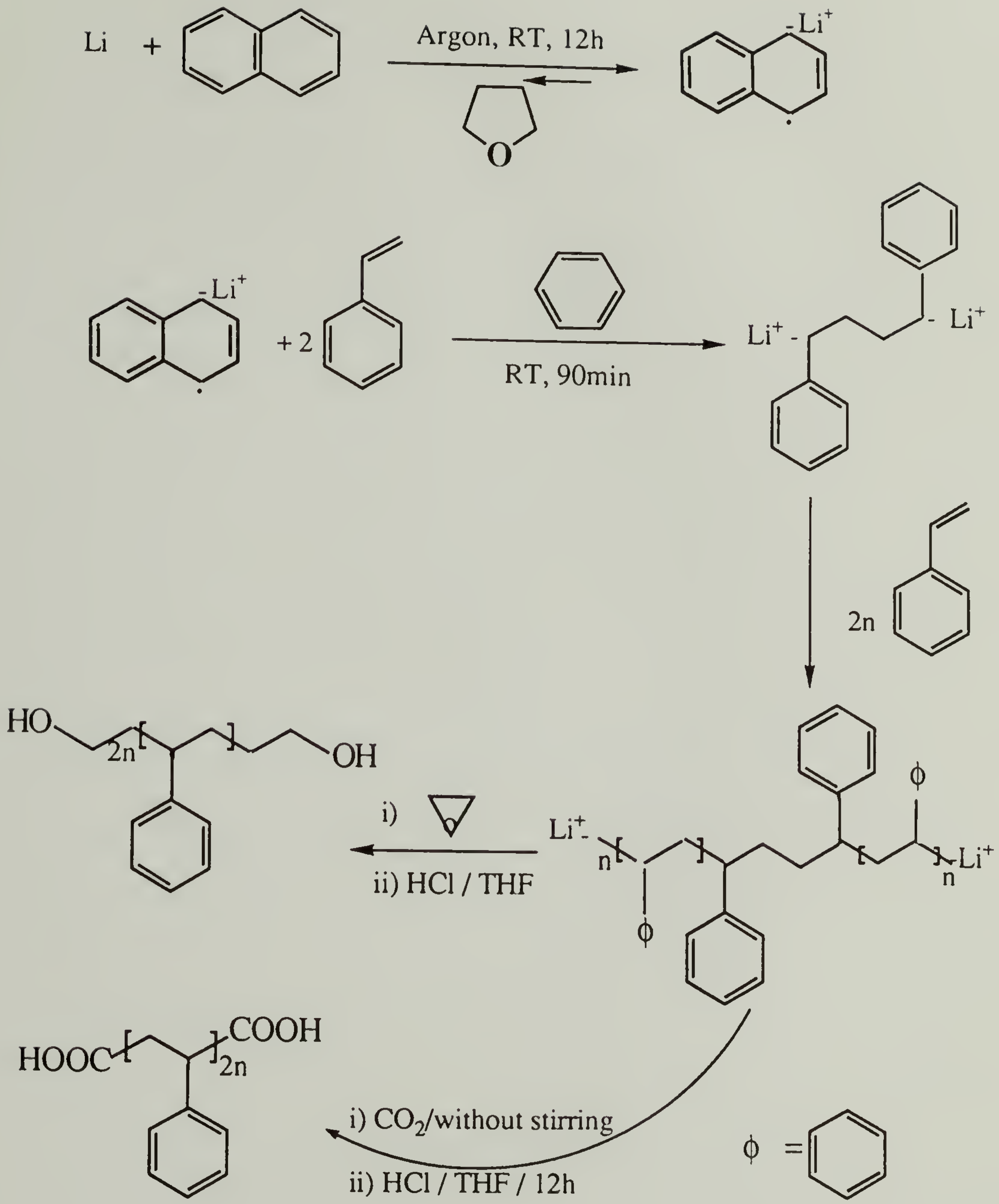


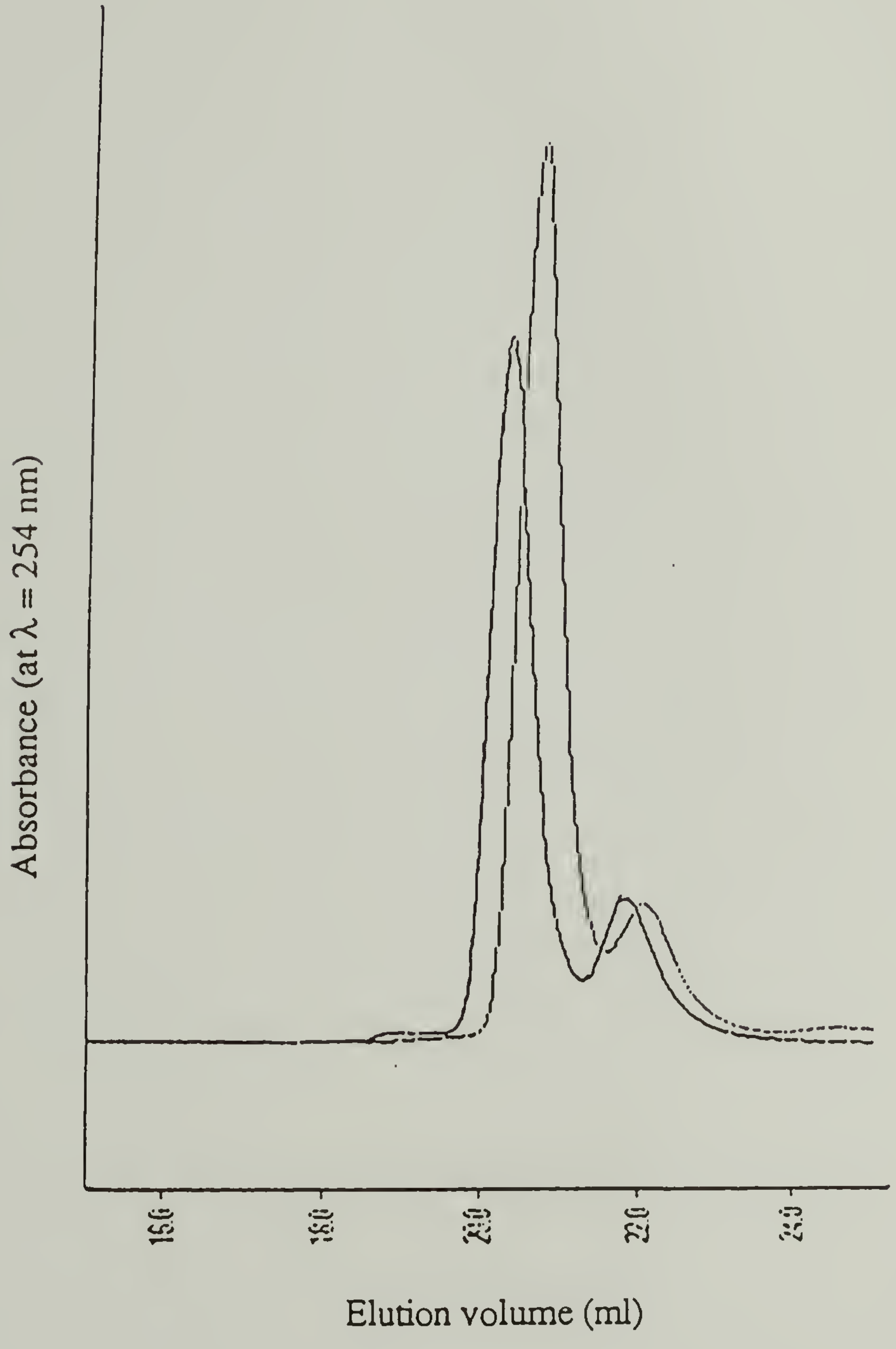
Figure 2.11 Synthesis of Functionalized Polystyrenes Initiated by Lithium Naphthalide

Tritium-Labelled polymers were prepared and fractionally purified by similar procedures. Non-radioactive polymers were prepared in parallel under identical experimental conditions and their characterization is assumed to reflect the properties of the radioactive polymers. Unless otherwise stated all polymers were purified by fractional precipitation.

Table 2.11 GPC Characteristics of Di-Functionally-Terminated Polystyrenes (HOOC-PS-COOH and HO-PS-OH)

Sample code	M_n	MWD	Lab. Note-Book reference
reaction #1 fraction 1	10000	1.09	synthesis alone NB #4 p 30-55
reaction #4 fraction 1	30000	1.06	synthesis alone NB #4 p 30-55
reaction #3 fraction 1	50000	1.05	synthesis alone NB #4 p 30-55
reaction #6 fraction 1	60000	1.05	synthesis alone NB #4 p 30-55
reaction #5 fraction 3	200000	1.04	synthesis alone NB #4 p 30-55
reaction #5 fraction 1	450000	1.04	synthesis alone NB #4 p 30-55
reaction #7 fraction 3	150000	1.05	synthesis alone NB #4 p 30-55
reaction #7 fraction 1	300000	1.04	synthesis alone NB #4 p 30-55

Note: Both HOOC-PS-COOH and HO-PS-OH samples were prepared in the same reaction in which styrene was polymerized in benzene using lithium naphthalide in THF as the initiator. This reaction invariably leads to the formation of a low molecular weight compound which appears as a tail in the GPC (see chapter 2). Therefore all samples were purified by fractional precipitation. The gel permeation chromatograms are stapled to synthesis alone note-book #4. The number average molecular weight of polystyrenes rounded to the nearest thousand alone are presented.



Number average molecular weight - 50430 (Cheng) and 66400 (Nakahama)
Poly dispersity index - 1.20 (Cheng and Nakahama)

Figure 2.12 GPC Chromatograms of Polystyrene Using Lithium Naphthalide Prepared According to Cheng (right) and Nakahama (left)

Number average molecular weight - 26300, PDI - 1.15 (PSH4)
Number average molecular weight - 44500, PDI - 1.18 (PSH3)

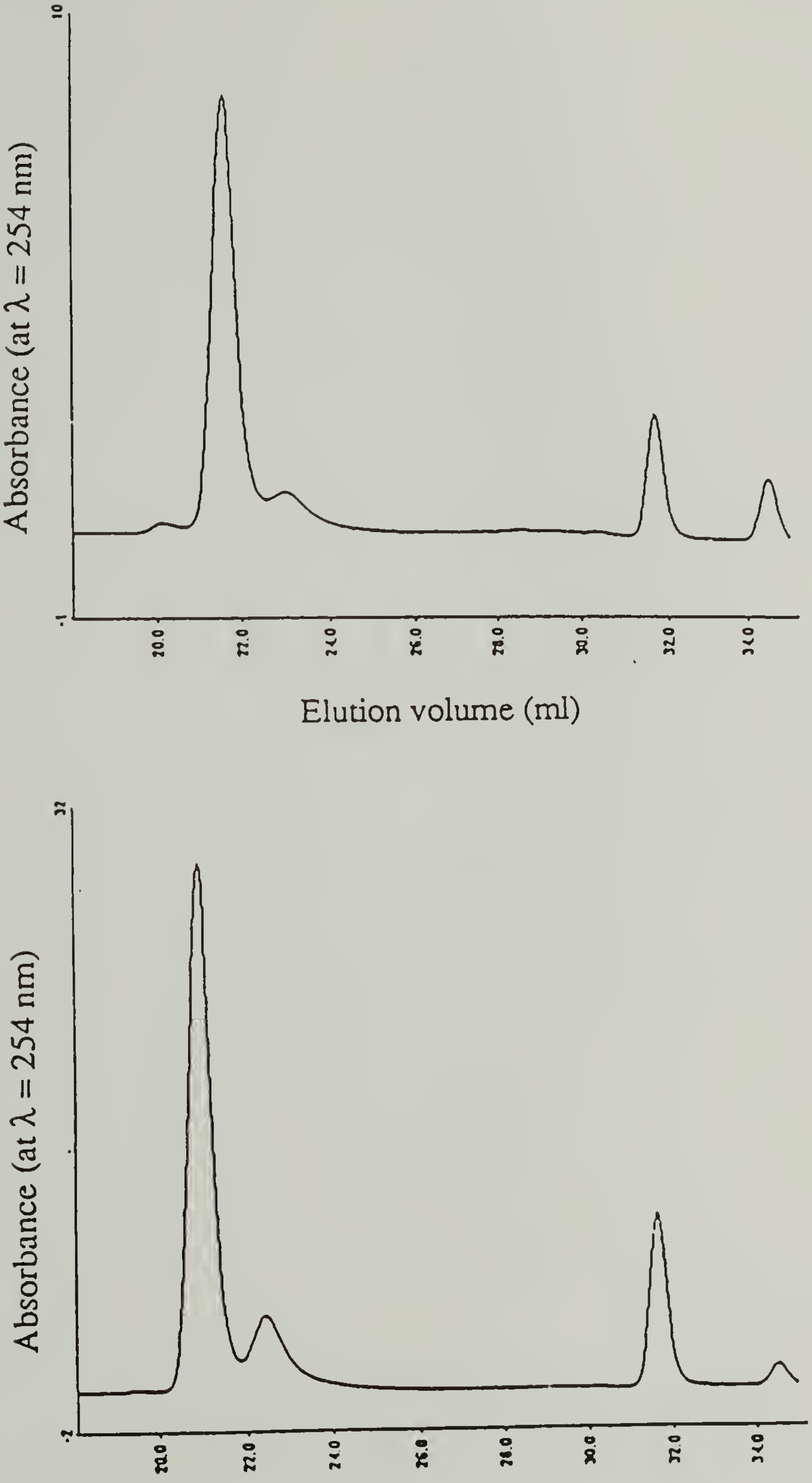
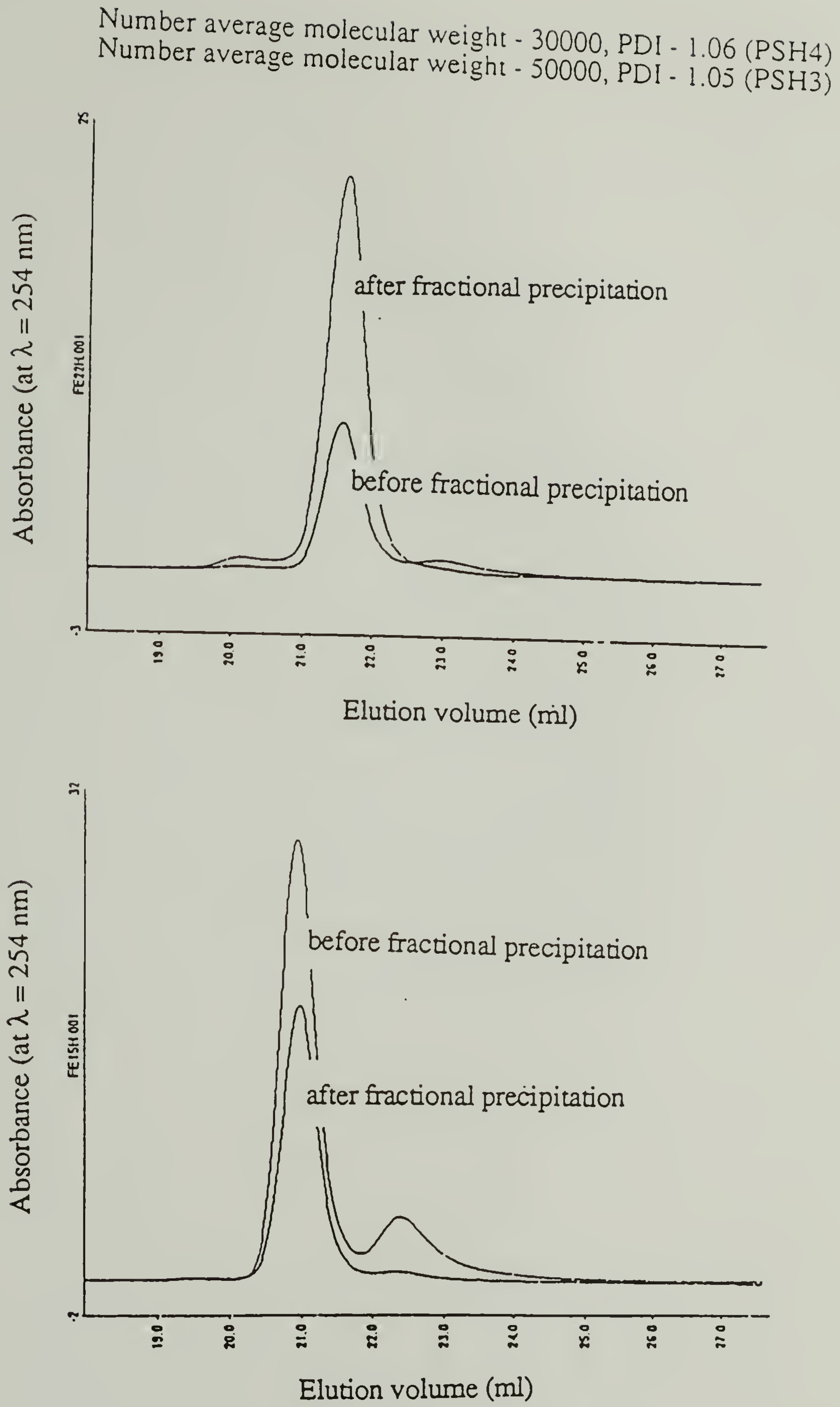


Figure 2.13 GPC Chromatograms of Polystyrene Prepared Using Lithium Naphthalide Prepared According to Nakahama, PSH4 (top) and PSH3 (bottom)



Number average molecular weight - 30000, PDI - 1.06 (PSH4)
Number average molecular weight - 50000, PDI - 1.05 (PSH3)

Figure 2.14 GPC Chromatograms of Polystyrene Prepared Using Lithium Naphthalide Prepared According to Nakahama after Fractional Precipitation, PSH4 (top) and PSH3 (bottom)

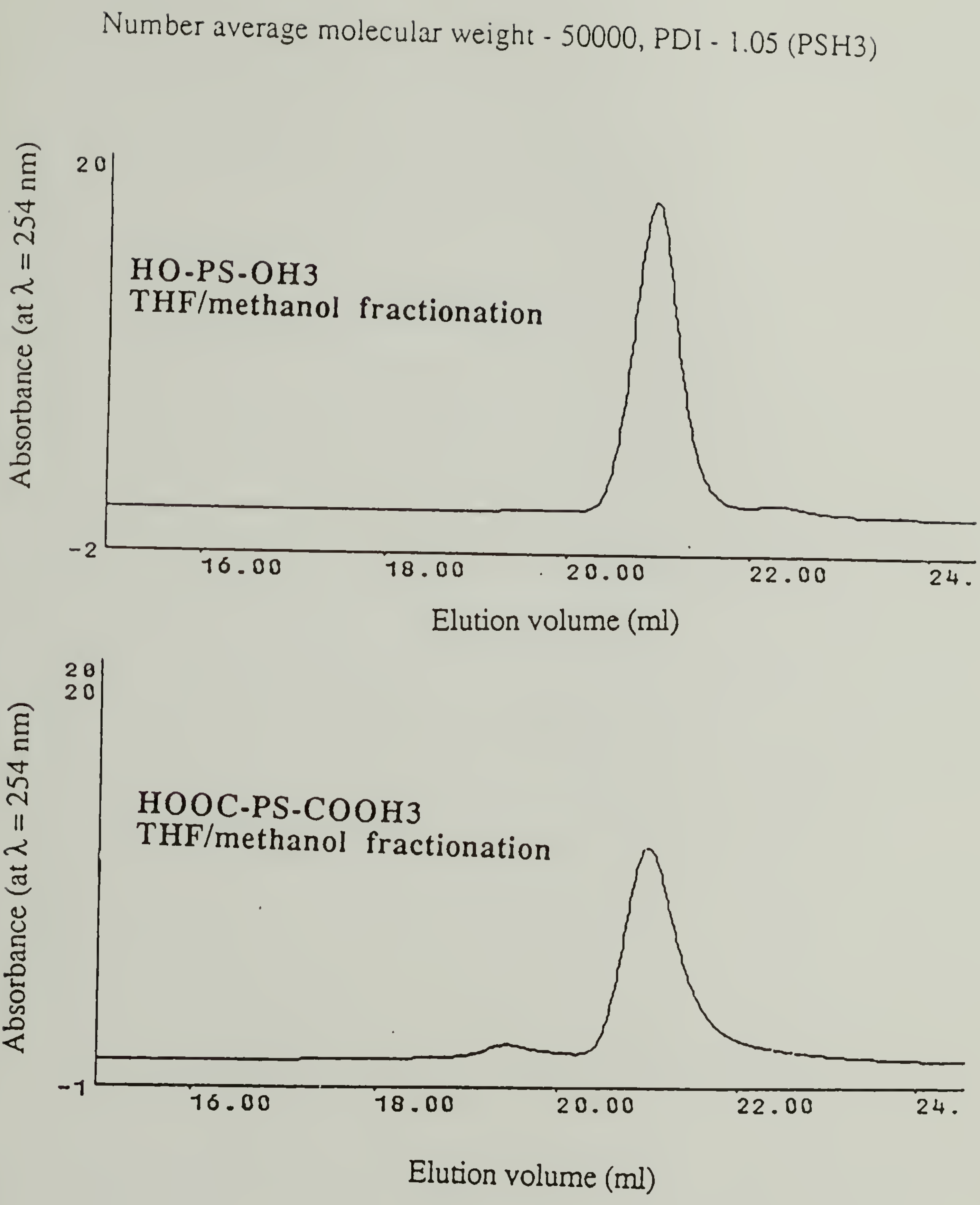


Figure 2.15 GPC Chromatograms of Hydroxyl and Carboxylic Acid-Terminated Polystyrenes after Fractional Precipitation, HO-PS-OH3 (top) and HOOC-PS-COOH3 (bottom)

2.5 Summary

The anionic synthesis of polystyrenes of narrow molecular weight distribution functionalized at one and both the chain ends, are reported. Polystyrene with a hydroxyl end-group (PS-OH) was synthesized according to Schulz and Milkovich and that with a carboxylic acid-end group (PS-COOH) was synthesized according to Quirk. A modified carbonylation procedure which essentially leads to the same result as that from Quirk's is reported. Di-functionally terminated polystyrenes of narrow molecular weight distribution were prepared by the anionic polymerization of styrene in benzene initiated by lithium naphthalide in THF. Polystyrenes terminated with hydroxyl groups at both the ends (HO-PS-OH) were prepared by the reaction of ethylene oxide with polystyrldilithium in the above reaction while that terminated with carboxylic acid-end groups (HOOC-PS-COOH) was prepared by the reaction of carbon dioxide in the absence of stirring. All the polymers prepared this way were fractionally precipitated by titrating a dilute solution in THF/toluene with methanol. The quantitative yield of the end-groups were confirmed by thin layer chromatography experiments. Perdeuterio polystyrenes and carboxylic acid-terminated polystyrenes were prepared from perdeuterio styrene by similar procedures. Tritiated polystyrenes and functionalized polystyrenes were prepared by the same procedure as well. The tritiated styrene necessary for the polymerization was prepared by the selective hydrogenation of phenylacetylene labelled at the β position by acid-base exchange reaction. It was reduced to styrene exclusively using an excess of carboxylic acid-terminated polystyrene, which competes with styrene formed in the reaction for catalytic sites eliminating its subsequent reduction to ethylbenzene. Radioactive polymers were synthesized using the tritium-labelled styrene, diluted 6-fold with cold styrene.

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CHAPTER 3

TRENDS IN ADSORPTION OF END-FUNCTIONALIZED POLYSTYRENES BY THIN LAYER CHROMATOGRAPHY

3.1 Introduction

Chromatography involves the transport of a mobile phase (eluent) along a stationary phase (adsorbent or substrate) in which the substance (adsorbate) of interest is exchanged between the two phases, both process taking place simultaneously and continuously.[1] The driving force for the transport of the eluent is the pressure differential occuring along the chromatographic bed (capillary forces) while that for the adsorbate is the difference in its activity in the mobile and stationary phase. At the leading edge of the the adsorbate band, the activity in the mobile phase exceeds that in the stationary phase while at the trailing edge the activity in the stationary phase is greater. The equilibrium of partition is not reached except at the center of the band. Adsorbates move rapidly if they prefer to stay in the mobile phase. The relative rate of migration of adsorbates is determined only by the time they spend in the stationary phase and not by their speed in the mobile phase. Different adsorbates spend different amounts of time in the stationary phase while the mobile phase is flowing past. This defines the retention time or retention value. Thin Layer Chromatography (TLC) involves a thin layer of a stationary phase in which the substance of interest is displaced by the eluent as it moves along the thin layer.

Chromatographic characterization of polymers on thin layers of adsorbents (usually porous), were carried out in the late 60's by Inagaki et al [2] at Kyoto University, Japan, and by Belenkii and Gankina [3] at St. Petersburg (formerly Leningrad., U.S.S.R) independently and simultaneously. Since that time, TLC has been used, to fractionate homopolymers according to their molecular weight, to determine molecular weight (number average molecular weight - M_n) and molecular weight distribution (MWD) of homopolymers, in the identification and separation of stereo-regular homopolymers, in the separation of random copolymers according to their composition, in the identification of linear polymers with specific endgroups, etc. Most of the work done in this field up to 1976 is summarized in the review articles of Inagaki [4], and Belenkii and Gankina.[5] A typical thin layer chromatographic experiment consists of a thin layer of adsorbent or restrainer supported or coated on a rigid glass plate or polyester film, on which the polymer of interest is deposited from solution, approximately an inch from the bottom of the film. A carrier solvent (also called eluent or developer) ascends the film by capillary action in a closed chamber and displaces the polymer to different degrees as shown in figure 3.1.1 (when compared to solvent flow). The degree of displacement is dictated by the net free energy change involved in the process and this includes the energy of interaction of the polymer segments with the surface in solution, and that of solvent molecules with the surface in solution. The differential restraining action exhibited by the thin layer of adsorbent has also been attributed to a combination of precipitation (phase separation) due to solvent depletion in the advancing front in addition to the adsorption-desorption mechanism at the restrainer-carrier interface.[4] The differential restraining action is characterized by the R_f value, defined as the ratio between the rate of migration of the sample divided by the rate of migration of the carrier (eluent).

R_f = migration rate of the sample / migration rate of the carrier

= distance travelled by the sample / distance travelled by the carrier.

Thin-layer Chromatography is a unique technique to characterize polymer adsorption as it is simple and highly sensitive to structural changes in the polymer backbone. It was illustrated earlier [6,7] that polymers with a single end group and isotopic mixtures can be detected and therefore separated in a TLC experiment. In addition this technique is inexpensive, rapid and polymers can be easily detected (as low as a μg). If the polymer contains a specific functionality (a group which interacts more strongly with the surface than the segments in a typical polymer chain - also referred to as sticky foot) at one end of a polymer chain, the rate of migration of that chain is reduced significantly when compared with that of the un-functionalized chain. This retardation is due to specific chemical interaction with the surface in question. This elegantly demonstrates the fact that the functional group in question is at the interface (particularly when the R_f changes from unity to zero on incorporating a chain end functionality) and the polymer chain is likely to be attached to the surface in a brush type configuration. An extension of this argument will be that if the migration rate of a particular polymer is retarded by the incorporation of a specific functionality at a particular location of the chain then it is most likely that the polymer is adsorbed to the surface with that part of the chain in contact with the surface. This implies that a range of polymer thin film architecture at interfaces can be synthesized using specific functionality in the polymer in well defined locations by performing thin layer chromatographic experiments (adsorption) from good solvents ($\chi_s < \chi_{sc}$ and $\chi \sim 0$).

This investigation was undertaken for two purposes: 1) to observe the trends in adsorption of end functionalized polystyrenes in different solvents and from the trends be able to rapidly select a solvent for adsorption studies and 2) to examine if it would be possible to synthesize different polymer architectures at interfaces, by the specific interaction between surface sites and organic functional groups such as hydroxyl (-OH) and carboxylic acid (-COOH) placed at the chain ends, by suitable organic synthesis. An attempt will also be made, to demonstrate, that trends in the adsorption energetics of end functionalized polystyrenes to different surfaces, from good solvent conditions can be understood qualitatively using thin layer chromatography.

It was reported earlier[8] that R_f values for polystyrene on silica and alumina from good solvent conditions are 1 and are independent of molecular weight up to 1.8×10^6. Mobility of polymers of molecular weights higher than this has not been reported from good solvent conditions (for that matter any solvent conditions), on any surface. It is possible that the earlier workers did not observe a molecular weight dependence of R_f, from good solvent conditions because the critical energy needed for adsorption [9,10] was probably not reached during the time scale of TLC measurements. One cannot wait for equilibrium adsorption to take place under TLC conditions as it might take a plate of infinitely long length and cumbersome experimental conditions. One way to accomplish this objective is to increase the number of segments on the polymer chain, i.e., to increase the molecular weight of the polymer so that the critical energy needed for adsorption could be reached during the time scale of TLC measurements (greater the number of segments per chain, greater is the probability of surface-segment contacts).

Towards the objectives, the molecular weight dependence of R_f from good solvents such as benzene are reported for polystyrene [PS-H], hydroxyl end-terminated polystyrenes [PS-OH and HO-PS-OH], and carboxylic acid end-terminated polystyrenes [PS-COOH and HOOC-PS-COOH], on silica and alumina thin layers. An attempt is made to explain qualitatively the molecular weight dependence of R_f for the end functionalized as well as the un-functionalized polymers, from the thermodynamics of polymer solutions and polymer adsorption theories. It is also proposed that TLC could be used to understand polymer architectures at interfaces from a plot of R_f vs Molecular weight for different degrees of functionalization in the molecular weight range $< 1 \times 10^6$.

3.2 Experimental

3.2.1 Materials

Polystyrenes of number average molecular weight (M_n) less than 100,000 and hydroxyl and carboxylic acid end - functionalized polystyrenes were synthesized by anionic polymerization of styrene. The synthetic procedures and the results of GPC characterization are discussed in detail in chapter 2. Anionic polymerization techniques enable the preparation of polymers of very high molecular weight and narrow molecular weight distribution, with or without specific end groups.[13, 14] Polystyrenes of M_n greater than 100,000 and molecular weight distribution (MWD) less than 1.10 were purchased from Polysciences, inc., and were used as received.

Several eluents, namely benzene (Aldrich sure seal grade), THF (Aldrich sure seal grade), chloroform, methylene chloride, pentane, ethyl acetate and toluene (Fisher spectroscopic grade) were used of which benzene, toluene, THF and chloroform were purified before use. Benzene and toluene were distilled from calcium hydride, chloroform from phosphorus pentoxide and THF from sodium benzophenone dianion. The rest of the solvents were used as received. The solvent strength values of these eluents are given Table 3.2.1.

3.2.2 Thin Layer Chromatography (TLC)

Silica gel thin layers (8 cm x 2 cm cut from Eastman Kodak Chromatogram sheet 13181) and aluminum oxide (IB-F thin layers, 8 cm x 2 cm purchased from J.T.Baker Chemical Co.) thin layers used for the characterization of individual polymers were conditioned in an oven between 150-200 °C for at least 7 days. Silica gel thin layers (250 µm thick, 60 Å mean pore diameter purchased from Aldrich) and preparative alumina thin layers (250 µm thick purchase from Analtech, Inc.) supported on 20 X 20 cm glass were used in the simultaneous characterization of polymer samples of different molecular weight, containing a particular functionality, say PS-OH. Both plate types were conditioned at 150-200 °C for at least 1 h prior to use. TLC was carried out by applying 5-10 µg of polymer as a circular spot of diameter 2 to 3 mm (10 µL GC syringe was used) 4 cm from the bottom of the plate. Elution (the solvent front was allowed to proceed 6 - 9 cm) was carried out in a filter-paper-lined TLC tank (Aldrich) filled to 3 cm depth with eluent. After elution the TLC plates were dried in an oven at 150-200 °C for 15 min and the samples were viewed as dark spots in a fluorescent background under a UV ($\lambda = 254$ nm) lamp. R_f values are reported in the standard fashion (R_f = elution distance of sample / elution distance of eluent). R_f values obtained on different TLC plates of the same adsorbent material were normalized to the R_f values of low molecular weight PS-H (freshly synthesized) run on the same plate. Two low molecular weight standards (benzophenone and 2,6-di-*tert*-butyl-4-methylphenol) were run on each plate to ensure that the activity of different plates was the same. R_f values are reproducible within 5% for TLC plates from a given source. The absolute R_f values obtained for a given polymer on a given adsorbent are dependent on the source of the TLC plate. Similar trends were seen on all plates regardless of the source. The eluents used and their properties are reported in Table 3.1.[11,15]

Table 3.1 Solvent Strength Values

Solvent	ε_o (silica gel)	ε_o (alumina)
pentane	0.0	0.0
benzene	0.25	0.32
chloroform	0.26	0.40
methylene chloride	0.32	0.42
ethyl acetate	0.38	0.58
tetrahydrofuran	0.35	0.45
toluene	0.22	0.29

3.3 Results and Discussion

Polystyrene (PS-H), hydroxyl-terminated polystyrene (PS-OH) and carboxylic acid-terminated polystyrene (PS-COOH) were prepared by anionic polymerization of styrene in benzene using *sec*-butyllithium as the initiator and reaction of the resulting polystyrllithium with methanol (for PS-H), ethylene oxide followed by HCl / THF (for PS-OH) or CO_2 (in the presence of TMEDA) followed by HCl / THF (for PS-COOH). Polystyrenes with hydroxyl and carboxylic acid functionality at both the chain ends were prepared by the anionic polymerization of styrene in benzene using lithium naphthalide in THF as the initiator and the reaction of the resulting polystyrllithium dianion with ethylene oxide followed by HCl / THF (for HO-PS-OH) or CO_2 (in the absence of stirring) followed by HCl / THF (for HOOC-PS-COOH). Samples of the di-functionally terminated polymers of narrow molecular weight distribution were obtained by fractional precipitation. The synthetic and purification procedures are discussed in detail in Chapter 2.

Thin-layer chromatography was carried out by using commercial silica and alumina chromatogram plates. Figure 3.1 shows plots of R_f vs molecular weight for PS-H (o), PS-OH (■), and PS-COOH(▲) eluted with benzene on silica and alumina thin layers, respectively. The data are shown in Table 3.2. The shapes of eluted samples of PS-H with number average molecular weight less than ~ 100,000 was close to the shape of the initial spot. PS-H with M_n between 100,000 and 600,000 exhibited a thin line (3-6 mm in length) with convex outer boundaries. PS-H with M_n greater than 600,000 exhibited an inverted ω-shape with polymer concentrated along the convex lines. All functionalized polymers that eluted had a convex lens type line shape. Because of this "spreading", all R_f values were computed from averages of the maximum and minimum elution distance. This difference ranged from 4 to 10 mm.

Benzene is a good solvent for PS-H, and high R_f values (o) are observed for samples with molecular weights less than ~ 10^5 on both alumina and silica. Samples with M_n values higher than these adsorb to the aluminum oxide or silica surface and exhibit lower R_f values. These samples are of the critical molecular weight (have the critical energy) necessary for adsorption on the "TLC time scale". Samples with M_n greater than 2,000,000 have R_f values equal to 0, and thus do not desorb from either silica or alumina into benzene. It should be recognized that adsorption/desorption kinetics play a critical role in TLC (R_f) measurements and that these conditions do not reproduce static adsorption experimental conditions but merely reflect relative propensity for adsorption and

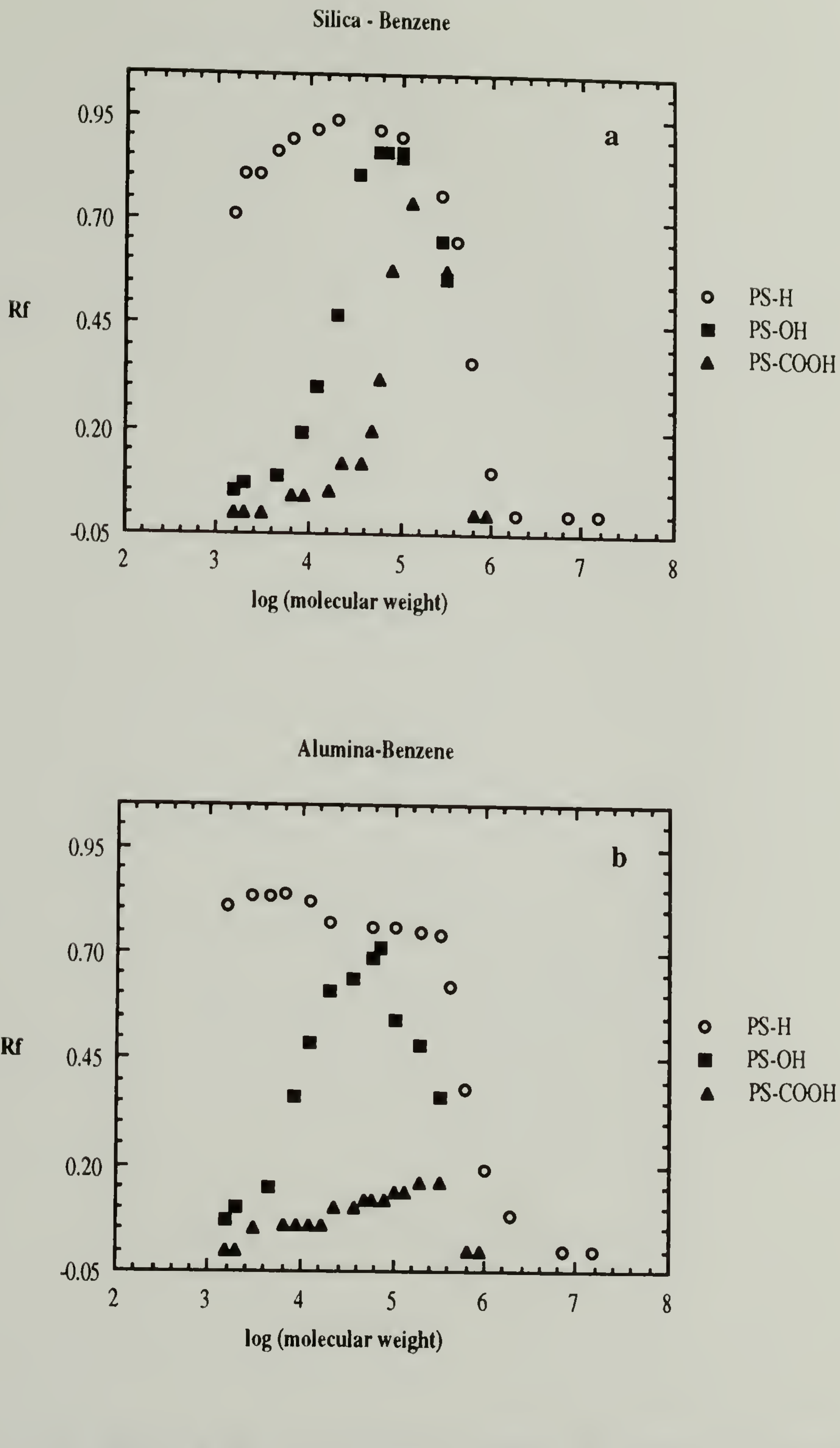


Figure 3.1 (a) Plots of R_f vs molecular weight for PS-H (o), PS-OH (■), and PS-COOH (▲) eluted with benzene on silica. (b) Analogous data on alumina

Table 3.2 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - benzene

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
1500	3.176	0.00	0.05	0.71	0.0	0.07	0.81
2000	3.301	0.0	0.07	0.81	0.0	0.10	
2800	3.447			0.81			0.83
3000	3.477	0.00			0.05		
4300	3.633			0.86			0.83
4400	3.643		0.09			0.15	
6500	3.813			0.89			0.84
7100	3.851	0.04			0.06		
8200	3.914		0.19			0.36	
9000	3.954	0.04			0.06		0.82
12000	4.079	0.04	0.30	0.92	0.06	0.49	
16800	4.225	0.05			0.06		
20000	4.301		0.47	0.94		0.61	0.77
23000	4.362	0.12			0.10		
36300	4.560		0.81			0.64	
37000	4.568	0.12			0.10		
47000	4.672	0.20			0.12		
58000	4.763		0.86	0.92		0.69	0.76
60000	4.778	0.32			0.12		
70500	4.848		0.86			0.71	

Continued, next page

Table 3.2 Continued

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
78000	4.892	0.58			0.12		
100000	5.0	0.85	0.86	0.90	0.14	0.54	0.76
133000	5.124	0.74			0.14		
200000	5.301				0.16	0.48	0.75
280000	5.447			0.76			
290000	5.462		0.65				
320000	5.505	0.58	0.56		0.16	0.36	0.74
400000	5.602			0.65			0.62
600000	5.778			0.36			0.38
624000	5.795	0.0			0.00		
825000	5.916	0.0			0.00		
980000	5.991			0.10			0.19
1860000	6.270			0.00			0.08
7000000	6.845			0.00			0.00
15000000	7.176			0.00			0.00
172 (S1)		0.34	0.29	0.33	0.54	0.48	0.45
220 (S2)		0.72	0.66	0.69	0.78	0.72	0.84

Note: S1 is benzophenone and S2 is 2,6-di-tert-butyl-4-methylphenol. The data was taken from p 60 - 70 of TLC - polymer adsorption and phase separation note book #1.

desorption. Under static adsorption conditions with greater contact time, samples with lower molecular weights than one would naively predict from these plots may adsorb from polymer solution and likewise higher molecular weight samples may desorb into solvent.

The low molecular weight samples of PS-OH and PS-COOH exhibit elution behavior markedly different from PS-H samples of the same molecular weight. PS-COOH samples with M_n less than 37,000 show R_f values less than 0.1 on silica (Figure 3.1a). The carboxylic acid group is an effective sticky foot in this molecular weight regime under these conditions. As the molecular weight is increased, adsorption becomes less favorable, and at $M_n = 99,000$, the observed R_f is essentially the same as a PS-H sample of similar molecular weight. At this molecular weight, the sticky foot/surface enthalpic interaction is not sufficient to overcome the combination of entropy loss of the large chain, the loss of polymer/solvent interactions, and the loss of solvent/surface interactions incurred on adsorption. This effect was observed for thiol-terminated polystyrenes (PS-SH) adsorbed to gold from THF solution.[22] Increasing the molecular weight further causes the R_f to decrease as the critical molecular weight for adsorption of un-functionalized PS-H is reached. The carboxylic acid is a strong sticky foot for alumina support (figure 3.1b), and only small differences in elution behavior are observed as the molecular weight is varied. The hydroxyl group is a relatively (to -COOH) weak sticky foot, and R_f value changes for PS-OH are observed at lower molecular weights than are observed for PS-COOH on both silica and alumina. All PS-OH samples elute to some extent under these eluent conditions.

Figures 3.2 to 3.5 show data analogous to that presented in Figure 3.1 for eluents THF, chloroform, ethyl acetate, and toluene. The corresponding data are shown in Tables 3.3 to 3.7, Table 3.7 being an additional table for a pentane/methylene chloride (3/7, v/v) mixture. All the eluents are good solvents for PS-H with the exception of pentane and interact strongly with silica and alumina as shown in Table 3.1.

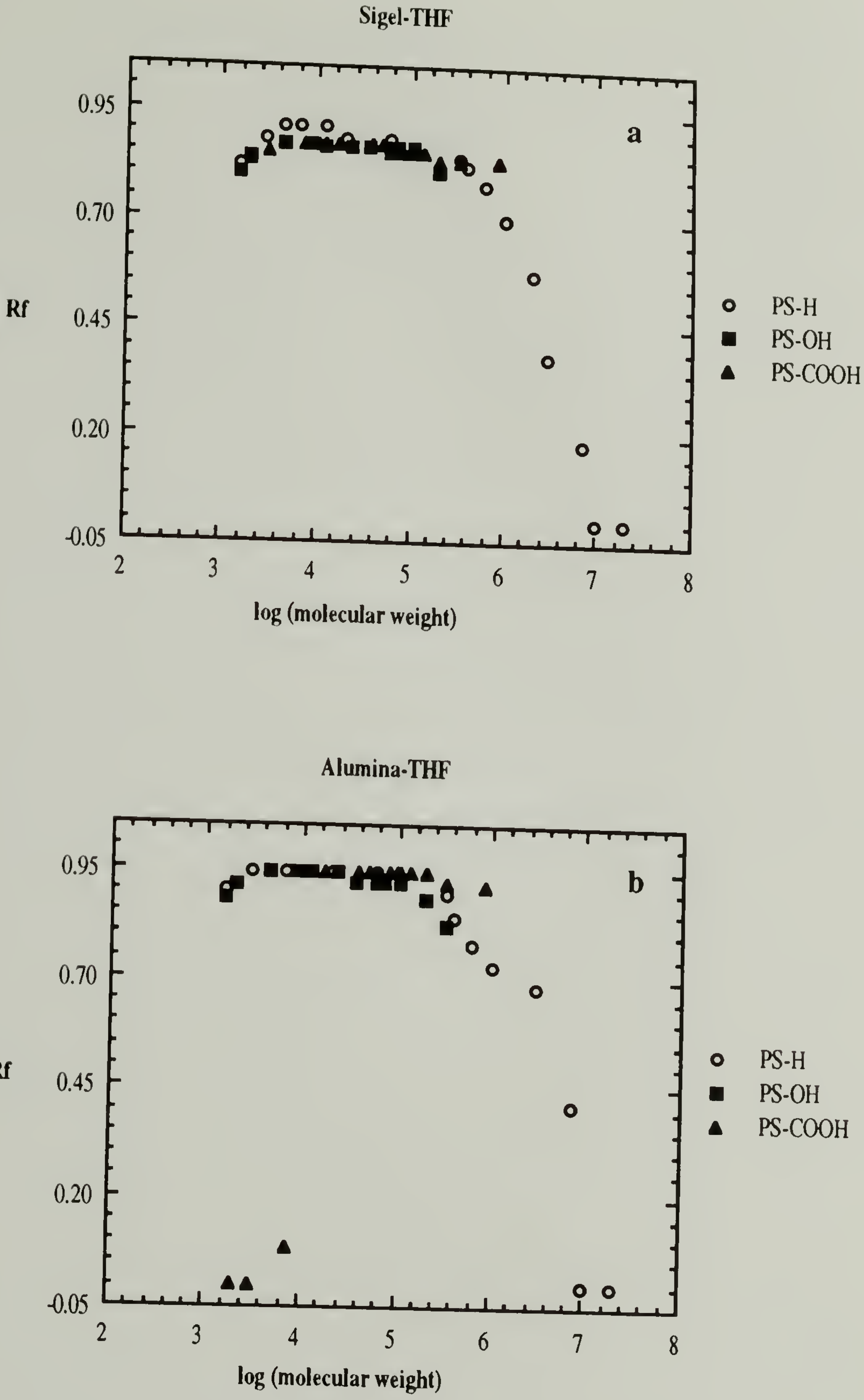


Figure 3.2 (a) Plots of R_f vs molecular weight for PS-H (o), PS-OH (■) and PS-COOH (▲) eluted with THF on silica. (b) Analogous data on alumina

Table 3.3 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - tetrahydrofuran

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
1500	3.176	0.83	0.80	0.82	0.0	0.88	0.90
2000	3.301	0.83	0.84			0.91	
2800	3.447			0.88			0.94
3000	3.477	0.85	0.85		0.0		
4300	3.633			0.91			0.94
4400	3.643		0.87			0.94	
6500	3.813			0.91			0.94
7100	3.851	0.87			0.08		
8200	3.914		0.87			0.94	
9000	3.954	0.87			0.94		
12000	4.079	0.87	0.86	0.91	0.94	0.94	0.94
16800	4.225	0.89			0.94		
20000	4.301		0.86	0.88		0.94	0.94
23000	4.362	0.87			0.94		
36300	4.560		0.86			0.92	
37000	4.568	0.87			0.94		
47000	4.672	0.89			0.94		
58000	4.763		0.86	0.88		0.92	0.94
60000	4.778	0.85			0.94	0.92	0.94
70500	4.848		0.86	0.86		0.92	

Continued, next page

Table 3.3 Continued

M_n (GPC)	$\log (M_n)$	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
78000	4.892	0.85			0.94		
100000	5.0	0.85	0.86		0.94	0.92	0.92
133000	5.124	0.85			0.94		
200000		0.83			0.94	0.88	
320000	5.505	0.83	0.86	0.84	0.92	0.82	0.89
400000	5.602			0.82			0.84
600000	5.778			0.78			0.78
624000	5.795	0.83			0.91		
825000	5.916	0.83			0.90		
980000	5.991			0.70			0.73
2000000	6.301			0.57			
3000000	6.477			0.38			0.68
7000000	6.845			0.18			0.41
10000000	7.000			0.00			0.00
20000000	7.301			0.00			0.00
172 (S1)		0.69	0.71	0.70	0.81	0.82	0.81
220 (S2)		0.74	0.75	0.76	0.83	0.84	0.83

Note: S1 is benzophenone and S2 is 2,6-di-tert-butyl-4-methylphenol. The data was taken from p 71 - 79 of TLC - polymer adsorption and phase separation note book #1.

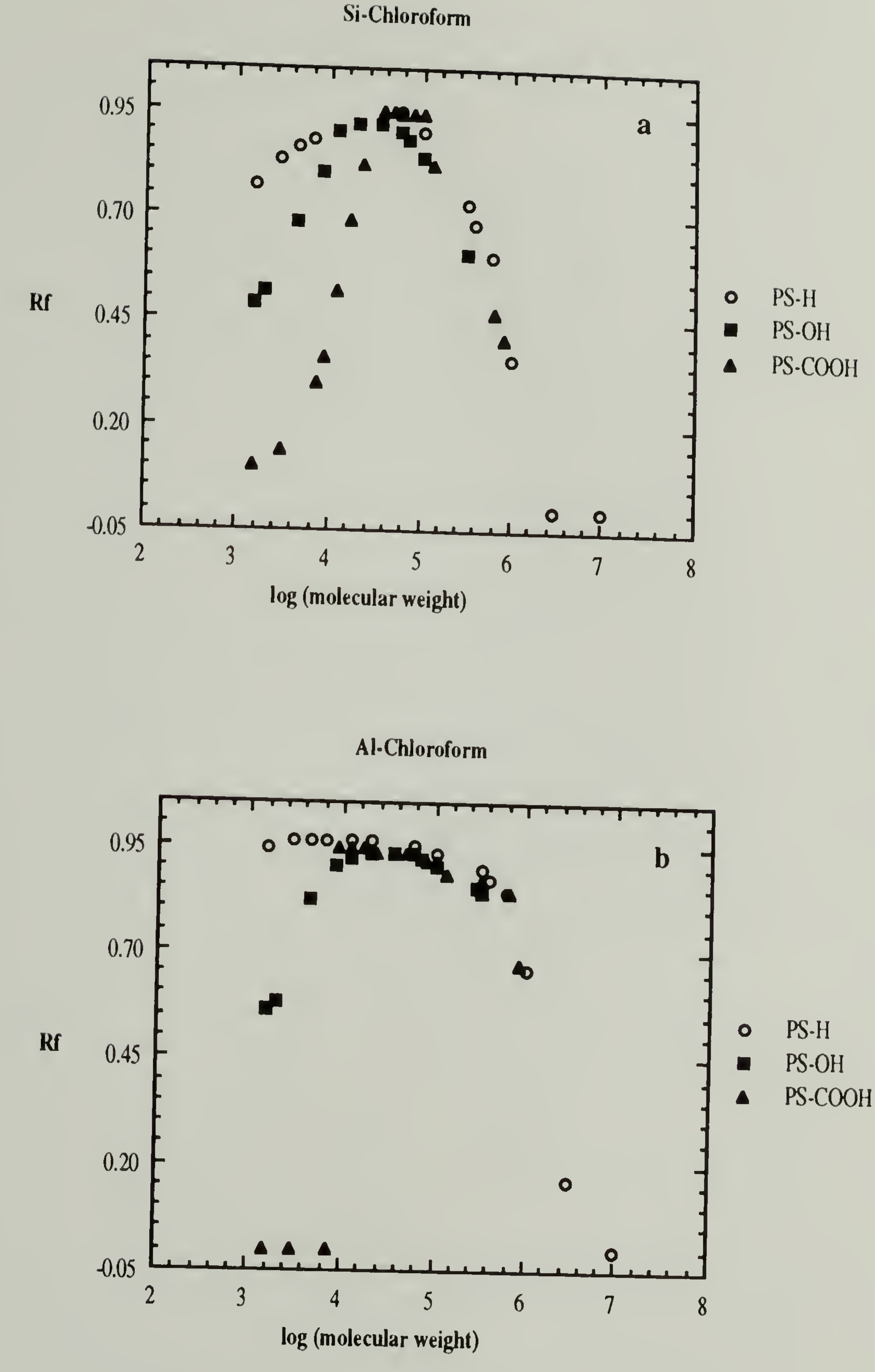


Figure 3.3 (a) Plots of R_f vs molecular weight for PS-H (o), PS-OH (■) and PS-COOH (▲) eluted with chloroform on silica. (b) Analogous data on alumina

Table 3.4 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - chloroform

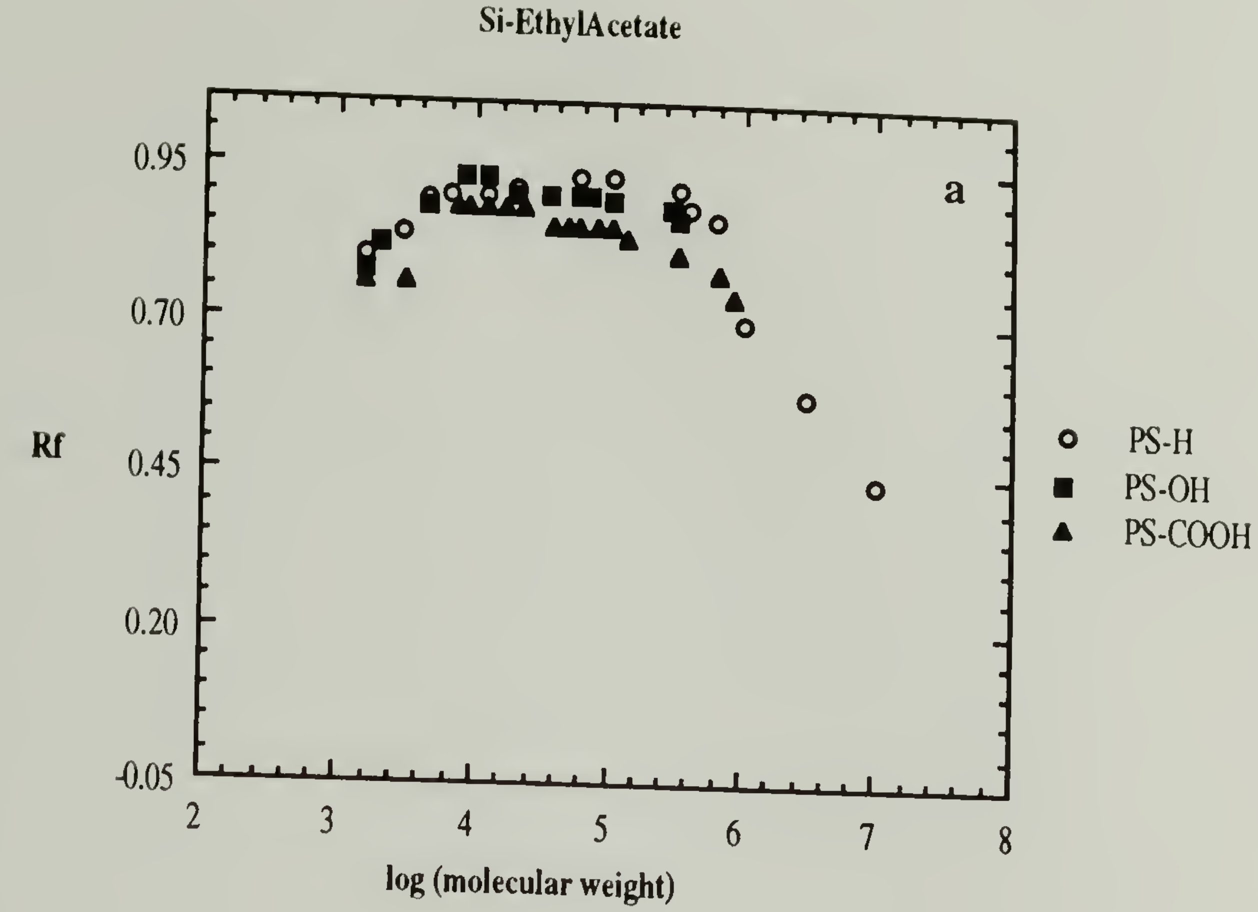
M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
1500	3.176	0.10	0.49	0.77	0.00	0.56	0.94
2000	3.301		0.52			0.58	
2800	3.447			0.83			0.96
3000	3.477	0.14			0.00		
4300	3.633			0.86			0.96
4400	3.643		0.68			0.82	
6500	3.813			0.88			0.96
7100	3.851	0.30			0.00		
8200	3.914		0.80			0.90	
9000	3.954	0.36			0.94		0.96
12000	4.079	0.52	0.90	0.90	0.94	0.92	
16800	4.225	0.69			0.94		
20000	4.301		0.92	0.90		0.93	0.96
23000	4.362	0.82			0.93		
36300	4.560		0.92			0.93	
37000	4.568	0.95			0.94		
47000	4.672	0.95			0.93		
58000	4.763		0.90	0.93		0.93	0.95
60000	4.778	0.94			0.93		
70500	4.848		0.88			0.92	

Continued, next page

Table 3.4 Continued

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
78000	4.892	0.94			0.91		
100000	5.0	0.94	0.84	0.90	0.91	0.90	0.93
133000	5.124	0.82			0.88		
200000							
280000							
290000	5.462		0.76			0.85	
320000	5.505	0.52	0.61	0.73	0.86	0.84	0.89
400000	5.602			0.68			0.89
600000	5.778			0.60			0.87
624000	5.795				0.84		
825000	5.916	0.41			0.67		
980000	5.991			0.36			0.84
3000000	6.477			0.00			0.66
10000000	7.000			0.00			0.16
20000000	7.301						0.00
172 (S1)		0.56	0.54	0.54	0.76	0.74	0.78
220 (S2)		0.72	0.69	0.69	0.86	0.86	0.88

Note: S1 is benzophenone and S2 is 2,6-di-tert-butyl-4-methylphenol. The data was taken from p 80 - 86 of TLC - polymer adsorption and phase separation note book #1.



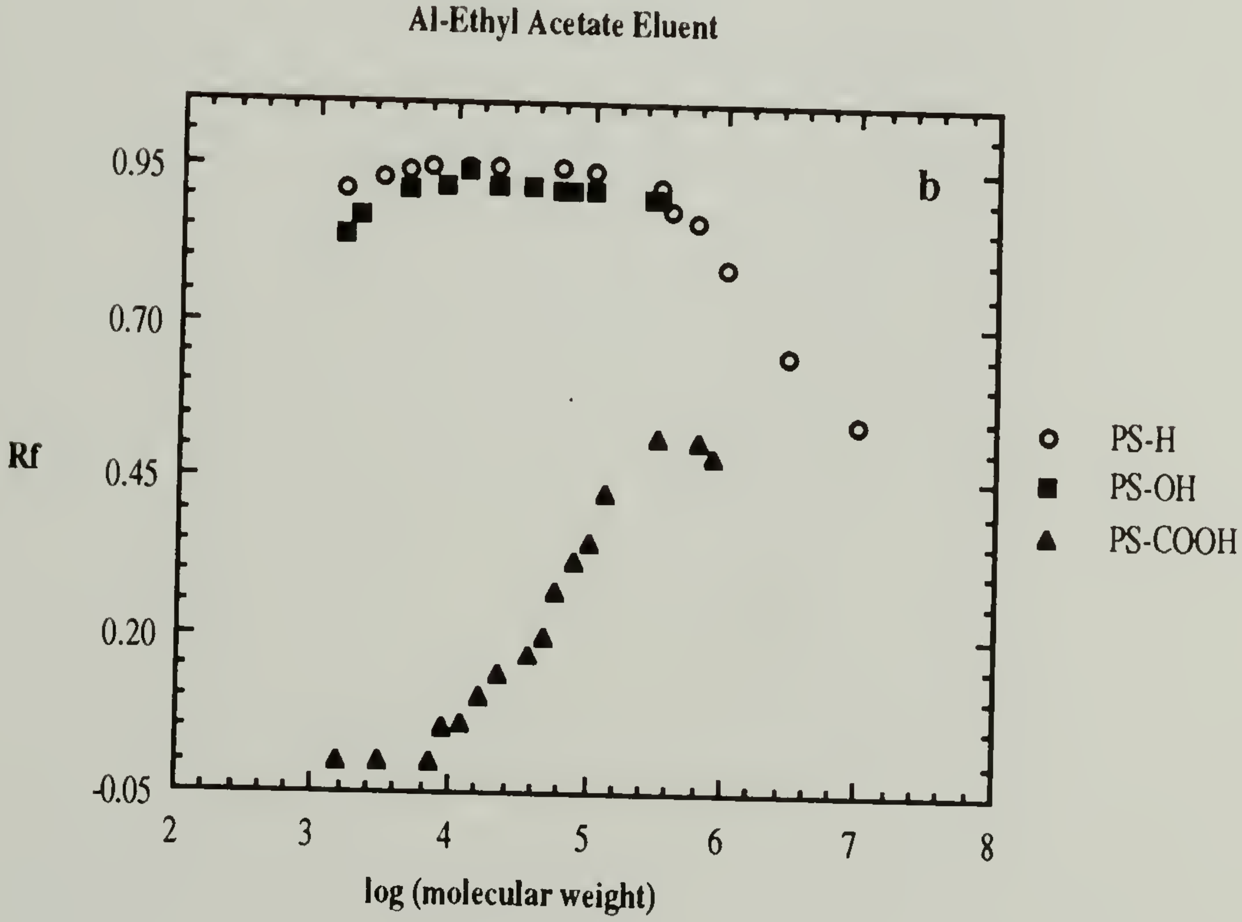


Figure 3.4 (a) Plots of R_f vs molecular weight for PS-H (o), PS-OH (■) and PS-COOH (▲) eluted with ethyl acetate on silica. (b) Analogous data on alumina

Table 3.5 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - ethyl acetate

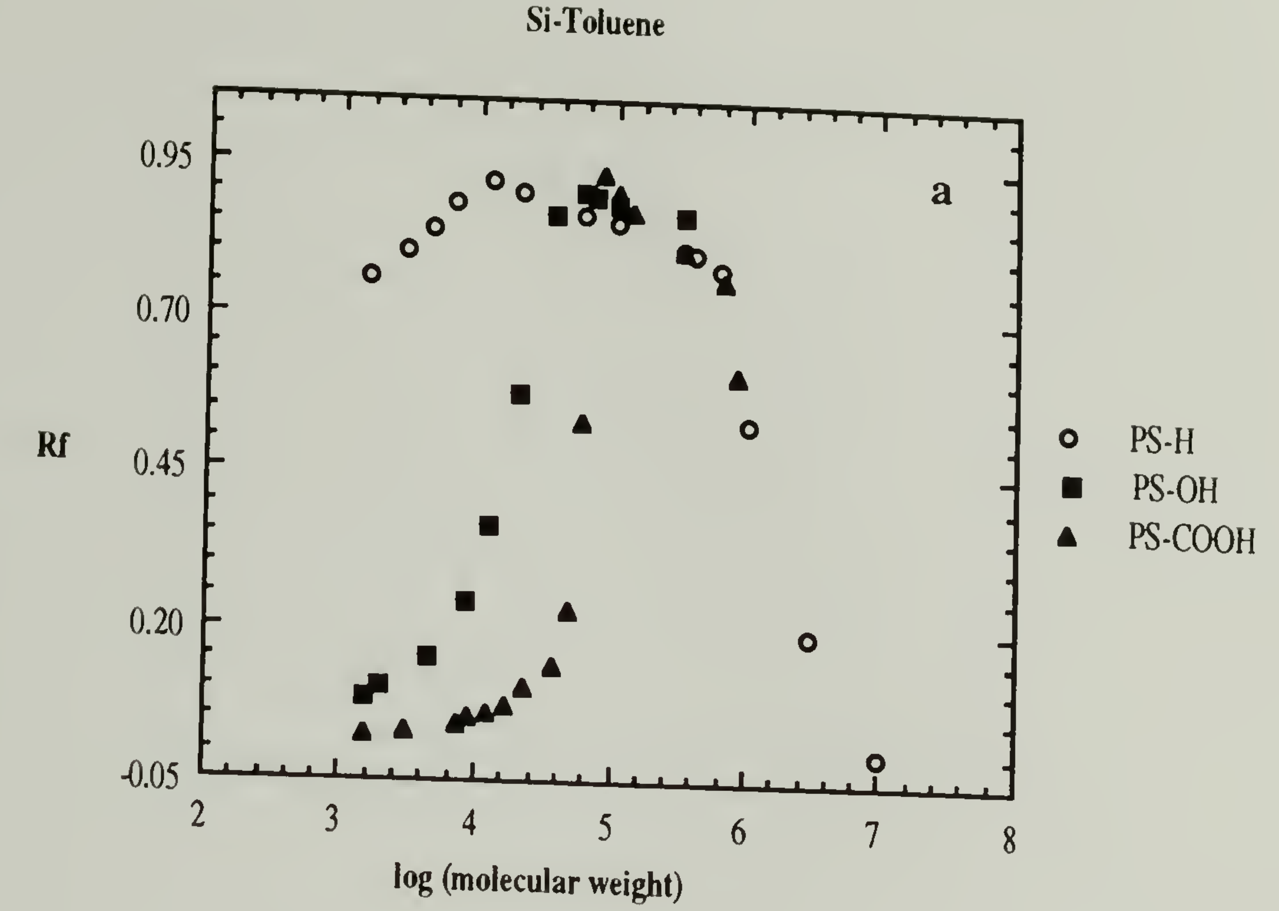
M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
1500	3.176	0.76	0.78	0.80	0.0	0.84	0.91
2000	3.301		0.82			0.87	
2800	3.447			0.84			0.93
3000	3.477	0.76			0.0		
4300	3.633			0.89			0.94
4400	3.643		0.88			0.91	
6500	3.813			0.90			0.95
7100	3.851	0.88			0.0		
8200	3.914		0.93			0.92	
9000	3.954	0.88			0.0		0.95
12000	4.079	0.88	0.93	0.90	0.06	0.94	
16800	4.225	0.88			0.1		
20000	4.301		0.90	0.91		0.92	0.95
23000	4.362	0.88			0.14		
36300	4.560		0.90			0.92	
37000	4.568	0.85			0.17		
47000	4.672	0.85			0.2		
58000	4.763		0.90	0.93		0.91	0.95
60000	4.778	0.85			0.27		
70500	4.848		0.90			0.91	

Continued, next page

Table 3.5 Continued

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
78000	4.892	0.85			0.32		
100000	5.0	0.85	0.89	0.93	0.35	0.91	0.94
133000	5.124	0.83			0.43		
200000			0.88				
280000				0.93			0.92
290000	5.462		0.88			0.90	
320000	5.505	0.81	0.86	0.91	0.52	0.90	0.88
400000	5.602			0.88			0.87
600000	5.778			0.86			0.86
624000	5.795	0.78			0.51		
825000	5.916	0.74			0.49		
980000	5.991			0.70			0.79
3000000	6.477			0.58			0.65
10000000	7.000			0.44			0.54
172 (S1)		0.70	0.71	0.70	0.82	0.82	0.82
220 (S2)		0.73	0.74	0.72	0.84	0.84	0.84

Note: S1 is benzophenone and S2 is 2,6-di-tert-butyl-4-methylphenol. The data was taken from p 89 - 96 of TLC - polymer adsorption and phase separation note book #1.



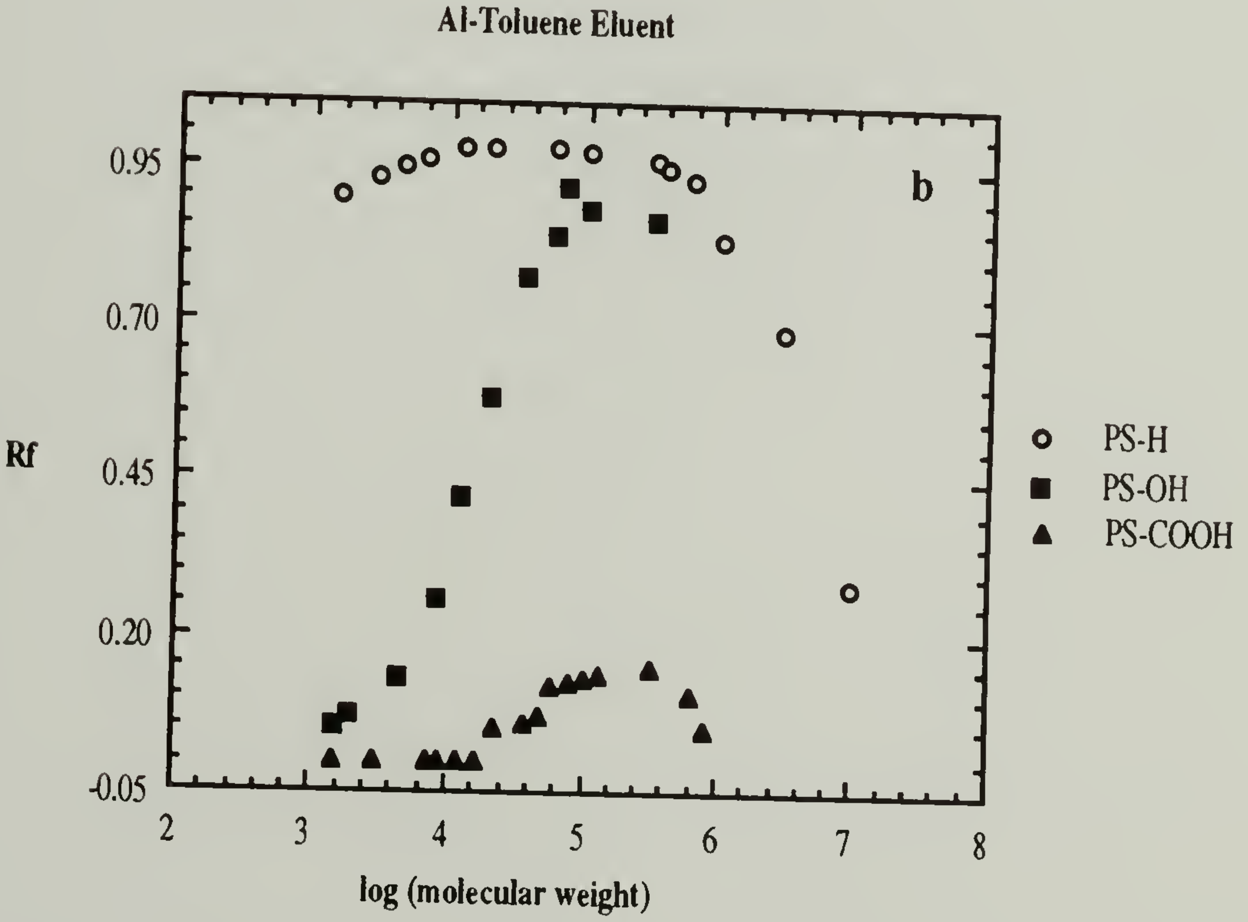


Figure 3.5 (a) Plots of R_f vs molecular weight for PS-H (o), PS-OH (■) and PS-COOH (▲) eluted with toluene on silica. (b) Analogous data on alumina

Table 3.6 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - toluene

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
1500	3.176	0.02	0.08	0.76	0.0	0.05	0.90
2000	3.301		0.10			0.07	
2800	3.447			0.80			0.93
3000	3.477	0.03			0.0		
4300	3.633			0.84			0.95
4400	3.643		0.15			0.13	
6500	3.813			0.88			0.96
7100	3.851	0.04			0.0		
8200	3.914		0.24			0.26	
9000	3.954	0.045			0.0		0.98
12000	4.079	0.06	0.36	0.92	0.0	0.42	
16800	4.225	0.07			0.0		
20000	4.301		0.57	0.90		0.58	0.98
23000	4.362	0.10			0.05		
36300	4.560		0.86			0.77	
37000	4.568	0.14			0.06		
47000	4.672	0.23			0.07		
58000	4.763		0.90	0.86		0.84	0.98
60000	4.778	0.53			0.12		
70500	4.848		0.89			0.92	

Continued, next page

Table 3.6 Continued

M_n (GPC)	$\log(M_n)$	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
78000	4.892	0.93			0.125		
100000	5.0	0.90	0.88	0.85	0.13	0.88	0.97
133000	5.124	0.87			0.14		
200000							
280000				0.83			0.96
290000	5.462		0.87			0.87	
320000	5.505	0.81	0.86	0.81	0.15	0.86	0.95
400000	5.602			0.80			0.94
600000	5.778			0.78			0.93
624000	5.795	0.76			0.11		
825000	5.916	0.61			0.05		
980000	5.991			0.53			0.83
3000000	6.477			0.19			0.69
10000000	7.000			0.00			0.28
172 (S1)		0.34	0.36	0.34	0.42	0.44	0.45
220 (S2)		0.72	0.72	0.71	0.82	0.84	0.84

Note: S1 is benzophenone and S2 is 2,6-di-tert-butyl-4-methylphenol. The data was taken from p 99 - 104 of TLC - polymer adsorption and phase separation note book #1.

Table 3.7 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - pentane / CH_2Cl_2, 3/7 (v/v)

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS-COOH	PS-OH	PS-H	PS-COOH	PS-OH	PS-H
1500	3.176	0.00			0.00		
2000	3.301		0.58			0.43	
3000	3.477	0.00			0.00		
4300	3.633						
4400	3.643					0.68	
7100	3.851	0.21			0.00		
8200	3.914		0.69			0.86	
9000	3.954	0.65			0.00		
12000	4.079	0.70			0.00	0.92	
17500	4.243			0.92			0.94
24200	4.384		0.81				
70500	4.848		0.84				
100000	5.0				0.19		
290000	5.462			0.84	0.73		
400000	5.602			0.60			0.86
600000	5.778			0.16			
825000	5.916						0.74

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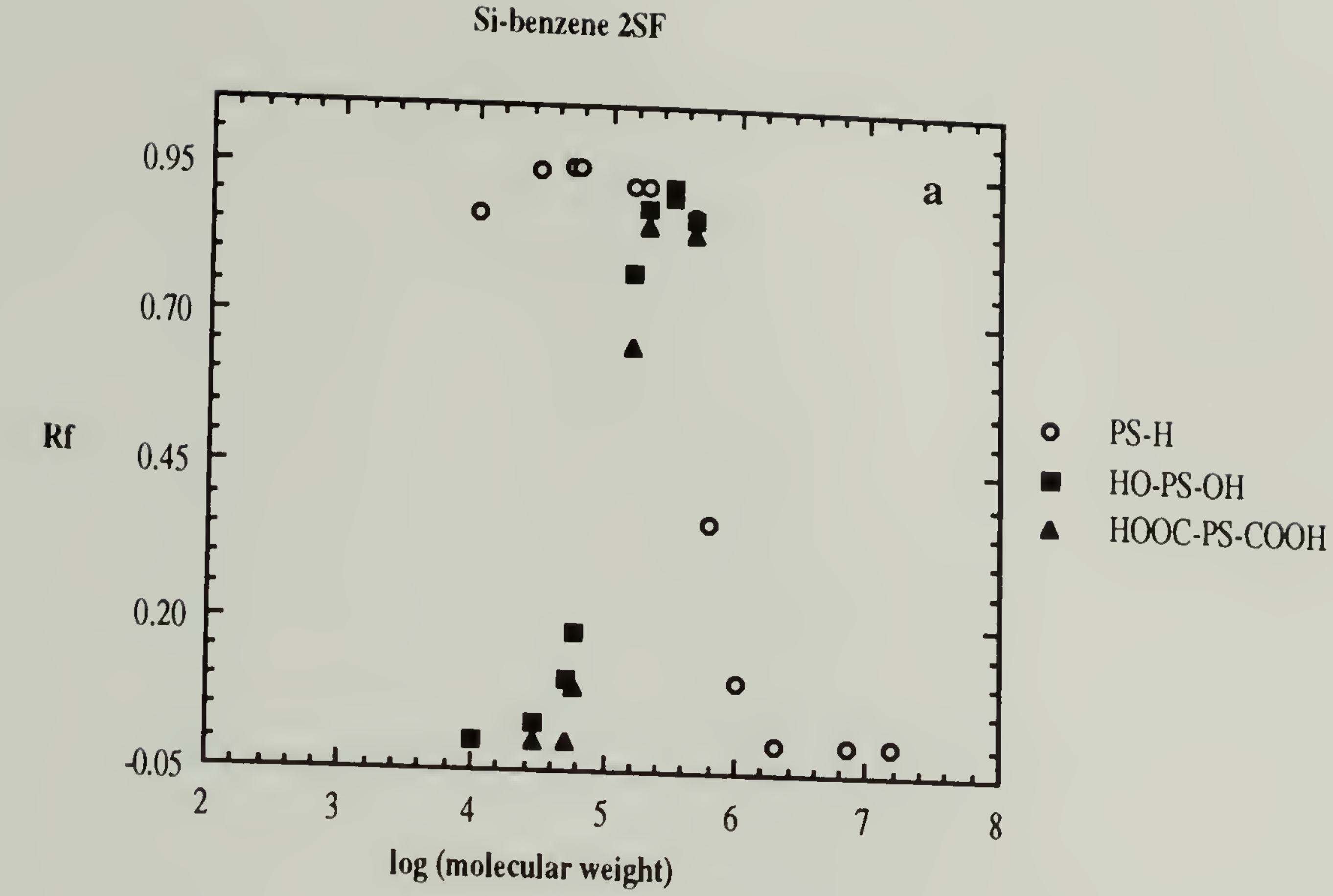
Table 3.7 Continued

M_n (GPC)	log (M_n)	R_f on silica PS-COOH	R_f on silica PS-OH	R_f on silica PS-H	R_f on alumina PS-COOH	R_f on alumina PS-OH	R_f on alumina PS-H
1860000				0.12			0.40
3000000	6.477			0.10			0.10
7000000							0.00
10000000	7.000			0.00			0.00
15000000	7.301			0.00			0.00

Note: Each entry point in this table was obtained by using silica gel supported on polyester sheet purchased from Eastman Kodak (cut to ~ 6 cm X 2.5 cm) and alumina supported on small glass plates (~ 6 cm X 2.5 cm) purchased from Baker, Inc. Small molecular weight standards were not run. Each data point is an average of 4 measurements two of which where obtained from one sheet (plate). The data was taken from p 44 - 45, p 79 - 89, p 104, and p 115 - 133 of synthesis alone note book #2.

In addition these eluents can also be regarded as neutral, acidic or basic and therefore interact specifically with silica (acidic) and alumina (amphoteric).[23-27] On silica, one terminal sticky foot has no apparent effect at any molecular weight with THF (basic) while on alumina only very low molecular weight PS-COOH samples adsorb. Figure 3.3 shows that chloroform (acidic) behaves as a displacer intermediate in strength between THF and benzene (weakly basic).[27] Although the solvent strength of ethyl acetate (basic) is greater than that of THF, the elution of PS-COOH on alumina with ethyl acetate is molecular weight dependent unlike with THF (figure 3.4b and 3.2b) . The analogous elution pattern on silica is indistinguishable (figures 3.4a and 3.2a). This indicates that the nature of the interaction between the carboxylic acid group from a given eluent to the adsorbent is responsible for the observed behavior. Figure 3.5 shows that toluene behaves as an eluent comparable to benzene.

TLC results of polystyrene and polystyrene terminated with hydroxyl and carboxylic acid groups at both the chain ends (HO-PS-OH and HOOC-PS-COOH) as a function of molecular weight from benzene on silica thin layers are shown in figure 3.6a while analogous results on alumina thin layers are shown in figure 3.6b as R_f vs log (molecular weight) plots. The data are presented in Table 3.8. The effect of the second functional group at the chain end is reduction in the R_f values (compare with figure 3.1). This indicates that during the "TLC time scale" the end-groups spend more time at the interface suggesting that in a static experiment the second end-group might bring the polymer to the interface by a two fold increase in the surface-functional group interaction. The analogous data obtained using THF as the eluent on silica and alumina thin layers are shown in figures 3.7a and 3.7b and the data are presented in Table 3.9. The presence of two carboxylic acid groups at the chain ends results in a molecular weight dependent elution pattern on the alumina thin layer as opposed to the molecular weight independent elution observed with one carboxylic acid end-group (compare with figure 3.2b). This clearly indicates that the second carboxylic acid group is necessary to bind the polystyrene molecule to the interface,



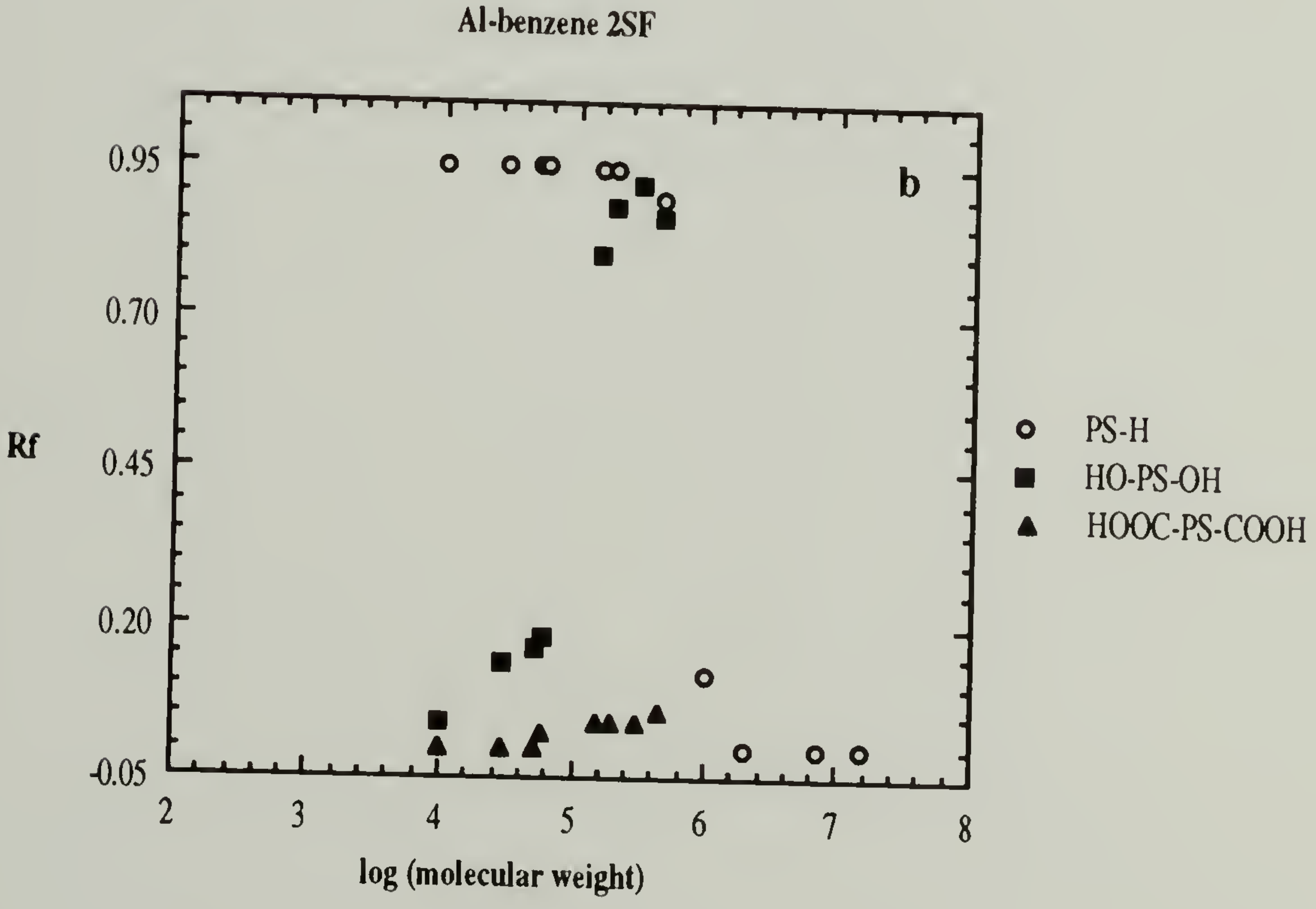


Figure 3.6 (a) Plots of R_f vs molecular weight for PS-H (o), HO-PS-OH (▪) and HOOC-PS-COOH (▴) eluted with benzene on silica. (b) Analogous data on alumina

Table 3.8 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - benzene

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		$PS(COOH)_2$	$PS(OH)_2$	PS-H	$PS(COOH)_2$	$PS(OH)_2$	PS-H
10000	4.000	0.00	0.00	0.87	0.00	0.04	0.95
20000	4.301			0.94			
30000	4.477	0.00	0.03	0.94	0.00	0.14	0.95
50000	4.699	0.00	0.10	0.95	0.00	0.16	0.95
60000	4.778	0.09	0.18	0.95	0.02	0.18	0.95
100000	5.0			0.90			
150000	5.176	0.65	0.77	0.92	0.04	0.80	0.94
200000	5.301	0.85	0.88	0.92	0.04	0.88	0.94
300000	5.477	0.90	0.92	0.90	0.04	0.92	0.92
450000	5.653	0.84	0.86	0.87	0.06	0.86	0.89
600000	5.778						0.38
980000	5.991			0.10			0.19
172 (S1)		0.38	0.39	0.40	0.50	0.46	0.45
220 (S2)		0.75	0.74	0.77	0.86	0.84	0.84

Note: S1 is benzophenone and S2 is 2,6-di-tert-butyl-4-methylphenol. The data was taken from p 47 - 48 of synthesis alone note book #4. The data for polystyrenes of molecular weight less than 10000 and greater than a million used in the figures are those obtained from the experiments discussed earlier.

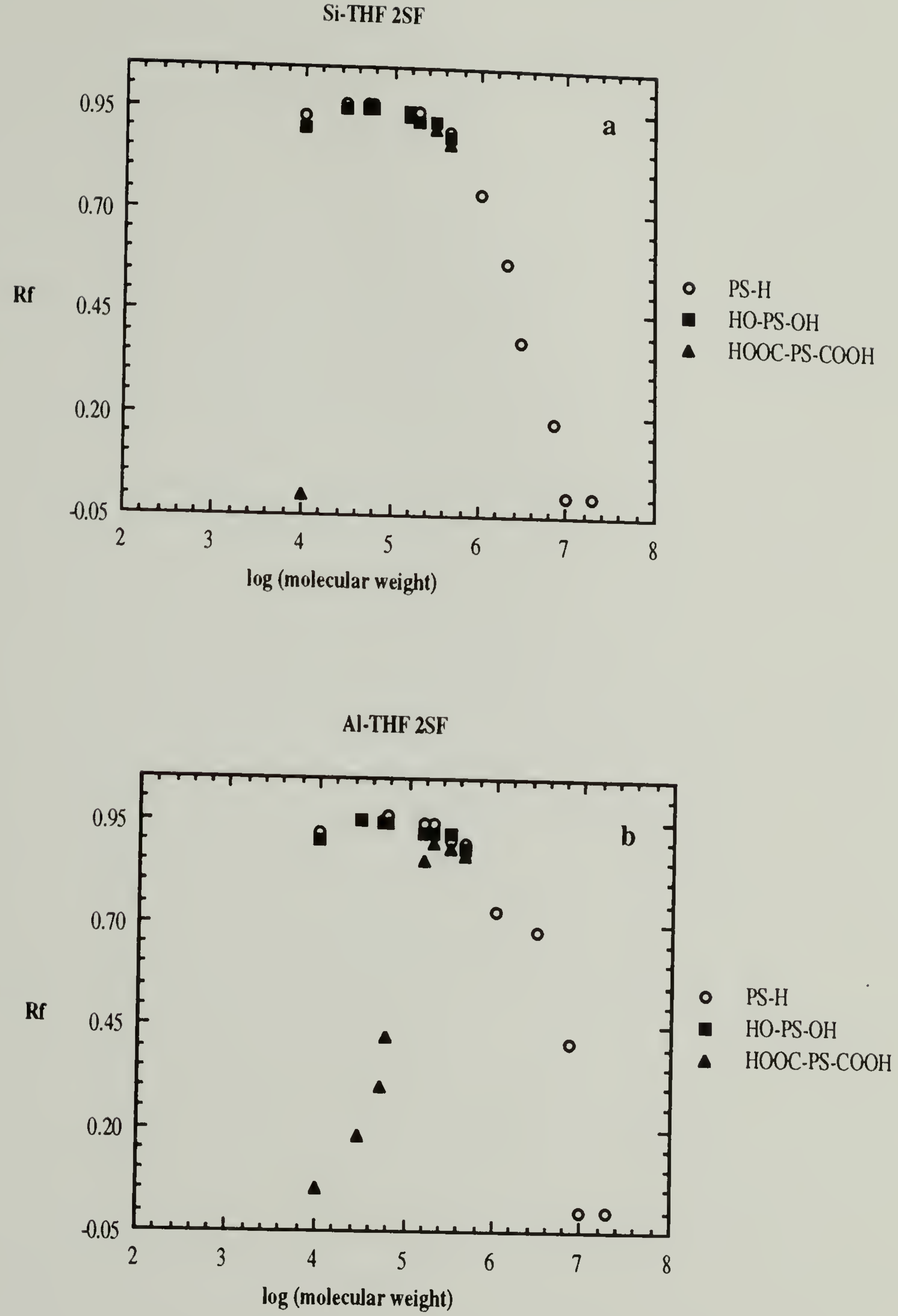


Figure 3.7 (a) Plots of R_f vs molecular weight for PS-H (o), HO-PS-OH (■) and HOOC-PS-COOH (▲) eluted with tetrahydrofuran on silica. (b) Analogous data on alumina

Table 3.9 R_f versus log (molecular weight) data

substrate - silica gel and alumina; eluent - tetrahydrofuran

M_n (GPC)	log (M_n)	R_f on silica			R_f on alumina		
		PS(COOH)$_2$	PS(OH)$_2$	PS-H	PS(COOH)$_2$	PS(OH)$_2$	PS-H
10000	4.000	0.00	0.90	0.93	0.05	0.90	0.92
20000	4.301			0.94			
30000	4.477	0.95	0.95	0.96	0.18	0.95	0.95
50000	4.699	0.95	0.95	0.96	0.30	0.94	0.95
60000	4.778	0.96	0.95	0.96	0.42	0.94	0.96
100000	5.0						
150000	5.176	0.93	0.94	0.94	0.85	0.92	0.94
200000	5.301	0.92	0.92	0.94	0.89	0.92	0.94
300000	5.477	0.90	0.92	0.92	0.88	0.92	0.92
450000	5.653	0.86	0.88	0.89	0.86	0.88	0.89
600000	5.778						0.38
980000	5.991			0.10			0.19
172 (S1)		0.76	0.79	0.78	0.83	0.86	0.93
220 (S2)		0.81	0.81	0.81	0.86	0.90	0.96

Note: S1 is benzophenone and S2 is 2,6-di-tert-butyl-4-methylphenol. The data was taken from p 45 - 46 of synthesis alone note book #4. The data for polystyrenes of molecular weight less than 10000 and greater than a million used in the figures are those obtained from the experiments discussed earlier.

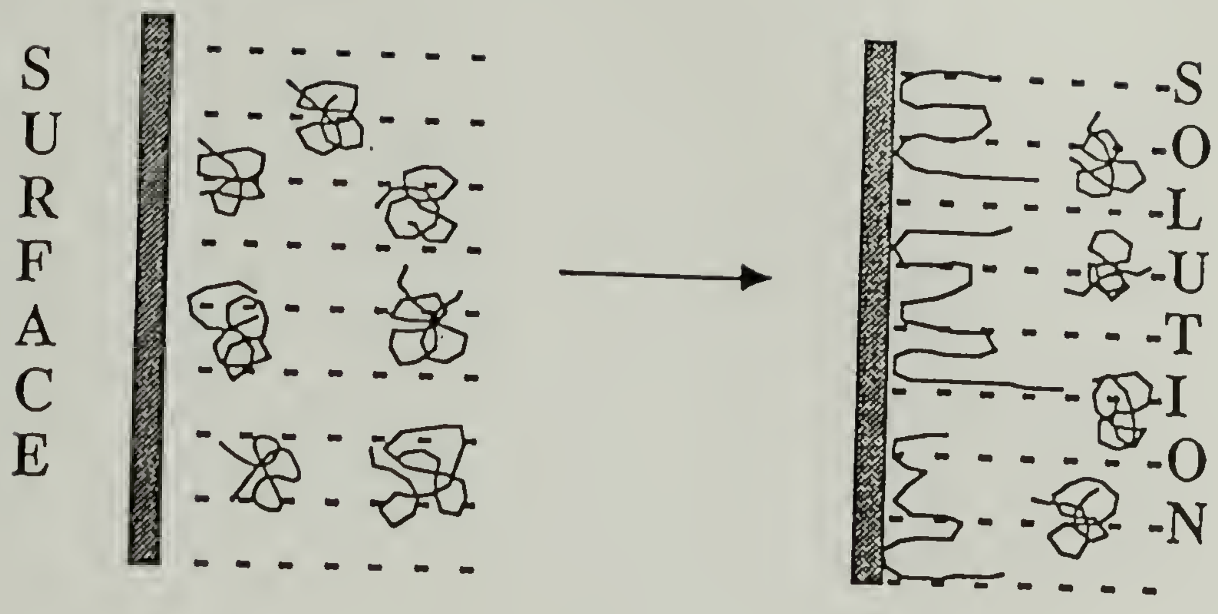
particularly from a good displacer like THF which happens to be a good solvent too. On silica gel thin layers, the displacement effect of THF is more prominent except at low molecular weights at which point the two carboxylic acid groups enable the binding of polystyrene molecules to the interface (due to the higher concentration of the end-group) resulting in zero R_f values. The incorporation of two hydroxyl groups at both the chain ends seem to have no impact on the adsorption of polystyrenes to silica and alumina interfaces from a good displacer and solvent such as THF. This result indicates that in a static experiment one can expect similar results and that the hydroxyl group is not an effective sticky foot when present in low concentrations (two per chain).

The observed molecular weight dependence of R_f values in functionalized polymers as a function of the nature and the degree of functionalization, the solvent nature and the nature of the substrate suggests that it is possible to design specific polymer architectures at interfaces by understanding the specific roles of different enthalpic factors and this is discussed in detail in Appendix A.

The observed elution pattern in solvents of different strength and displacing ability (polarity) can be qualitatively explained by the following model: A polymer molecule will spontaneously adsorb from solution to a surface if the net free energy of the adsorption process is less than zero [eq. 1].

$$\Delta G_1 + \Delta G_2 = \Delta G = \Delta H - T\Delta S \quad \ldots\ldots\ldots\ldots\ldots \ (1)$$

where, ΔG_1 is the decrease in free energy due to the formation of adsorbed (condensed) polymer phase; ΔG_2 is the increase in free energy accompanying the removal of polymer from solution to form more dilute polymer solution; ΔG is the net free energy change and ΔH and ΔS are the enthalpic and entropic changes accompanying adsorption. The contribution of individual terms can be best understood, if adsorption is thought of as an equilibrium process as depicted in figure 3.8.



Surface..Solvent + dilute polymer solution(3D Coil)

K ⇅

Surface-Polymer condensed phase(2D Coil)
+ more dilute polymer solution.

Figure 3.8 Adsorption - Desorption Equilibrium

The net free energy change ΔG, is then given by the equation 2.

$$\Delta G = [\Delta H_{12} + \Delta H_{14} + \Delta H_{22} + \Delta H_{13} + \Delta H_{34} + \Delta H_{23} + \Delta H_{33}] \quad .....$$

$$- T[\Delta S_{trans}\ (\text{polymer}) + \Delta S_{conf}\ (\text{polymer}) + \Delta S_{trans}\ (\text{Solvent})] \quad ....(2)$$

where 1 stands for a surface site, 2 for the segment on the polymer backbone, 3 for a solvent molecule and 4 for an organic functional group on the polymer. ΔH_{12} is the surface-segment interaction energy given by $\varepsilon_{12} * n$, where n is the number of surface-segment contacts (if p is the fraction of segments in contact with the surface and r the degree of polymerization then n = pr) and ε_{12} is the surface-segment interaction energy per segment. For adsorption to occur a finite adsorption potential is assumed to exist and ΔH_{12} is therefore always negative. ΔH_{12} is exothermic and arises from the non-bonded interaction of the segment with the surface through a combination of dispersive and van der Walls type of interactions. It has been predicted that a certain critical energy of about 0.7 kT per segmental contact [7] with the surface, must be exceeded for adsorption to occur. The point is that the contribution of ΔH_{12} to the free energy of adsorption is proportional to the number of surface-segment contacts made, and therefore is a function of molecular weight. ΔH_{14} is the surface-functional group interaction energy, and is always negative (exothermic) as the functional group in question forms some kind of bond (equivalent to or greater than hydrogen bonded interactions) with the surface. The magnitude of this energy depends both on the functional group and the surface in question. This may involve the formation of a chemical bond or a hydrogen bond. It's magnitude can vary from 5 k cal /mole to 100 k cal/mole (In cases where strong chemical bonds are formed, we can say that, it's only a matter of time before the functional group finds the appropriate surface-sites and binds irreversibly to it).

ΔH_{22} is the enthalpic contribution from the increased segment-segment contact in the condensed phase. ΔH_{22} is an attractive interaction at short distances of the order of few bond lengths and repulsive at long ranges. It's contribution to free energy of adsorption is small as the short-range attractive forces annul the long range repulsive forces between segments far apart in the adsorbed layer[9], and is independent of molecular weight. ΔH_{23} is the enthalpic change, due to fewer segment-solvent contacts upon adsorption (Flory-Huggins). ΔH_{34} is the enthalpic change due to a solvated functional group losing its solvent sphere upon adsorption and its magnitude depends on the polarity of the solvent. It is an endothermic contribution to the net free energy change. ΔH_{13} is the enthalpy change due to the desorption of the solvent from the surface, which in turn is followed by adsorption of a polymer segment for each solvent molecule desorbed. This is an endothermic interaction and is equal in magnitude and opposite in sign to the enthalpy of surface-solvent interaction. It is an indirect function of the molecular weight and this is always positive (endothermic).

ΔH_{33} is the enthalpy change due to the formation of more solvent-solvent contacts upon adsorption and is very small. ΔS_{trans} (polymer) is the translational entropy lost when a polymer with 3 dimensional mobility is bound to the surface through a functional group or through a segment and the motions of the segments are limited to two dimensions. This is of the order of kT. The greater the number of segmental contacts, the greater is the loss of two dimensional segmental translational entropy (even if the polymer molecule is bound to a surface its segments can still translate about their mean center of gravity as all the segments are not bound). The higher the molecular weight of the polymer, the greater is the probability of contact and therefore this is a function of molecular weight. ΔS_{conf} (polymer) is the conformational entropy lost, when large # of conformational states per chain are lost due to various degrees of attachment of the chain. This in turn is also a function of molecular weight ($kTpr\chi_{sc}$). ΔS_{trans} (solvent) is the translational entropy gained by the solvent [~ - kTpr ln (volume fraction of solvent in the adsorbed layer/volume fraction of solvent in the bulk solution)] when it is displaced by polymer segments due to specific and various degree of attachments to the surface and is a function of the fractional number of segments attached and the molecular weight (through the degree of polymerization, r).

The net free energy change has many terms whose magnitude cannot be determined experimentally although several attempts have been made to calculate the algebraic sum of $\Delta H_{22} + \Delta H_{33} + \Delta H_{23}$ (χ parameter), using Flory-Huggins lattice theory of polymer solutions. One such work estimates that under good solvent conditions the above sum, for each surface-segment contact is of the order of 0.5 kT.[10] Some researchers have also obtained the algebraic sum of $\Delta H_{12} + \Delta H_{13}$ (χ_s) by the displacement of adsorbed polymers[22], by microcalorimetry[23] and by thin-layer chromatography[24]. ΔH_{13} has been calculated for several surface-solvent pairs and the values are listed in a reference.[11] ΔH_{14} has also been measured experimentally for several functional small molecules such as CH_3OH, CH_3CN, CH_3COOH, and CH_3NH_2 adsorbed to single crystal metal oxide surfaces in the gas phase.[12] But the enthalpy of interaction in solution is not known.

Cohen Stuart, et al.,[20] have given a simple expression for the net free energy change using the same arguments as presented above and represented in equation 2 based on Flory-Huggins theory of polymer solutions and Scheutjens and Fleer theory of polymer adsorption (Appendix A). From the efforts of Cohen Stuart, et al., it is clear that this is a complex problem to be simplified by analytical expressions and therefore we neither make any attempt to simplify equation 2 to an analytical equation (usually this is the most acceptable form of any physical picture) nor do we calculate adsorption energy parameters. Our efforts are focussed on interpreting trends in adsorption that can be obtained fairly quickly for a given set of solvents, while retaining the physical form as expressed in detail in equation 2 and the information that TLC provides about the possible location of the functionalized part of the chain (i.e chain architecture).

Let us consider some of the cases that are encountered in a real adsorption experiment. The first simplification stage involves the surface-solvent interaction. Let us say that the solvent-surface bond is not strong enough, i.e $\Delta H_{13} \approx T\Delta S_{trans}$ (solvent). For weakly bound solvents both the enthalpic and entropic contribution from surface-solvent interaction do not contribute to the free energy of adsorption (note that for $\Delta H_{13} < T\Delta S_{trans}$

(solvent) the solvent will not bind to the surface, and a depletion layer is observed). For strongly adsorbing solvents, the enthalpic term overrides the entropic contribution; i.e $\Delta H_{13} >> T\Delta S_{trans}$ (solvent) and $T\Delta S_{trans}$ (solvent) term can be ignored. Therefore, the net free energy of adsorption ΔG is given by,

$$\Delta G = \Delta H_{12} + \Delta H_{14} + \Delta H_{13} - \Delta H_{23} - T\,[\Delta S_{trans}+\Delta S_{conf}]$$

after ignoring the small contributions from the other two enthalpic terms ΔH_{33} and ΔH_{34}, the entropic terms being exclusively from the polymer. All the terms except ΔH_{13} and ΔH_{23} are negative. In the case of a neutral polymer and a neutral solvent the excess enthalpy of mixing is usually zero (ΔH_{23} is zero and mixing occurs because of the entropic gain in going from an entangled solid to a solution) and therefore this term can be ignored.

Case (i) Let $\Delta H_{13} > \Delta H_{12} + \Delta H_{14} - \Delta H_{23}$

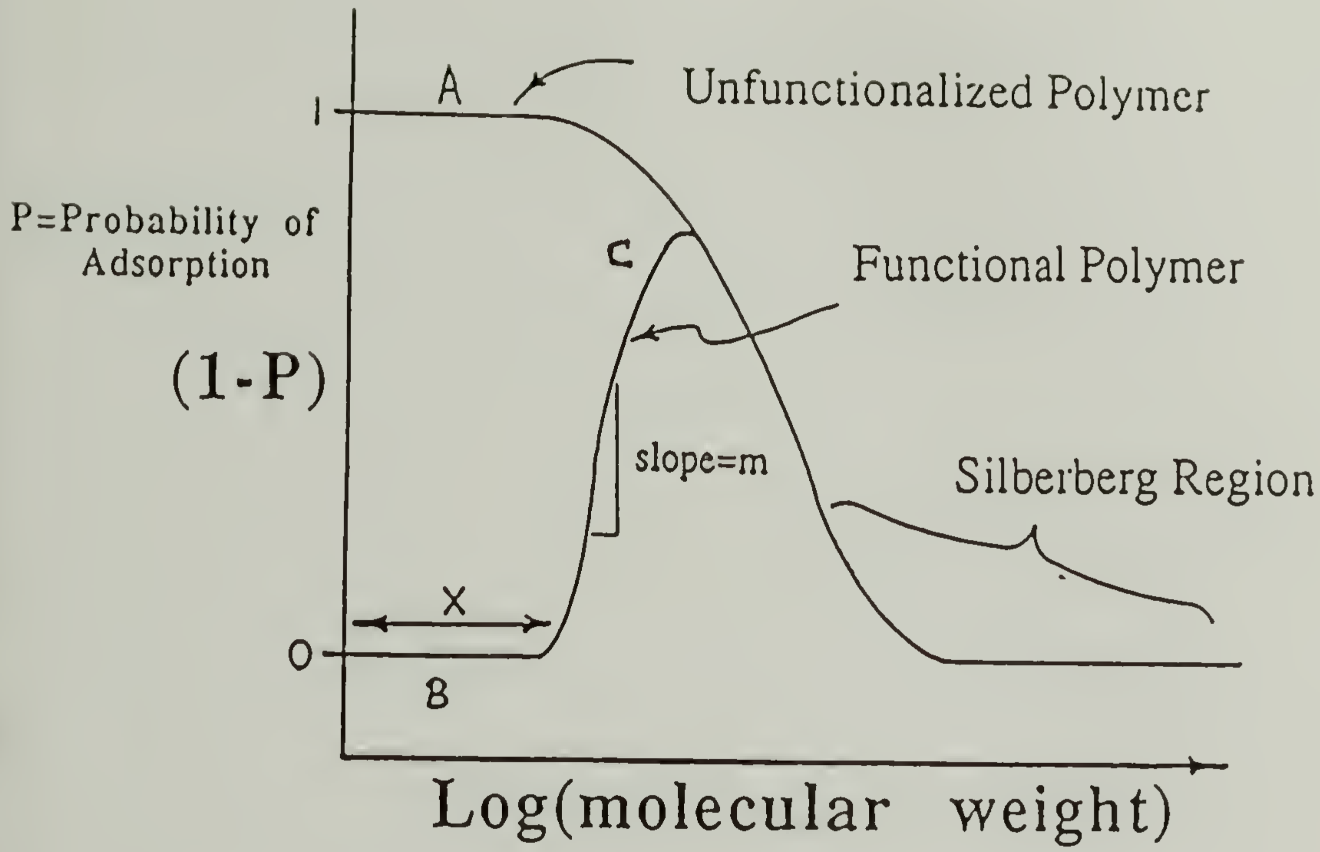
No adsorption would occur for the above condition for any molecular weight with and without any kind of functional group as the rest of the terms (entropic) would only increase the free energy. e.g. PS-H does not adsorb to alumina from ethyl acetate and THF. No polymer adsorbs to iron surface from acetonitrile (CH_3CN).

Case (ii) Let $\Delta H_{13} = \Delta H_{12} + \Delta H_{14} - \Delta H_{23}$

No adsorption would take place in this case too, as the entropic terms again lead to an increase in free energy.

Case (iii) Let $\Delta H_{13} < \Delta H_{12} + \Delta H_{14} - \Delta H_{23}$

In this case, adsorption is governed by polymer solution energetics and surface functional group interaction energies. For this case one should observe a curve for the probability of desorption (1-P, where P is the probability of adsorption) vs molecular weight as shown in figure 3.9 (note that this curve is identical to R_f vs molecular weight that one would obtain from a TLC experiment since R_f is proportional to (1-P) and this is derived in the appendix). The justification for the shape of the un-functionalized polymer is that at low molecular weights the critical adsorption energy is not reached within the "TLC" time scale and therefore the probability of adsorption remains at zero. As the molecular weight is



$X \sim \Delta H_{\text{surface-functional group}} + \Delta H_{\text{solvation of the coil}}$

m ~ Parameter indicating the goodness of the solvent

Figure 3.9 Prediction of Adsorption Behavior From the Model Proposed

increased the critical adsorption energy is reached within the "TLC time scale" and the probability of desorption goes down as $\approx \exp(-Np\chi_s)$.

Sub case (a) Let $\Delta H_{14} = 0$, i.e m = 0. Then the free energy of adsorption is governed by, $\Delta G = \Delta H_{12} + \Delta H_{13} + \Delta H_{14} - \Delta H_{23} - T(\Delta S_{trans} + \Delta S_{conf})$, where $\Delta H_{12} = n \times \varepsilon_{12}$ and $\Delta H_{14} = m \times \varepsilon_{14}$ (m = number of functional groups interacting with the surface; ε_{14} is the enthalpy of interaction of a functional group with the surface). Except ΔH_{14} the rest of the terms depend on the number of surface-segment contacts made and are therefore functions of molecular weight. For small n's the loss of free energy due to enthalpic interactions of the segments with the surface cannot overtake the loss of entropy due to adsorption. Therefore adsorption does not occur and the probability of adsorption is not a function of molecular weight for these n's. However as n increases, at some n, the enthalpic interactions overtake the loss of entropy due to adsorption, and therefore adsorption occurs. Beyond this limit, adsorption must occur for any n and therefore in this range the probability of adsorption depends on molecular weight as discussed above. This behavior is shown as curve A in figure 3.9. From the equation for the free energy it is clear that at what "n" the probability of adsorption begins to depend on molecular weight, and therefore the shape of the curve depends on ΔH_{13} (however small it might be) and ΔH_{23} (how good or bad a solvent is).

Sub case **(b):** Let $\Delta H_{14} \neq 0$ and be significant.(< 0 or exothermic)

Then for small n's, if ΔH_{12} and ΔH_{23} and ΔS terms are insignificant compared to ΔH_{14} adsorption takes place. (If not, that condition is as good as Sub-case (a)). As n increases, two possibilities arise.

1. $\Delta H_{14} + \Delta H_{12} - \Delta H_{23} > T\Delta S$
2. $\Delta H_{14} + \Delta H_{12} - \Delta H_{23} < T\Delta S$

The first possibility considers a strong surface-functional group bond (ΔH_{14}) and the second a relatively weak surface-functional group bond. If surface-functional group interaction is strong enough to overtake the increasing loss of entropy that occurs when the chain length is increased, adsorption would occur for any molecular weight. This possibility is shown as curve B in figure 3.9. However if ΔH_{14} is relatively weak there will be an "n" (molecular weight) at which possibility 2 would arise and at this n, the adsorption behavior would approach that of the un-functionalized polymer (i.e. end group effects are negligible). The probability of adsorption would follow that of the un-functionalized polymer above this "n". This possibility is shown as curve C in figure 3.9.

To summarize, the equation $\Delta H_{12} + \Delta H_{14} = \Delta H_{13} + \Delta H_{23} + T\,[\Delta S_{trans}+\Delta S_{conf}]$ governs adsorption. The terms on the left favour adsorption while those on the right oppose it. In the case of neutral un-functionalized polymers in a neutral solvent, the competition between the first term on the left hand side and the entropic term on the right hand side decides adsorption (e.g. polystyrene in cyclohexane). In the case of a neutral polymer with an end-functional group in a neutral solvent the competition between the two terms on the left hand side and the entropic term determines adsorption (e.g. PS-COOH in cyclohexane). Introduction of a polar solvent (THF) or a polar polymer brings in the additional terms ΔH_{23} and ΔH_{13} and their absolute magnitude in comparison with ΔH_{14} decides adsorption and therefore the elution pattern on a thin-layer of adsorbent.

Let us look at the results in the light of the model discussed above keeping in mind that some of the solvents used in the experiments reported interact specifically with the substrate and to some extent with the polymer (as in the case of chloroform). Unlike a neutral polymer and a neutral solvent the effects of the ΔH_{23} term cannot be ignored in such cases and so is the the effect of ΔH_{13} term. The carboxylic acid-end group interacts specifically with alumina (interaction energy is stronger than a hydrogen bond) while its interaction with silica is of the order of a hydrogen bond.

TLC results for polystyrene, hydroxyl end-capped polystyrene, and carboxylic acid end-capped polystyrene of different molecular weights in different good solvents on alumina thin layer are shown in figures 3.1b to 3.5b as R_f vs log (molecular weight) plots. From the figures it is apparent that the R_f vs molecular weight curves for PS-H follows qualitatively the shape proposed in the model for the un-functionalized polystyrene (case (iii) and $\Delta H_{14} = 0$). Up to a molecular weight of 100,000 the R_f value for PS-H is 1 or close to 1 as reported earlier.[6] Above this molecular weight, R_f is a function of molecular weight up to a molecular weight of 10^6, beyond which it is independent of molecular weight in all the solvents tried justifying the predicted and observed plateau region. The molecular weight at which the curve plateau's depends on the goodness of the solvent. As expected the curve begins to plateau at higher molecular weights in specifically interacting solvents such as THF and ethyl acetate than in benzene or toluene.

Carboxylic acid and hydroxyl end-functionalized polymer's TLC behavior follows, case (iii), sub case (b) (possibility 1 for -COOH and 2 for -OH) of the proposed model. Carboxylic acid end-functionalized polymer of any molecular weight has a lower R_f value than hydroxyl end-functionalized polymer of the same molecular weight because $(\Delta H_{14})_{COOH} > (\Delta H_{14})_{OH}$, i.e the enthalpy of interaction of the -COOH group with alumina is much greater than that of the enthalpy of interaction of the -OH group.[11] From the figures and the tables, the quality of eluents for adsorption, during flow on alumina thin layer decreases in the following order benzene ≈ toluene > CH_2Cl_2/pentane (7/3) ≥ $CHCl_3$ > ethyl acetate > THF. If the eluents had functioned just as displacers then the order must have followed the solvent strength parameter ε_0 of Snyder [11]as CH_2Cl_2/pentane (7/3) > benzene ≈ toluene > $CHCl_3$ > THF > ethyl acetate. Further if the thermodynamic quality of the solvent was the only criterion, then adsorption should be favoured in this order; CH_2Cl_2/pentane (7/3) > ethyl acetate > $CHCl_3$ > THF ≥ benzene > toluene.[27] That the R_f value does not follow either of the trends in general suggests that for adsorption to take place from good solvents one has to consider not only the thermodynamic quality of the solvent but also the magnitude of the surface-solvent interaction energy and the polymer-solvent interaction energy. The complete elution of all polymer samples in THF with the exception of low molecular weight PS-COOH on alumina indicates that as a rule the surface-solvent term (ΔH_{13}) and probably the polymer-solvent term (ΔH_{23}) dominate and prevent adsorption except at low molecular weights (where the concentration of the end-group turn the table). PS-COOH samples elute with molecular weight dependent R_f's while PS-OH samples do not. Although ethyl acetate is a better displacer than THF it is a poorer solvent and therefore cooperative effect of segments { n x (ΔH_{12} - ΔH_{23})} leads to molecular weight dependent adsorption. Chloroform is an acidic solvent which interacts specifically with basic sites on alumina and with the polymer itself[22] in addition to being a very good solvent. Therefore all the enthalpic parameters are important in this case and we see an elution pattern in between that of a poor displacer and a good displacer (solvent quality being in between ethyl acetate and benzene).

The shape of the eluted samples (circular at $R_f = 0$ and convex lens shape at $R_f > 0$) and the change in shape of the R_f vs log(molecular weight) curve from the un-functionalized samples indicates that below a molecular weight of 10^5, adsorption-desorption is the mechanism, operating in the TLC of functional polymers. The increase of R_f with molecular weight for functionalized polymers in solvents which interact strongly with alumina such as THF and ethyl acetate,[11] rules out phase separation due to depletion of solvent in the advancing solvent front, thus confirming the above mechanism.

Figures 3.1a to 3.5a describe the TLC behavior of polystyrene, hydroxyl end-functionalized polystyrene, and carboxylic acid end-functionalized polystyrene on silica gel thin layer in different good solvents as a function of molecular weight. From Table 3.1 the solvent strength of the different solvents used decreases in the following order: ethyl acetate > $CHCl_3$ > benzene ≈ toluene > CH_2Cl_2/pentane (7/3). The thermodynamic goodness of the solvent decreases in the following order: benzene ≈ toluene ≥ THF > $CHCl_3$ > ethyl acetate > CH_2Cl_2/pentane (7/3). The experimental results suggest that adsorption decreases in the following order: benzene ≈ toluene > CH_2Cl_2/pentane (7/3) > $CHCl_3$ > ethyl acetate ≈ THF. These results in general suggest the competitive nature of adsorption. All the solvents as well as the -COOH end-group interact less strongly with silica than alumina.[11] In the absence of strong solvent-surface interactions, we observe a molecular weight-dependent R_f value in benzene and toluene dictated by surface-functional group interaction. Since the carboxylic acid group interacts more strongly with silica than does the hydroxyl group, lower R_f values are observed for the former. In THF and ethyl acetate surface-solvent interactions become important in the absence of strong surface-functional group interaction and therefore functionalized polymers elute with a molecular weight independent R_f values up to the critical molecular weight. The elution behavior of hydroxyl end-functionalized polymers follows case (iii), sub-case b, condition 2 where R_f values were predicted to be molecular weight dependent (region below the critical molecular weight) being determined by a critical balance between surface-solvent and surface-functional group interaction.

To summarize, for a given molecular weight, R_f values are considerably lower for carboxylic acid end-functionalized polystyrenes on alumina compared to silica gel thin layer because of the alumina-COOH specific interaction. In the case of the hydroxyl end-functionalized polystyrenes higher R_f values are usually observed in alumina because the solvent-surface interaction is greater. The R_f values of polystyrenes with two end-groups is lower than those with one because both the chain ends adsorb in the case of the former. The R_f values for the di-carboxylic acid-terminated polystyrenes are lower than those for the di-hydroxyl-terminated polystyrenes because of the higher enthalpy of interaction of the carboxylic acid group with silica and alumina.

3.4 References and Notes

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CHAPTER 4

ADSORPTION OF END-FUNCTIONALIZED POLYSTYRENES TO GLASS FROM Θ AND GOOD SOLVENT CONDITIONS MONITORED BY LIQUID SCINTILLATION COUNTING

4.1 Introduction

This chapter deals with adsorption experiments performed with radioisotope-labeled polystyrenes (functionalized and un-functionalized), the synthesis of which is discussed in detail in Chapter 2. The substrate used was glass and the solvents were cyclohexane and toluene. At 36.7 °C, cyclohexane is a theta solvent (slightly better) for polystyrene; i.e the polymer coil in solution is well described by random walk or gaussian statistics. Toluene is a good solvent for polystyrene at 23 °C; i.e the polymer coil interacts favorably with the solvent and exhibits dimensions higher than that in a poor solvent. Because of this favorable polymer segment-toluene interaction the segments of a given coil and different coils avoid each other as well (the so called excluded volume interaction).

The rates of adsorption and the adsorbance of several end-functionalized polystyrenes of different molecular weights to clean glass surfaces from dilute solutions of different concentrations were determined by liquid scintillation counting. The graft densities (# of polymer chains/unit area divided by the number of monomers that will occupy the same area) were determined from the adsorbance data as well.

The radioactivity of tritium-labeled polymers, displaced from glass surfaces (to which the polymer was adsorbed previously) using a suitable displacer mixture, was determined by the fluorescence activity of a scintillation cocktail. The scintillation cocktail, in a liquid scintillation counting experiment, converts part of the radiation energy of the primary particle emitted by the sample into light which in turn is converted to a charge pulse by a phototube. This is amplified and counted by a scaling circuit.[1-3] The amount of radiation energy converted to light depends on the molecules that make up the cocktail and is given by its efficiency. The efficiency of a cocktail in turn is determined by the charge pulse counts/min obtained for radio-labeled samples of previously known activity (disintegrations/minute). Tritium-labelled polystyrene was used by several researchers in the past to study the adsorption of polystyrene.[4-7] Following reported procedures and precautions the adsorption of end-functionalized polystyrenes to glass surfaces were performed.[7, 8]

Briefly, the chapter is organized as follows: following this section is the experimental section which discusses the materials used and the methods. A large volume of data was obtained in view of the number of variables used in the experiments. Most of the data on the kinetics of adsorption did not reveal any new physical phenomena. Therefore a summary of the results in the form of equilibrium adsorbances alone are presented in the results section. After this section the results of the kinetics of adsorption for some specific and novel cases, the adsorption isotherms, molecular weight effects, the graft density vs. end-group concentration, and the surface excess for some samples are presented and discussed in detail in the discussion section. The summary of the chapter is presented in the following section, followed by conclusions. The bulk of the raw data in the form of counts per min/geometric area vs. time and the graft density data obtained from the adsorbance values are presented in Appendix B.

4.2 Experimental

4.2.1 Materials and Methods

Tritiated water and toluene of specific activities 100 mCi/ml and 0.93 μCi/ml were purchased from New England Nuclear. Tritiated styrene, polystyrene and end-functionalized polystyrenes were synthesized according to the detailed procedure reported in Chapter 2. Cold (non-radioacitve) samples were prepared in parallel under identical experimental conditions and the characteristics of the cold sample are assumed to reflect those of the hot samples. The polymer samples prepared and their GPC characteristics are reported in Table 4.1

Liquid Scintillation Counting was performed using an LKB Wallac Rackbeta LS Counter, Model 1217-001 for samples containing a single sticky foot and a Beckmann LS 3801 for samples containing two sticky feet.

Liquid scintillation counting of eight different polymer samples (4 different molecular weight with one and two functional end-groups) of different masses, prepared from styrene of the same specific activity, on an average, lead to the following general equation for the counts obtained vs. mass of the polymer: cpm = 773.93 ± 50.55 x, where x is the mass of the polymer in μg. The data for each of the samples are presented in Appendix B. Based on the definition of 1 μCi being equal to 2.22 x 10^6 dpm and the fact that 1 dpm is equal to 0.475 cpm (from the efficiency of the cocktail determinations discussed in Appendix B), the average specific activity of the polymers synthesized was calculated to be 733.94 ± 47.94 μCi/g. This means that lowest adsorbance that can be detected above the background with 95% confidence is 3 nanograms/cm^2.

Typically, a liter of cocktail was prepared by adding 657.5 ml of toluene, 200 ml of benzene and 100 ml of tetrahydrofuran to 42.5 ml of "liquifluor" (a concentrated solution of cocktail supplied by New England Nuclear) which on dilution contains 4 g of PPO (poly(phenyloxazole)) and 50 mg of POPOP (1,4-bis-2-(5-phenyloxazolyl)benzene per liter. This solution was immersed in a warm water bath for an hour following which it was degassed with nitrogen for an hour. 10 ml of this cocktail gave a background count of 7 to 12.5 counts per minute (cpm) in plastic scintillation vials (nylon or polyethylene) and 12 to 19 cpm in glass scintillation vials. The efficiency of the cocktail, determined by the internal standard method,[9, 10] was 47.5 ± 1.5 % and was unaltered by the presence of small amount of polystyrenes (up to several μg).

Table 4.1 Characteristics of Tritium-Labeled Polystyrenes

sample	R_g (CH)	R_g (Tol)	M_n	PDI
PS-COOH	20	22	5000	1.03
PS-OH	20	22	5000	1.03
PS-H	20	22	5000	1.03
PS-COOH	28.5	33	10000	1.03
PS-OH	28.5	33	10000	1.03
PS-H	28.5	33	10000	1.03
HOOC-PS-COOH	28.5	33	10000	1.07
HO-PS-OH	28.5	33	10000	1.06
PS-COOH	49.3	62.9	30000	1.04
PS-OH	49.3	62.9	30000	1.04
PS-H	49.3	62.9	30000	1.04
HOOC-PS-COOH	49.3	62.9	30000	1.05
HO-PS-OH	49.3	62.9	30000	1.03
HOOC-PS-COOH	69.8	94.2	60000	1.04
HO-PS-OH	69.8	94.2	60000	1.04
PS-COOH	108.1	157	140000	1.06
PS-OH	108.1	157	140000	1.06
PS-H	108.1	157	140000	1.06
HOOC-PS-COOH	108.1	157	140000	1.05
HOOC-PS-COOH	108.1	157	140000	1.05

Note: M_n is the number average molecular weight rounded to the nearest thousand and PDI is the poly dispersity index determined by gel permeation chromatography using cold samples prepared in parallel under identical experimental conditions. R_g stands for the radius of gyration in angstroms, CH for cyclohexane and Tol for toluene.

Early experiments also indicated that benzene and tetrahydrofuran in the cocktail functioned as displacers and completely desorbed polymers (known amount) cast as thin films on glass slides. This suggested that benzene and tetrahydrofuran in the cocktail will completely desorb the adsorbed polymers (functionalized and un-functionalized polymers) into the cocktail solution.

4.2.2 Substrate Preparation

Glass microscope slides (Fisher, ~ 6.0 cm x 1.5 cm) were cut to dimensions of ~ 1.5 cm x 1.5 cm using Dyna-cut abrasive cut off machine. About 5000 slides thus prepared were washed thoroughly in tap water to remove fine glass particles. They were oven dried (200 - 250 °C, 12 h), cooled and weighed. The weight of the glass slides ranged from 0.4450 to 0.4650 g. They were separated in to five groups based on their weight and these groups were 0.4450±0.0025 g, 0.4500±0.0025 g, 0.4550±0.0025 g, 0.4600±0.0025 g, and 0.4650±0.0025 g. The geometric area of a given glass slide was calculated from its weight by the equation given below:

$[\text{weight (g)} \times 2 / \{\text{density of glass } (2.434 \text{ g/cm}^3) \times \text{thickness } (0.094 \text{ cm})\}] + 0.5 \text{ cm}^2$

The last term being a correction for the four sides that are not taken into account by the formula given within the square brackets and this was determined using a vernier caliper.

Glass slides from a particular group, for adsorptions from a given polymer solution, were immersed in an acid bath containing 50 g of nochromix powder (Aldrich) for every liter of concentrated sulfuric acid (36 N), for at least 24 h. After this they were rinsed in flowing distilled water for ~ 2 min. Subsequently the slides were heated to about 80 °C in double-distilled water (~ 35 to 45 min for 150 ml of water at 4 to 5 °C/min heating rate) and the hot water was discarded. The above step was repeated with a fresh aliquot of double-distilled water (150 ml). This time the slides were sonicated after the appropriate heating time for 10 to 15 min (as the water was cooling). After discarding the water, sonication was performed in spectroscopic grade methanol (10 min, twice) and in cyclohexane or toluene as the case may be (10 min, thrice). The clean slides were equilibriated for 2 h at 36.7 ± 0.1 °C in cyclohexane before use while they were used immediately in toluene.

The cleaning ability of the acid bath was periodically monitored as follows: A drop of the acid solution at the end of a glass rod was allowed to touch a brown paper towel. If the paper towel charred instantly on contact, it was taken that the acid bath was active. A glass slide immersed in such a solution for 30 sec, followed by distilled water wash and nitrogen drying exhibited a water contact angle of 12° - 14° / 0° (θ_A/θ_R) while advancing and receding the (water) drop.

4.2.3 Adsorption Experiments

The polymer solution of the highest concentration (1.0 mg/ml or 2.5 mg/ml) used for a particular sample (molecular weight and sticky foot type) was prepared by weighing the appropriate amount in a volumetric flask (25 ml), followed by the addition of the solvent (spectroscopic grade). After 48 h, a 5 to 25 μl aliquot of the solution was withdrawn and was counted in 10 ml of the cocktail for 10 min. The experiments were performed in triplicate. The average cpm obtained was used in the appropriate equation for that sample (shown in Table 4.3.9) to obtain the exact concentration of the solution. Solutions of lower concentrations were prepared by serial dilution from the concentrated solutions. The exact concentration of each of the solutions was obtained by counting three aliquots of 25 μl each as described above.

A typical adsorption experiment conducted in cyclohexane is described below. About 12 to 15 ml of a particular polymer solution (say 1 mg/ml) was taken in a cylindrical glass tube, sealed at one end. The open end was closed tightly with an aluminum foil and was secured with a rubber band. This tube was then placed in a thermostated bath (water + ethylene glycol) maintained at 36.7 ± 0.1 °C, for 12 to 14 h for temperature equilibriation. Clean glass slides, after the 2 h temperature equilibriation, were placed in the polymer solution using tweezers (~ 5 sec transport through air). After the appropriate time, the slides were withdrawn carefully (the polymer solution in contact with the glass slide was removed by bringing an edge of the glass slide against the wall of the tube as it was being withdrawn) and were rinsed in pure solvent placed in three different glass tubes at 36.7 ± 0.1 °C. The precision of this method was checked by repeating the same experiment under the same conditions on several occasions and by performing the experiment in an inert atmosphere (in Schlenk tubes under nitrogen, using steel cannulas to transport polymer solution and pure solvent). The data thus acquired fell within 4% of each other, and therefore the adsorptions were performed in glass tubes covered with aluminum foil.

After three rinses, the slides were placed in 10 ml of the cocktail in a 20 ml scintillation vial (for 16 to 30 h to allow complete desorption) and subsequently counted for 10 min.

4.2.4 Error Propagation[11]

The following factors can contribute towards errors in the adsorption measurements: 1) radioactive decay is a random process in time. Therefore the error that arises by counting a sample at different points of time follows a Poisson distribution.[9] Such an error is calculated by the appropriate mathematical function by the computer interfaced to the instrument and is printed along with the counts per minute. These numbers divided by the geometric area were used in the adsorbance calculations. 2) Systematic error that arises during the cpm vs mass (μg) calibration of different samples (weighing error and volume error associated with serial dilution of the appropriate amounts of each sample). For the single sticky foot samples this was estimated to be 3.9% from the scatter in the data obtained for the four different molecular weights (all of them were prepared from the same stock of styrene) and for the double sticky feet samples it was estimated to be 5.7% from similar calculations. 3) Procedural error arising from the techniques used to clean, temperature equilibriate, perform adsorption experiments and rinse glass slides was estimated to be ± 4% from the cpm/geometric area obtained from glass slide to glass slide under exact experimental conditions. In other words the precision of our technique is ± 4%. 4) The geometric area of the glass slides obtained from their mass and density with the appropriate correction for the area of the sides of the slide (0.5 cm^2) was used in all calculations. The true surface area of glass is definitely different from this number and need not scale exactly with the geometric area, from glass slide to glass slide. This error is the area normalization error and we do not include it in our calculations because surface area determination by BET measurements can be applied only to small molecules. Individual polymer chains occupy larger dimensions and this increases with molecular weight and the goodness of the solvent. Therefore roughness scales less than the chain dimension are irrelevant and those greater than the chain dimensions are relevant. Currently the exact mapping of a given glass surface has not been established well and therefore we ignore the effect of surface roughness though we realize its importance. The counts per minute versus time obtained with different glass slides for the same adsorption experiment at times between 6 and 48 h, depending on the polymer sample, varies ± 10 to 15%, indicating that surface roughness effect is significant. However this includes all the above said errors and therefore its effect cannot be separated. Based on the contributions of 1, 2 and 3, this is probably in the range 1 to 2%. 5) Instrumental error: The countings were performed using the "Rackbeta" counter for the samples with a single sticky foot and the "Beckman" counter for the samples with two sticky feet. The background obtained with the "Beckman" counter is 5 times that of the "Rackbeta" counter. Based on the average counts obtained with ten different samples of toluene (^3H) standard we estimate this error to be in the range 3 to 5%. 6) Different amounts of cocktail in the counting mixture can bring in additional error. Since a 10 ml aliquot of the cocktail was pipetted out each time and the typical variation in the counts for a volume change of ± 0.5 ml is ± 2.0 (Rackbeta) to ± 5.0 (Beckman), this is negligible.

4.3 Results

The amount of polymer adsorbed to glass versus time was followed for all the samples till equilibrium adsorbance was recorded. Equilibrium adsorbance means counts per minute obtained from samples with time are within 3σ of each other, where σ is the random error encountered due to the nature of the radioactive decay process. All the raw data (LSC notebooks #1 to #3) obtained after background subtraction were divided by the geometric area of the respective glass slides to obtain per unit area numbers. All the polymer samples were prepared from styrene of the same specific activity and therefore the cpm/geometric area of different samples can be compared within experimental error.

The variables involved in the experiments were: two types of solvents, two types of sticky foot, two locations, un-functionalized control, five different molecular weights, at least five different concentrations and ten different times. This resulted in a large volume of data. Most of the data concerning the kinetics of adsorption were not interesting as they did not reveal any new physical phenomenon. The polymers with sticky feet adsorbed much faster than those without, a well known result. Therefore most of the cpm/geometric area vs. time data are presented in Appendix B. An example (M_n = 10 K and conc. = 1 mg/ml) in cyclohexane and toluene is presented (Table 4.2 and 4.3) and discussed in the following section. However equilibrium adsorbances for each of the samples at all the concentrations and molecular weights are presented in Tables 4.4 (cyclohexane) and 4.5 (toluene) and these were calculated from the cpm/geometric area numbers using the calibration curve for each of the sample (see Appendix B, Tables B.4 to B.11).

Table 4.2 Counts Per Minute Per Square Centimeter Obtained after Adsorption as a Function of Time

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; $M_n = 10000$

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration =				1.51 mg/ml	1.45 mg/ml
0.25					203.6 ± 5.3	53.3 ± 3.3
0.50					212.7 ± 5.5	50.1 ± 3.3
1.0					228.8 ± 5.8	44.2 ± 3.2
2.0					230.2 ± 5.8	47.7 ± 3.2
3.0					231.5 ± 5.8	50.3 ± 3.3
6.0					234.5 ± 5.9	56.0 ± 3.4
12.0					243.0 ± 6.0	50.7 ± 3.3
24.0					242.2 ± 5.9	51.7 ± 3.3
	concentration = 1.0 mg/ml				0.94 mg/ml	0.94 mg/ml
0.25	261.8 ± 5.3	41.5 ± 2.5	29.4 ± 2.3	0.25	59.9 ± 3.2	26.0 ± 2.8
0.50	376.5 ± 6.2	49.0 ± 2.7	36.1 ± 2.4	0.50	72.8 ± 3.7	31.1 ± 2.9
1.0	324.1 ± 5.8	54.8 ± 2.8	49.7 ± 2.7	1.0	63.0 ± 3.2	28.5 ± 2.8
3.0	313.1 ± 5.7	69.3 ± 3.1	64.1 ± 3.0	2.0	71.0 ± 3.7	27.9 ± 2.8
6.0	317.9 ± 5.8	79.1 ± 3.2	77.1 ± 3.2	3.0	72.8 ± 3.7	26.9 ± 2.8
16.0	332.6 ± 5.9	81.2 ± 3.3	74.9 ± 3.2	6.0	73.2 ± 3.7	25.2 ± 2.7
24.0	329.5 ± 5.9	80.0 ± 3.2	76.0 ± 3.2	12.0	73.6 ± 3.7	26.6 ± 2.8
				24.0	72.0 ± 3.7	27.3 ± 2.8
	concentration = 0.1 mg/ml				0.15 mg/ml	0.19 mg/ml
0.25	160.7 ± 4.4	22.0 ± 2.1	30.9 ± 2.3	0.25	36.5 ± 3.0	16.5 ± 2.5
0.5	167.4 ± 4.5	28.8 ± 2.3	36.1 ± 2.5	0.50	34.5 ± 3.0	19.4 ± 2.7
1.0	178.3 ± 4.6	41.3 ± 2.6	41.3 ± 2.6	1.0	32.6 ± 2.9	16.9 ± 2.6
3.0	181.1 ± 4.6	45.4 ± 2.7	51.4 ± 2.8	3.0	35.7 ± 3.0	19.3 ± 2.6
6.0	177.4 ± 4.6	43.8 ± 2.7	48.5 ± 2.6	6.0	41.2 ± 3.1	17.9 ± 2.6
12.0	182.4 ± 4.7	45.5 ± 2.8	51.8 ± 2.8	12.0	34.1 ± 3.0	15.9 ± 2.5
24.0	184.6 ± 4.7	46.0 ± 2.8	50.9 ± 2.8	24.0	35.4 ± 3.0	14.1 ± 2.5
48.0	189.8 ± 4.7					

Continued, next page

Table 4.2 Continued

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; M_n = 10000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
concentration = 0.01 mg/ml					0.015 mg/ml	0.019 mg/ml
0.5	54.6 ± 2.8	31.5 ± 2.3	28.1 ± 2.2	0.25	26.5 ± 2.8	11.2 ± 2.5
1.0	44.6 ± 2.6	32.8 ± 2.3	29.3 ± 2.2	0.50	23.0 ± 2.8	14.6 ± 2.5
2.0	61.0 ± 2.9	36.5 ± 2.4	33.7 ± 2.4	1.0	20.1 ± 2.7	13.3 ± 2.5
4.0	64.0 ± 3.0	38.4 ± 2.5	34.4 ± 2.4	3.0	20.9 ± 2.7	13.2 ± 2.5
6.0	60.3 ± 2.9	38.9 ± 2.5	35.1 ± 2.4	6.0	23.9 ± 2.8	10.4 ± 2.4
15.0	67.6 ± 3.0	42.5 ± 2.5	2.6 ± 2.3	12.0	22.9 ± 2.8	13.4 ± 2.5
24.0	61.1 ± 2.9	39.3 ± 2.5	31.8 ± 2.3	24.0	26.9 ± 2.8	11.1 ± 2.5
48.0	64.2 ± 3.0	39.8 ± 2.5	34.1 ± 2.4			
concentration = 0.001 mg/ml						
0.25	30.0 ± 2.3	17.0 ± 1.8	10.2 ± 1.7			
0.5	33.2 ± 2.3	19.0 ± 1.9	13.1 ± 1.8			
1.0	35.8 ± 2.4	23.6 ± 2.1	16.6 ± 1.9			
2.0	38.7 ± 2.4	26.7 ± 2.2	19.6 ± 1.9			
3.0	39.5 ± 2.5	31.5 ± 2.2	25.7 ± 2.2			
4.0	49.9 ± 2.7	33.1 ± 2.3	29.3 ± 2.3			
8.0	41.2 ± 2.5	34.3 ± 2.3	30.7 ± 2.3			
24.0	39.4 ± 2.4	33.0 ± 2.3	30.5 ± 2.3			

Table 4.3 Counts Per Minute Per Square Centimeter Obtained after Adsorption as a Function of Time

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 10000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration =				1.5 mg/ml	
0.083					161.8 ± 4.8	
0.25					169.2 ± 4.9	
0.50					144.6 ± 4.6	
1.0					196.3 ± 5.2	
2.0					185.3 ± 5.1	
3.0					164.3 ± 4.8	
6.0					168.1 ± 4.9	
12.0					198.9 ± 5.2	
24.0					160.5 ± 4.8	
	concentration = 1.0 mg/ml				1.05 mg/ml	1.06 mg/ml
0.25	428.6 ± 6.6	18.0 ± 2.0	4.4 ± 1.4	0.083	163.3 ± 4.8	83.6 ± 3.8
0.50	189.8 ± 4.6	19.8 ± 2.0	7.6 ± 1.6	0.25	147.4 ± 4.6	113.3 ± 4.2
1.0	180.4 ± 4.5	21.7 ± 2.1	8.8 ± 1.6	0.50	151.1 ± 4.7	105.6 ± 4.1
3.0	203.6 ± 4.8	22.1 ± 2.1	11.2 ± 1.7	1.0	135.9 ± 4.5	103.7 ± 4.1
6.0	177.5 ± 4.5	22.8 ± 2.1	11.6 ± 1.7	2.0	141.5 ± 4.6	100.8 ± 4.1
12.0	159.1 ± 4.3	25.1 ± 2.2	14.9 ± 1.9	3.0	133.1 ± 4.4	88.7 ± 3.9
12.0	175.6 ± 4.5	21.8 ± 2.1	12.1 ± 1.8	6.0	166.9 ± 4.9	89.1 ± 3.9
24.0	145.5 ± 4.1	23.1 ± 2.1	12.3 ± 1.8	12.0	157.6 ± 4.8	101.4 ± 4.1
48.0	137.9 ± 4.1	22.8 ± 2.1	12.9 ± 1.8	24.0	162.3 ± 4.8	99.2 ± 4.0
120.0	134.4 ± 4.0	21.5 ± 2.1	12.2 ± 1.8			
360.0	138.7 ± 4.1					
	concentration =				0.56 mg/ml	0.5 mg/ml
				0.083	172.5 ± 4.9	61.6 ± 3.5
				0.25	160.4 ± 4.8	69.3 ± 3.6
				0.50	137.1 ± 4.6	64.4 ± 3.5
				1.0	148.2 ± 4.7	72.8 ± 3.7
				2.0	143.7 ± 4.6	70.4 ± 3.6
				3.0	149.0 ± 4.7	65.8 ± 3.5
				6.0	157.1 ± 4.8	62.2 ± 3.5
				12.0	140.2 ± 4.6	66.6 ± 3.5
				24.0	153.6 ± 4.7	69.5 ± 3.6

Continued, next page

Table 4.3 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 10000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
concentration = 0.1 mg/ml					0.12 mg/ml	0.12 mg/ml
0.083	95.7 ± 3.4	6.3 ± 1.5	1.6 ± 1.3	0.083	149.2 ± 4.7	46.5 ± 3.2
0.25	76.6 ± 3.2	8.0 ± 1.6	2.0 ± 1.3	0.25	120.9 ± 4.3	49.4 ± 3.4
0.5	72.9 ± 3.1	5.7 ± 1.5	2.0 ± 1.3	0.50	114.7 ± 4.3	53.6 ± 3.3
1.0	68.4 ± 3.0	5.1 ± 1.4	4.8 ± 1.4	1.0	127.6 ± 4.4	50.7 ± 3.3
2.0	75.1 ± 3.1	5.2 ± 1.4	3.4 ± 1.4	2.0	130.3 ± 4.5	50.2 ± 3.2
3.0	72.5 ± 3.1	7.8 ± 1.6	3.7 ± 1.4	3.0	125.2 ± 4.4	52.9 ± 3.3
4.0	73.1 ± 3.1	6.5 ± 1.5	3.5 ± 1.4	6.0	124.5 ± 4.4	49.8 ± 3.3
15.0	71.7 ± 3.1	7.2 ± 1.5	4.7 ± 1.4	12.0	130.8 ± 4.5	54.4 ± 3.4
24.0	76.9 ± 3.2	8.0 ± 1.6	5.6 ± 1.5	24.0	123.8 ± 4.4	47.9 ± 3.2
48.0	80.5 ± 3.2	7.0 ± 1.5	5.5 ± 1.5			
336.0	75.6 ± 3.1					
concentration =					0.067 mg/ml	0.056 mg/ml
				0.083	151.5 ± 4.6	30.7 ± 2.8
				0.25	142.6 ± 4.6	31.0 ± 2.8
				0.50	128.5 ± 4.4	34.7 ± 3.2
				1.0	116.5 ± 4.2	31.7 ± 2.9
				2.0	120.3 ± 4.3	29.0 ± 2.7
				3.0	110.5 ± 4.1	26.0 ± 2.7
				6.0	103.9 ± 4.1	33.4 ± 2.9
				14.0	113.0 ± 4.2	28.8 ± 2.7
				24.0	108.6 ± 4.1	31.1 ± 2.8
concentration = 0.01 mg/ml					0.015 mg/ml	0.019 mg/ml
0.25	19.8 ± 2.0	Below detection limit	Below detection limit	0.083	89.0 ± 3.8	19.7 ± 2.5
0.5	18.6 ± 2.0			0.25	63.7 ± 3.4	24.7 ± 2.7
1.0	16.8 ± 1.9			0.50	51.5 ± 3.2	19.8 ± 2.5
2.0	17.1 ± 1.9			1.0	78.8 ± 3.7	19.4 ± 2.5
4.0	15.2 ± 1.8			2.0	59.7 ± 3.3	16.6 ± 2.4
				3.0	68.2 ± 3.5	14.1 ± 2.3
				6.0	74.6 ± 3.6	16.5 ± 2.4
15.0	13.8 ± 1.8			14.0	60.2 ± 3.4	16.1 ± 2.4
24.0	13.0 ± 1.8			24.0	47.6 ± 3.2	15.5 ± 2.4
48.0	14.5 ± 1.8			48.0	45.4 ± 3.2	14.4 ± 2.3
96.0	12.9 ± 1.8			96.0	50.2 ± 3.2	13.5 ± 2.3
120.0	13.5 ± 1.8			120.0	47.7 ± 3.2	13.4 ± 2.3

Continued, next page

Table 4.3 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; $M_n = 10000$

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 0.001 mg/ml					
0.25	7.3 ± 1.6	Below detection limit	Below detection limit			
0.5	7.0 ± 1.5					
1.0	6.4 ± 1.5					
2.0	6.2 ± 1.5					
4.0	5.7 ± 1.5					
8.0	4.1 ± 1.4					
24.0	4.2 ± 1.4					
48.0	3.4 ± 1.4					
72.0	3.6 ± 1.4					

Table 4.4 Summary of Adsorbance versus Concentration for the Functionalized and Un-Functionalized Samples in Cyclohexane

conc (mg/ml)	PS-COOH (μg/cm^2)	PS-OH (μg/cm^2)	PS-H (μg/cm^2)	PS(COOH)$_2$ (μg/cm^2)	PS(OH)$_2$ (μg/cm^2)
Number average molecular weight - 5K					
0.001	0.071 ± 0.013	0.036 ± 0.007	0.031 ± 0.007		
0.013	0.114 ± 0.018	0.044 ± 0.008	0.036 ± 0.007		
0.115	0.259 ± 0.035	0.053 ± 0.009	0.044 ± 0.008		
0.530	0.320 ± 0.043	0.073 ± 0.012	0.060 ± 0.011		
1.05	0.366 ± 0.048	0.081 ± 0.013	0.068 ± 0.011		
Number average molecular weight - 10K					
0.001	0.057 ± 0.010	0.049 ± 0.008	0.046 ± 0.008		
0.012	0.092 ± 0.015	0.059 ± 0.009	0.050 ± 0.009		
0.015				0.031 ± 0.009	
0.019					0.015 ± 0.006
0.106	0.254 ± 0.035	0.066 ± 0.011	0.073 ± 0.012		
0.150				0.046 ± 0.011	
0.190					0.023 ± 0.008
0.520	0.393 ± 0.051	0.089 ± 0.015	0.081 ± 0.013		
0.937				0.095 ± 0.019	0.036 ± 0.009
1.12	0.432 ± 0.057	0.110 ± 0.017	0.105 ± 0.016		
1.51				0.317 ± 0.056	0.068 ± 0.015
Number average molecular weight - 30K					
0.001	0.108 ± 0.017	0.070 ± 0.012	0.072 ± 0.012		
0.012	0.156 ± 0.023	0.091 ± 0.015	0.092 ± 0.015		
0.016				0.035 ± 0.008	
0.027					0.013 ± 0.004
0.110	0.372 ± 0.050	0.114 ± 0.017	0.103 ± 0.016		
0.150				0.051 ± 0.011	
0.203					0.021 ± 0.005
0.530	0.491 ± 0.065	0.165 ± 0.026	0.153 ± 0.022	0.209 ± 0.036	0.050 ± 0.011
1.06	0.563 ± 0.073	0.182 ± 0.026	0.172 ± 0.025	0.278 ± 0.048	0.092 ± 0.018
2.43				0.610 ± 0.106	
2.71					0.265 ± 0.046

Continued, next page

Table 4.4 Continued

conc (mg/ml)	PS-COOH ($\mu g/cm^2$)	PS-OH ($\mu g/cm^2$)	PS-H ($\mu g/cm^2$)	$PS(COOH)_2$ ($\mu g/cm^2$)	$PS(OH)_2$ ($\mu g/cm^2$)
Number average molecular weight - 60K					
0.013				0.118 ± 0.025	
0.017					0.067 ± 0.016
0.101				0.150 ± 0.031	
0.120					0.096 ± 0.021
0.567				0.366 ± 0.066	
0.711					0.247 ± 0.046
1.050				0.446 ± 0.079	0.302 ± 0.055
1.922					
2.234				0.640 ± 0.110	0.380 ± 0.066
Number average molecular weight - 140K					
0.001	0.158 ± 0.023		0.152 ± 0.023		
0.014	0.193 ± 0.027		0.181 ± 0.026	0.300 ± 0.053	0.148 ± 0.028
0.118	0.257 ± 0.035		0.208 ± 0.029	0.368 ± 0.066	0.178 ± 0.036
0.530	0.379 ± 0.049		0.252 ± 0.035		
0.570				0.485 ± 0.087	
0.620					0.215 ± 0.041
1.150	0.434 ± 0.057		0.277 ± 0.037	0.610 ± 0.108	
1.294					0.270 ± 0.050
2.410				0.600 ± 0.106	
2.553					0.320 ± 0.059

Note: conc stands for concentration in mg/ml. For adsorbance entries in any particular row the stated value of concentration is the average of the exact concentrations used in the experiments (deviation ≤ ± 10%). The exact concentration of the solutions in mg/ml was obtained by the liquid scintillation counting of 3 aliquots each of 25 μl before adsorption. The adsorbances of polystyrenes with one end-group at a concentration of ~ 0.5 mg/ml is an average of the counts obtained from two glass slides after 48 h and no kinetic measurements were performed. The error associated with the adsorbance is the summation of the random, systematic and other errors mentioned in section 4.2.4.

Table 4.5 Summary of Adsorbance versus Concentration for the Functionalized and Un-Functionalized Samples in Toluene

conc (mg/ml)	PS-COOH (μg/cm^2)	PS-OH (μg/cm^2)	PS-H (μg/cm^2)	PS(COOH)$_2$ (μg/cm^2)	PS(OH)$_2$ (μg/cm^2)
Number average molecular weight - 5K					
0.002	0.006 ± 0.003	below detection limit (b. d. l.)	below detection limit (b. d. l.)		
0.010	0.013 ± 0.004				
0.053	0.079 ± 0.013				
0.103	0.132 ± 0.019				
0.150	0.139 ± 0.021				
1.050	0.142 ± 0.021				
Number average molecular weight - 10K					
0.001	0.010 ± 0.004	(b. d. l.)	(b. d. l.)		
0.012	0.023 ± 0.006	(b. d. l.)	(b. d. l.)		
0.015				0.065 ± 0.015	
0.019					0.019 ± 0.006
0.060	0.058 ± 0.010	0.006 ± 0.003	0.005 ± 0.003	0.144 ± 0.028	0.041 ± 0.010
0.120	0.108 ± 0.017	0.014 ± 0.004	0.012 ± 0.004	0.168 ± 0.031	0.065 ± 0.015
0.497					0.091 ± 0.019
0.570	0.155 ± 0.022	0.029 ± 0.006	0.017 ± 0.005	0.201 ± 0.037	
1.050				0.210 ± 0.039	0.130 ± 0.026
1.150	0.185 ± 0.026	0.036 ± 0.009	0.022 ± 0.005		
1.500				0.215 ± 0.039	
Number average molecular weight - 30K					
0.001	0.006 ± 0.003	b. d. l.	b. d. l.		
0.014	0.010 ± 0.004	0.010 ± 0.004	0.009 ± 0.004		0.011 ± 0.004
0.021				0.087 ± 0.017	
0.050	0.023 ± 0.006	0.019 ± 0.005	0.017 ± 0.005		
0.120	0.042 ± 0.009			0.126 ± 0.023	
0.150		0.026 ± 0.006	0.022 ± 0.005		0.019 ± 0.005
0.479				0.187 ± 0.033	
0.510	0.110 ± 0.017				0.030 ± 0.007
0.709				0.268 ± 0.046	
1.050	0.136 ± 0.020	0.043 ± 0.009	0.036 ± 0.008		0.048 ± 0.010
2.210					0.048 ± 0.010
2.600				0.270 ± 0.047	

Continued, next page

Table 4.5 Continued

conc (mg/ml)	PS-COOH (μg/cm^2)	PS-OH (μg/cm^2)	PS-H (μg/cm^2)	PS(COOH)$_2$ (μg/cm^2)	PS(OH)$_2$ (μg/cm^2)
Number average molecular weight - 60K					
0.013				0.066 ± 0.015	0.013 ± 0.005
0.119				0.080 ± 0.018	
0.129					0.015 ± 0.007
0.603				0.106 ± 0.023	
0.649					0.066 ± 0.016
0.965					0.116 ± 0.023
1.020				0.132 ± 0.026	
1.890				0.143 ± 0.029	
1.900					0.118 ± 0.024
Number average molecular weight - 140K					
0.001	0.007 ± 0.003		0.006 ± 0.003		
0.012	0.016 ± 0.005		0.014 ± 0.005		
0.015					0.010 ± 0.007
0.021				0.042 ± 0.012	
0.056	0.021 ± 0.005		0.019 ± 0.005		
0.125	0.032 ± 0.007		0.030 ± 0.006		0.012 ± 0.007
0.164				0.102 ± 0.022	
0.600	0.074 ± 0.012		0.065 ± 0.011	0.137 ± 0.029	0.036 ± 0.011
1.200	0.090 ± 0.014		0.058 ± 0.010		
1.269				0.222 ± 0.042	
1.294					0.072 ± 0.018
2.342				0.225 ± 0.043	
2.553					0.084 ± 0.020

Note: conc stands for concentration. Adsorbances along a particular row are from solutions of different exact concentrations but the average concentration (deviation ≤ ±10 %) is given at the extreme left column in an effort to prepare a compact table. The exact concentration of the solutions were determined from the liquid scintillation cocktail of three aliquots each of 25 μl. The adsorbances of polystyrenes with one end-group at concentrations of ~ 0.05, ~0.15, and ~ 0.5 mg/ml is an average of the counts obtained from four glass slides after 360 h and no kinetic measurements were performed. The error associated with the adsorbance is the summation of the random, systematic and other errors mentioned in section 4.2.4.

4.4 Discussion

4.4.1 Kinetics of the Adsorption of End-Functionalized Polystyrenes to Glass from Cyclohexane just above "Theta" Solvent Condition

The amount of end-functionalized polystyrenes (represented by the counts per minute obtained after background subtraction divided by the geometric area) adsorbed to glass from cyclohexane at 36.7±0.1 °C for the 10 K sample at a solution concentration of ~ 1 mg/ml as a function of time are shown in figures 4.1a and 4.1b. The data is presented in Table 4.2. It is evident from the figures that carboxylic acid end-functionalized samples adsorb rapidly to glass and maximum adsorbance is reached within 0 to 15 min of contact. Polystyrene with two hydroxyl end-groups adsorbs as rapidly as the carboxylic acid end-functionalized polystyrenes. The polymer with a hydroxyl end-group (PS-OH) and the un-functionalized polymer (PS-H) adsorb at the same rate and reach equilibrium adsorbance within 3 to 4 h. Their rate of adsorption is smaller when compared to the carboxylic acid end-functionalized polystyrene and the difference is not that significant to warrant a discussion.

In general the rate of adsorption in cyclohexane follows the following trend: HOOC-PS-COOH ~ PS-COOH ~ HO-PS-OH > PS-OH ≥ PS-H. The rate of adsorption also decreases with concentration and increasing molecular weight. The observed decrease in the equilibriation time with decrease in concentration is well documented [12] and is believed to be the effect of the rearrangement of the segments at the surface so as to achieve a flatter conformation. Small molecular weight polymers adsorb rapidly compared to polymers of large chain length because equilibriation is not only limited by material transport but also by the large number of molecular rearrangements that are hypothesized to take place in order to reach a state of minimum energy.

solvent - cyclohexane; M_n = 10000; c = 1.0 mg/ml; T = 36.7 ± 0.1°C; a - 1SF; b - 2SF

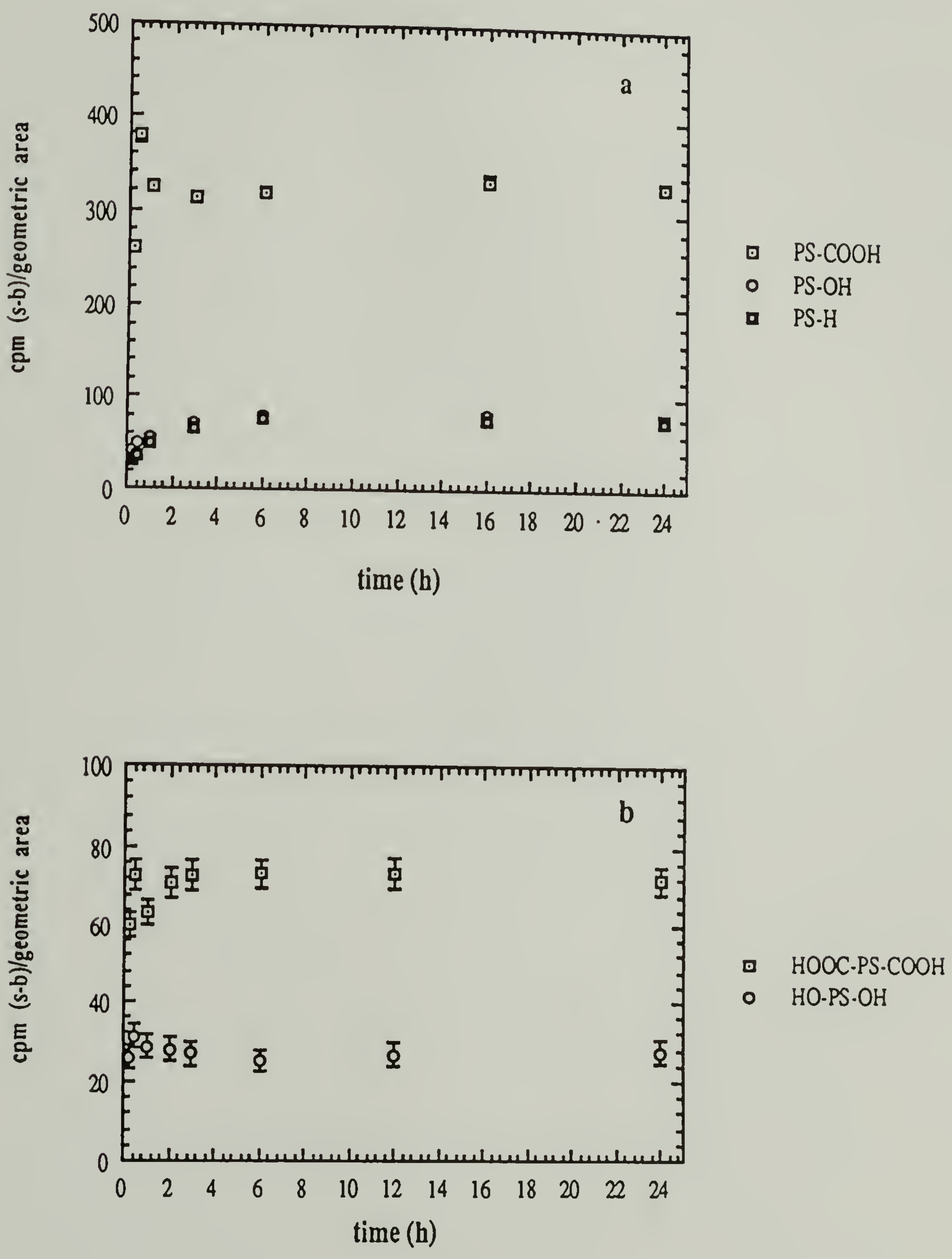


Figure 4.1 cpm / geometric area versus time

4.4.2 Kinetics of the Adsorption of End-Functionalized Polystyrenes to Glass from Toluene under "Good" Solvent Conditions

The amount of end-functionalized polystyrenes (represented by the counts per minute obtained after background subtraction divided by the geometric area) adsorbed to glass from a solution of concentration ~ 1 mg/ml as a function of time for the 10 K samples are shown in figures 4.2a and 4.2b. The data are presented in Table 4.3.

Polystyrenes with carboxylic acid and hydroxyl functional groups at both the chain ends adsorb rapidly to glass and equilibrium adsorbances are recorded within a few hours. The kinetics of the adsorption of PS-COOH sample exhibits an interesting feature; an initial maximum in the amount adsorbed occurs 5 to 15 min into the experiment following which it declines to an equilibrium value in about 24 - 48 h. This phenomenon is reproducible in its trend as well as in the absolute cpm obtained within ± 10%. Earlier this was reported for the adsorption of poly(styrene-b-ethylene oxide) from cyclopentane solution to glass by Gast.[13] However theory predicts a rapid initial adsorption to a mushroom type conformation (diffusion controlled) from which a denser coverage is obtained by the penetration of the sticky block to the interface to form a more brushy conformation over longer times (logarithmic change).[14] Experimental results on the kinetics of the adsorption of poly(styrene-b-ethylene oxide) block copolymer to silicon dioxide from toluene monitored by ellipsometry seem to agree with the above prediction.[15] However one cannot escape noticing a statement made by the authors, that "The maximum adsorbed amount at long times decreases with increasing lengths of the nonadsorbing tail". This suggests that for a given enthalpy of interaction with the surface the amount adsorbed would go through a maximum as one goes through a conformational transition from strongly stretched brushes through weakly stretched brushes to mushroom type structures.

solvent - toluene; M_n = 10000; c = 1.0 mg/ml; T = 23.0 ± 1.0 °C; a - 1SF; b - 2SF

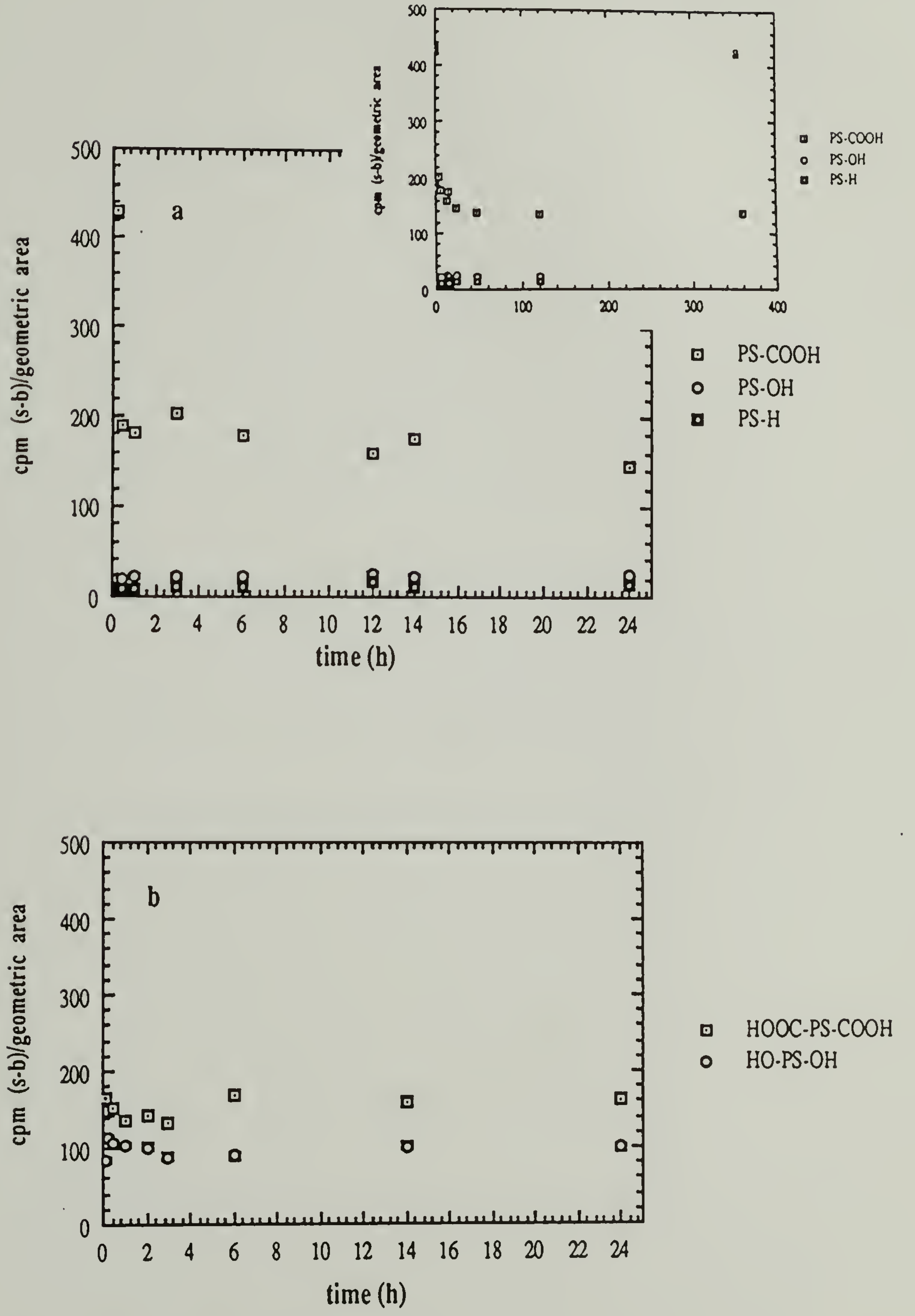


Figure 4.2 cpm / geometric area vs time

In our case the differential enthalpy of interaction of the -COOH group with the surface is ~ 4 kT (it is 5 kT in cyclohexane[16] and since toluene interacts with the surface it is less) and therefore this interaction energy is not capable of stretching the chains strongly. Experimental fact is that these chains desorb to different extents, depending on contact time and molecular weight, on contact with pure toluene after adsorption. Also, polystyrene segments interact with silica with an interaction energy of the order 0.3 kT.[17] Combining these factors we hypothesize that PS-COOH chains form weakly stretched brushes at low time scales which eventually rearrange to an energetically more stable mushroom type structures on the surface at longer times. This is clearly counter-intuitive and contradicts theoretical predictions. The justification for the hypothesis is as follows: The backbone structure of the polystyrene is similar to the structure of toluene. Therefore it is reasonable to assume that the enthalpy of interaction of the polystyrene segment with the surface is approximately equal that of toluene. The polymer segments possess an additional advantage in that once a molecule is bound by a few segments in a cooperative fashion its probability of desorption is lower than that of an isolated toluene molecule. In all probability there is a stiff competition between the -COOH and the solvent molecules during the initial stages of the adsorption (0 to 5 min) for the surface sites. This is understandable from the fact that the concentration of the -COOH group at a solution concentration of 1 mg/ml is 2×10^{-4} moles/liter and its differential enthalpy of interaction with the surface is ~ 4 kT while the concentration of the solvent molecules is ~ 9.4 moles/liter and its differential enthalpy of interaction is = 0.3 kT. In addition the number of -COOH groups at the surface is also limited by the hydrodynamic size of the polystyrene backbone to which it is attached, being less the larger the size of the molecule as a whole. With time polystyrene segments (with similar enthalpy of interaction and solution concentration of 9.6×10^{-3} moles/liter) bind "co-operatively" to the surface displacing some solvent molecules and polystyrene molecules bound either with a terminal group or with a terminal group and a few segments.

The above hypothesis does result in fewer chains being attached with time. Solvent binding to the surface is supported by the fact that some of the bound polymer is desorbed when brought in contact with fresh solvent for 15 min (three washes), but still leaves a significant amount on the surface as analyzed by x-ray photoelectron spectroscopy (PS-COOH, 5K, 1 mg/ml leaves about 5 Å of polymer after three washes).

PS-OH and PS-H adsorb to glass at a smaller rate but reach equilibrium adsorbance faster as the unusual kinetics observed with PS-COOH sample is not observed here. We think that the hydroxyl group is not as effective a competitor for the surface sites as the carboxylic acid group and therefore the initial orientation of the chains followed by the subsequent "cooperative" binding of the segments to kick out loosely bound chains is not observed.

The familiar adsorption maximum followed by the decline to a steady state value observed for PS-COOH samples is not observed with HOOC-PS-COOH samples. It is possible that this phenomenon takes place at time scales shorter than that tried (5 min). If that is the case we do not know why it takes place that fast. In general we are unable to account for this phenomenon in a discrete manner but believe that at this end group concentration and the enthalpy change per chain (~ 8 kT) brought about by the carboxylic acid groups alone is sufficient for adsorption and probably the segments with an enthalpy of interaction of a fraction of kT do not compete for the surface.

In general the rate at which equilibrium adsorbance is reached follows the following trend: HOOC-PS-COOH ~ HO-PS-OH > PS-OH ~ PS-H > PS-COOH. This rate also decreases with decreasing concentration and molecular weight for the same reasons as explained earlier (see section 4.4.1).

4.4.3 Adsorption Isotherms in Cyclohexane

The adsorption isotherms for all the functionalized and un-functionalized polystyrenes in the order of increasing molecular weight are shown in figures 4.3 to 4.7. The data is presented in section 4.3, Tables 4.4 and 4.5. All the adsorbance data are presented in the units of $\mu g/cm^2$. The units used in most of the publications in the adsorption literature is mg/m^2 the reason being the use of high surface area adsorbents. The multiplication of the adsorbance data presented here by 10 converts it to the mg/m^2 units.

An inspection of the isotherms reveals the following facts: 1) Adsorbance increases with concentration of the polymer in solution for the un-functionalized and functionalized polystyrenes. All the samples exhibit high affinity isotherms, i.e at very low solution concentrations adsorbance maximum is reached. 2) The derivative of the adsorbance with respect to the concentration (dA/dC or the slope of A vs. C) as a function of concentration of the polymer in solution exhibits interesting features for PS-COOH, HOOC-PS-COOH, and HO-PS-OH. 3) The adsorbance of polystyrene with a hydroxyl end-group (PS-OH) is the same as that of un-functionalized polystyrene within experimental error and therefore a hydroxyl end-group doesn't function as an effective sticky foot. 4) The ratio of the adsorbances of functionalized polystyrene to un-functionalized polystyrene is a function of the concentration of the polymer in solution, type of the functional end-group and its location. Each of the observed facts is discussed in detail in the following paragraphs.

The amount of polymer adsorbed increases with concentration for all the polymers as observed earlier.[12] This is because of the change in the conformation of the adsorbed chain as a function of increasing solution concentration. At low solution concentration the average conformation of the chains in the adsorbed state consists of a large number of segments in trains, some in small loops and tails. At very high solution concentration (say at the maximum adsorbance) the average conformation of the adsorbed chain consists

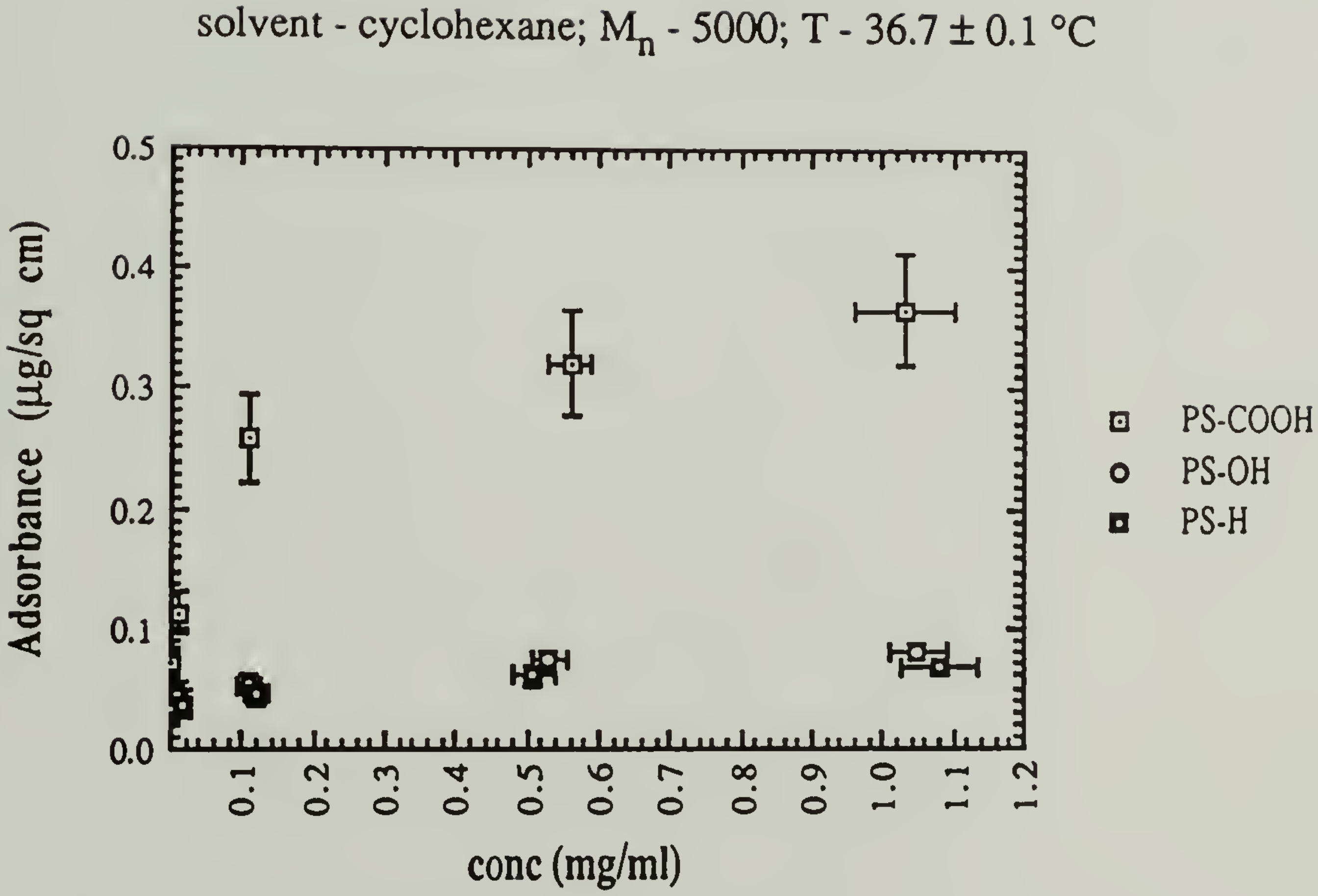


Figure 4.3 Adsorption Isotherms

solvent - cyclohexane; M_n - 10000; T - 36.7 ± 0.1 °C; top - 1SF; bottom - 2SF

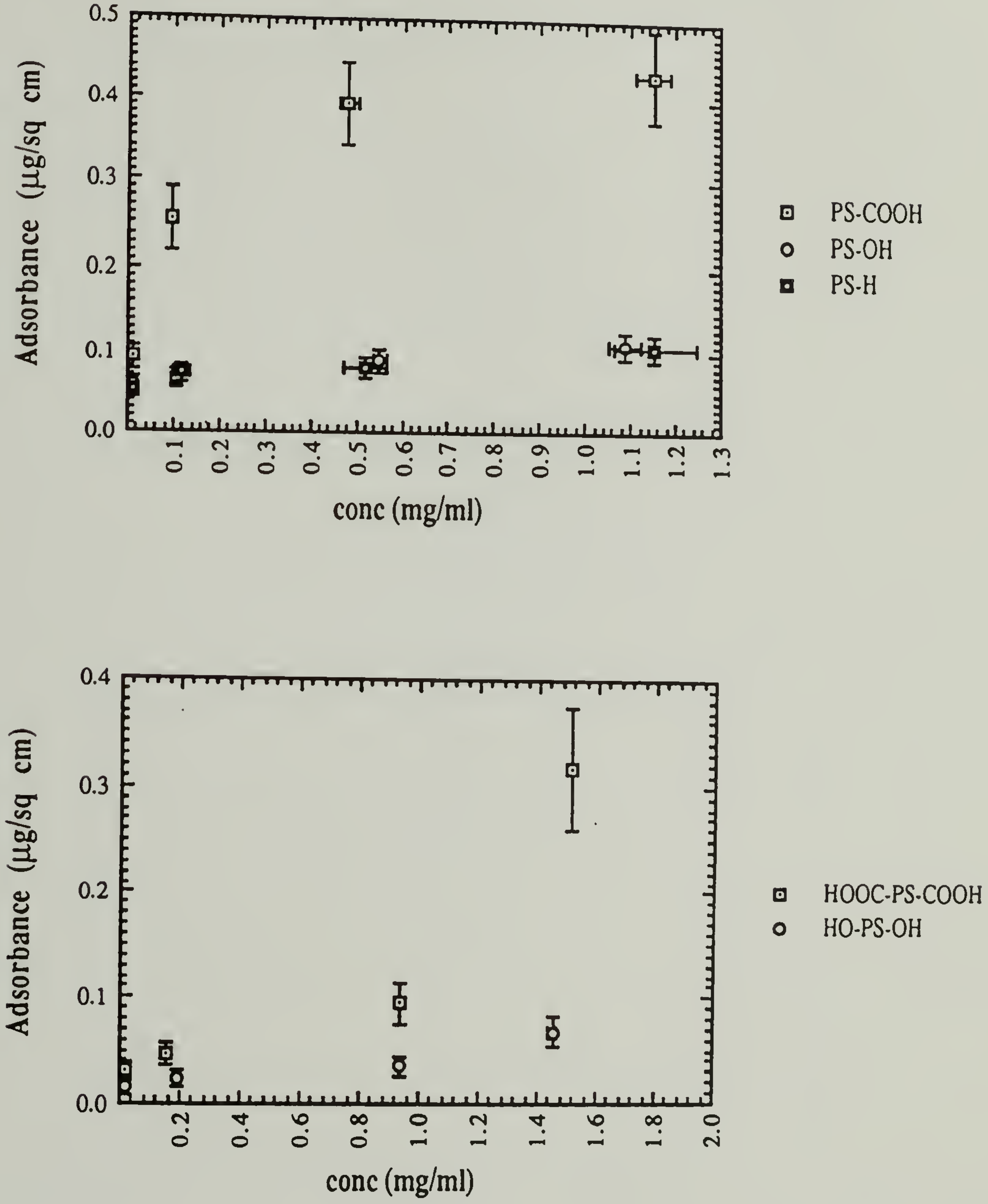


Figure 4.4 Adsorption Isotherms

solvent - cyclohexane; M_n - 30000; T - 36.7 ± 0.1 °C; top - 1SF; bottom - 2SF

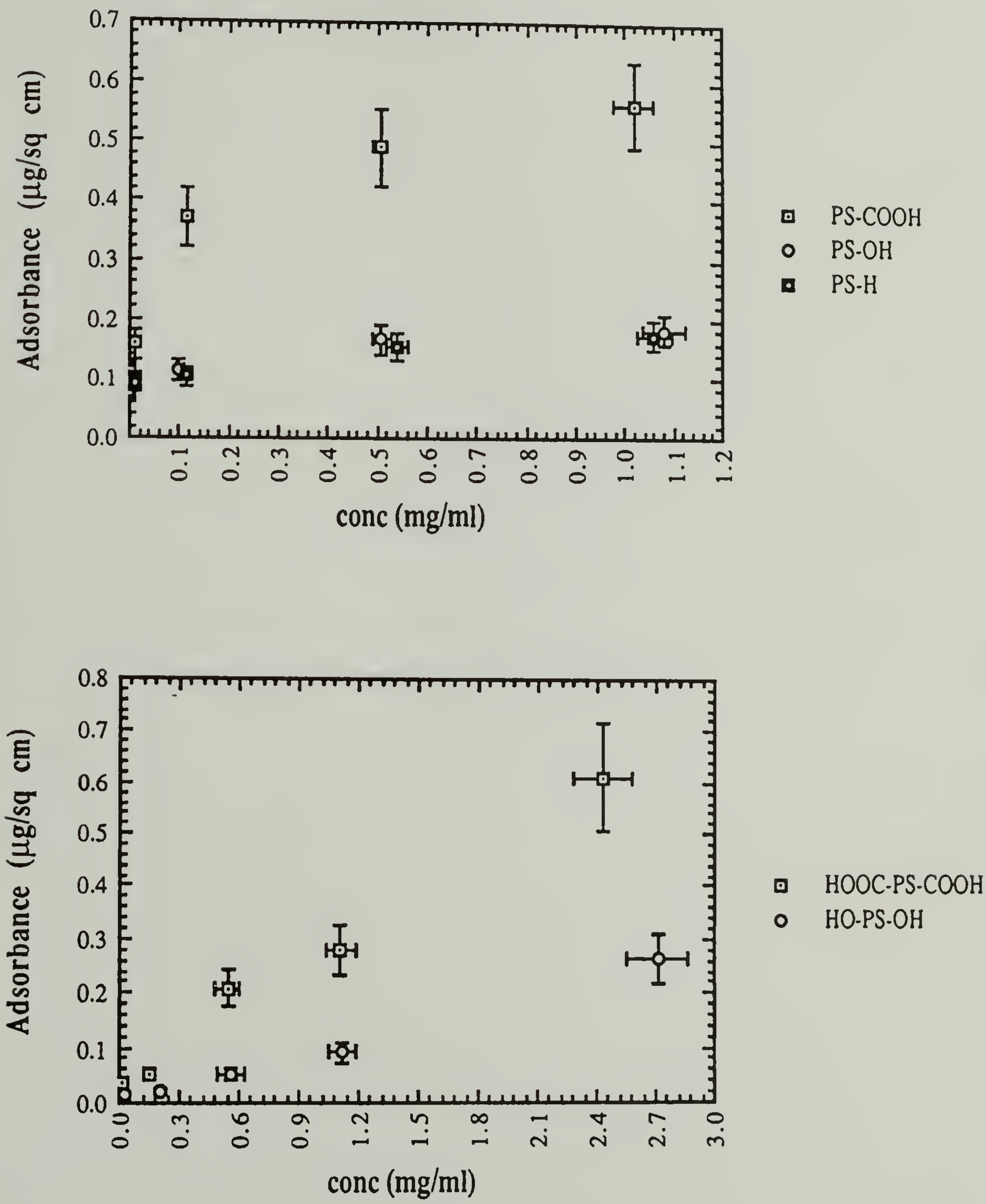
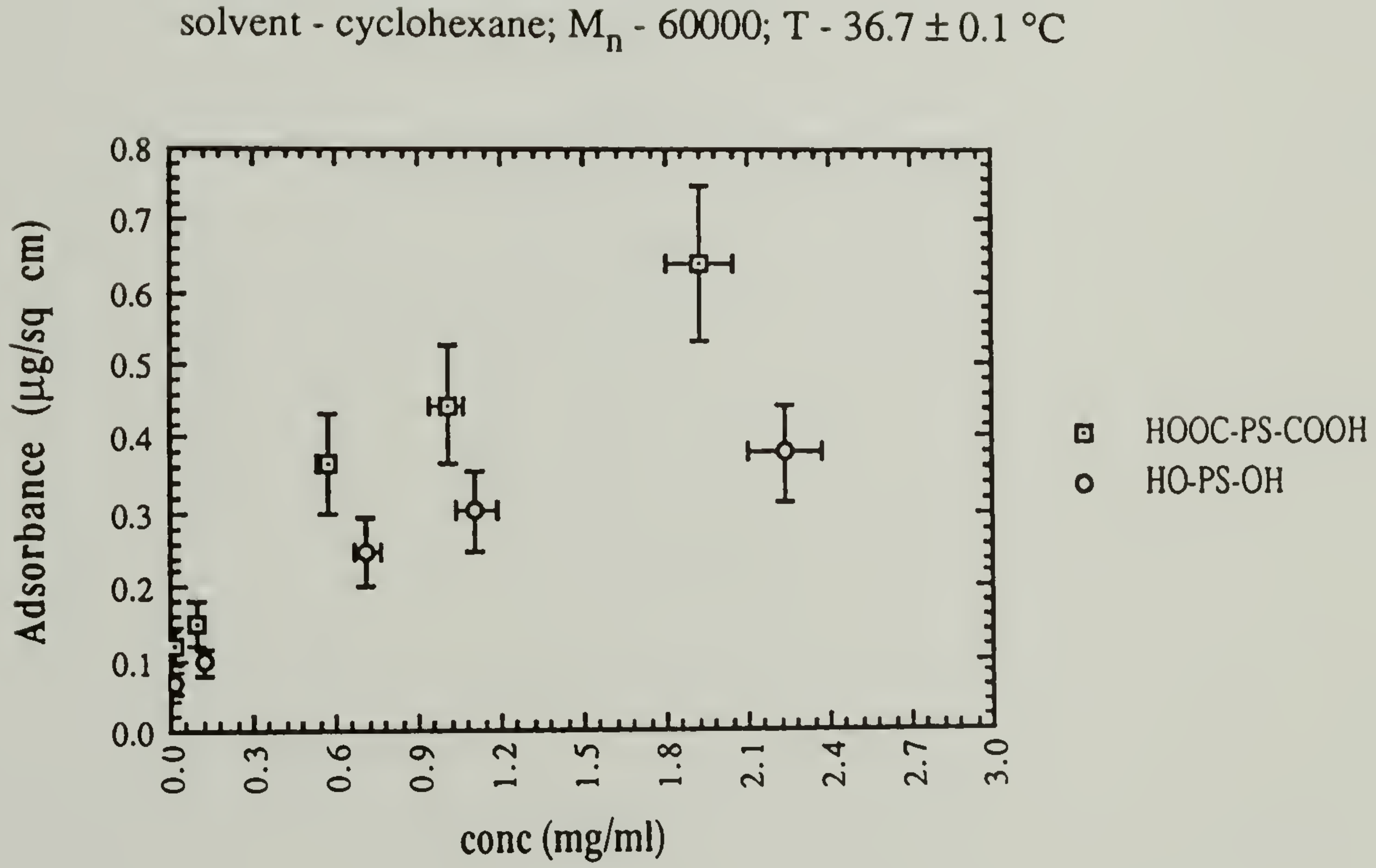


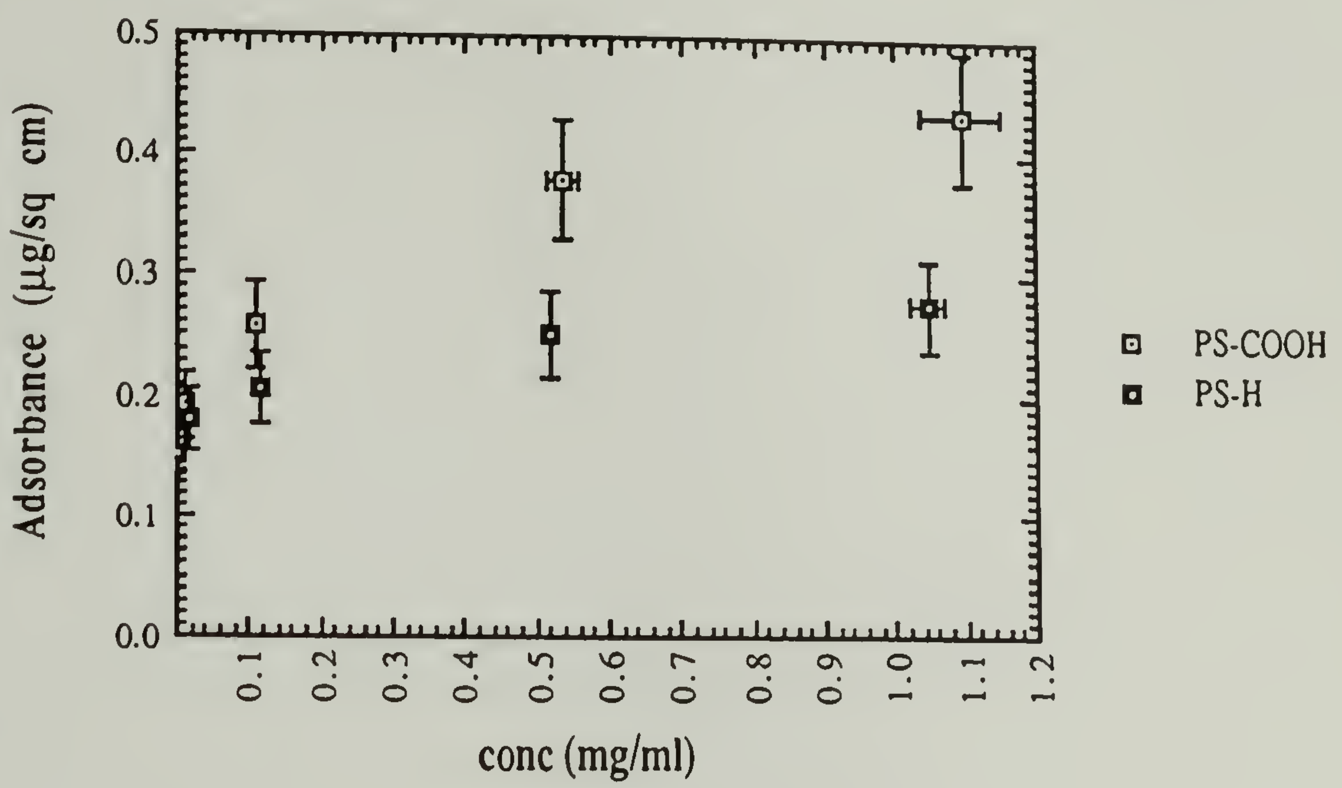
Figure 4.5 Adsorption Isotherms



solvent - cyclohexane; M_n - 60000; T - 36.7 ± 0.1 °C

Figure 4.6 Adsorption Isotherms

solvent - cyclohexane; M_n - 140000; T - 36.7 ± 0.1 °C; top - 1SF; bottom - 2SF



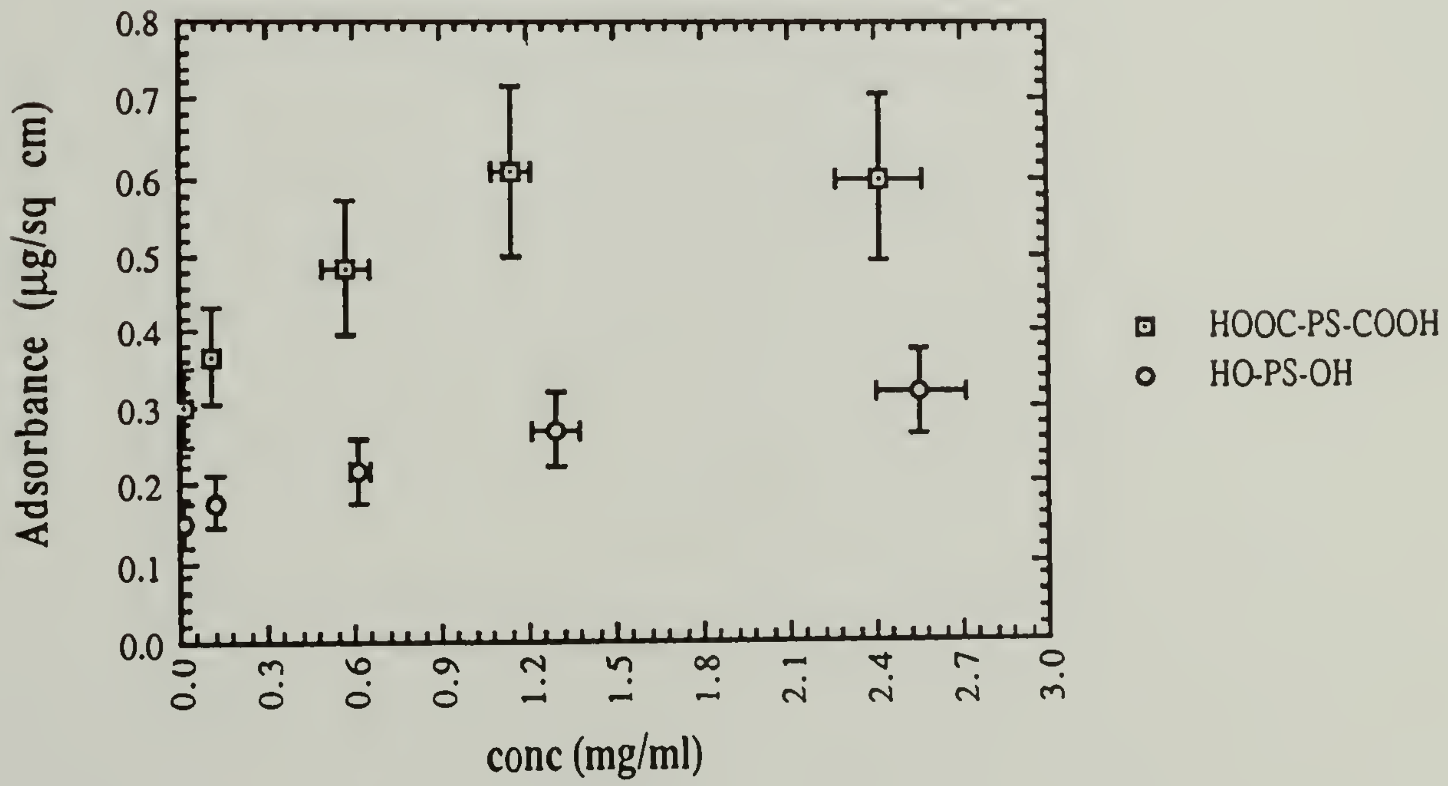


Figure 4.7 Adsorption Isotherms

of a smaller number of segments in trains and larger number of segments in bigger loops and longer tails. This explanation also follows directly from the adsorbance data if one calculates the effective surface area per chain as a function of concentration (assuming uniform surface coverage). The amount of un-functionalized polystyrene adsorbed as a function of concentration and molecular weight is consistent in magnitudes and trends with previously reported results of Stromberg,[4, 12] Granick,[18] and Takahashi [19] within experimental error.

The slope of A vs. C for PS-COOH, HOOC-PS-COOH and HO-PS-OH follows that of polystyrene at very low solution concentration and increases abruptly at some intermediate concentration before levelling off just as observed with polystyrene. The slope changes are functions of molecular weight and therefore are functions of end-group concentration.

The reason why hydroxyl end-group is not an effective sticky foot is probably due to its weak enthalpic interaction with the surface even though its magnitude might be marginally higher than the interaction energy of a polystyrene segment with the surface. This in principle might bring one end of the chain to the surface but its interaction energy may not pay for the stretching of the chains in order to accommodate more end-groups at the surface. Therefore polystyrenes with one hydroxyl end-group adsorb in conformations similar to that of polystyrene resulting in almost the same adsorbances at all the concentrations and molecular weights. In addition it is possible that one end of the hydroxyl end-functionalized polystyrene is at the surface.

The ratio of the adsorbances of functionalized polystyrene to un-functionalized polystyrene is a function of the concentration of the polymer in solution, type of the functional end-group and its location. Each of these cases are discussed for a particular molecular weight (10K) in the following paragraphs.

As the concentration of the polymer in solution is increased, the ratio of the adsorbances of PS-COOH to PS-H increases rapidly as shown in the next page.

concentration (mg/ml)	segment concentration (moles/liter)	end-group conc. (moles/liter)	$A_{PS\text{-}COOH} / A_{PS\text{-}H}$ ratio
0.0011 ± 0.003	1.06×10^{-5}	1.1×10^{-7}	1.24
0.010 ± 0.040	9.6×10^{-5}	1.0×10^{-6}	1.84
0.095 ± 0.010	9.12×10^{-4}	9.5×10^{-6}	3.47
0.480 ± 0.022	4.61×10^{-3}	4.80×10^{-5}	4.85
1.150 ± 0.040	1.10×10^{-2}	1.15×10^{-4}	4.11

At the lowest concentration the ratio is 1.24. This suggests that the conformation of adsorbed chains of PS-COOH and PS-H are similar. As the concentration of the polymer in solution is increased, the adsorbance of PS-COOH sample increases much more rapidly than that of the PS-H samples ($A_{PS\text{-}COOH} / A_{PS\text{-}H}$ ratio). For any given solution concentration the concentration of the segments is the same for PS-COOH and PS-H while the end-group concentration increases with increasing solution concentration. The increase in the ratio is therefore due to the increase in the absolute concentration of the carboxylic acid end-group and these groups compete with the segments of the backbone for the surface sites. The result of this argument is that PS-COOH chains adsorb with much of their backbone extended normal to the surface in order to accommodate more carboxylic acid end-groups at the surface. The energy of extension of the backbone or stretching of the chain is then paid for by the surface-carboxylic acid interaction enthalpy. The fact that a similar phenomenon does not take place at lower polymer concentration is probably due to the fact that the absolute concentration of the end-group is much smaller than that of the segments, which must compete effectively for surface sites as evidenced by the adsorption of the un-functionalized polystyrene.

The maximum amount adsorbed at this molecular weight (0.432 µg/sq cm) is consistent with that reported by Satija, et al.,[20] for the adsorption of PS-COOH of number average molecular weight 14K from deuteriocyclohexane to silicon dioxide. They used neutron reflection technique to determine the adsorbance and reported a value of 0.41 μg/sq cm at ~ 21 °C and also found it to be independent of temperature up to 42 °C.

Comparing the variation of the chain architecture with that of un-functionalized polystyrene (i.e. comparing the area occupied per chain from the adsorbance data) we can conclude that the transformation of the chain conformation from that dominated by trains to those dominated by loops and tails takes place at a much lower solution concentration for the PS-COOH sample.

The ratios of the adsorbances of polystyrene with two carboxylic acid end-groups to the un-functionalized one as a function of concentration are given below. The adsorbances of un-functionalized polymers at any given concentration were interpolated from the adsorbance isotherm of the 10K sample.

concentration (mg/ml)	segment concentration (moles/liter)	end-group conc. (moles/liter)	$A_{HOOC\text{-}PS\text{-}COOH} / A_{PS\text{-}H}$ ratio
0.015 ± 0.002	1.44×10^{-4}	3.0×10^{-6}	0.62
0.150 ± 0.005	1.44×10^{-3}	3.0×10^{-5}	0.82
0.938 ± 0.014	9.01×10^{-3}	1.9×10^{-4}	0.95
1.510 ± 0.020	1.45×10^{-2}	3.0×10^{-4}	3.00

The ratio increases with increasing solution concentration being lower than one at all concentrations below ~ 1 mg/ml. This indicates that a significant number of HOOC-PS-COOH chains might have adsorbed with both their ends at the interface, resulting in fewer number of tails in the average structure of the adsorbed layer and therefore lower adsorbed amount.

The ratios of the adsorbances of polystyrene with two hydroxyl end-groups and to the un-functionalized one as a function of concentration are given below. The adsorbances of un-functionalized polymers at any given concentration were interpolated from the adsorbance isotherm of the 10K sample.

concentration (mg/ml)	segment concentration (moles/liter)	end-group conc. (moles/liter)	$A_{HO\text{-}PS\text{-}OH} / A_{PS\text{-}H}$ ratio
0.019 ± 0.002	1.82×10^{-4}	3.8×10^{-6}	0.27
0.190 ± 0.006	1.82×10^{-3}	3.8×10^{-5}	0.32
0.935 ± 0.012	8.98×10^{-3}	1.9×10^{-4}	0.38
1.450 ± 0.016	1.40×10^{-2}	2.9×10^{-4}	0.65

The ratio increases with increasing solution concentration being lower than one at all the concentrations. This indicates that most of the HO-PS-OH chains might have adsorbed with both their ends at the interface, resulting in a fewer number of tails in the average structure of the adsorbed layer and therefore lower adsorbed amount. Hydroxyl end-groups probably interact with the surface with an enthalpy of interaction marginally greater than the polystyrene segments. This might result in chain structures devoid of tails. As tails contribute significantly to the adsorbed amount this results in adsorbances lower than those for un-functionalized polystyrene.

On comparing the adsorbance ratios of dicarboxylic acid and dihydroxyl terminated polystyrenes at low concentrations we infer that the dicarboxylic acid adsorbs with longer and a larger number of loops.

4.4.4 Adsorption Isotherms in Toluene

The adsorption isotherms for the functionalized and un-functionalized polystyrenes are shown in figures 4.8 to 4.12 and are presented in the order of increasing molecular weight. The data are listed in Table 4.5. Adsorbances are in the units of μg/cm^2 which on multiplication by 10 converts it in to units of mg/m^2.

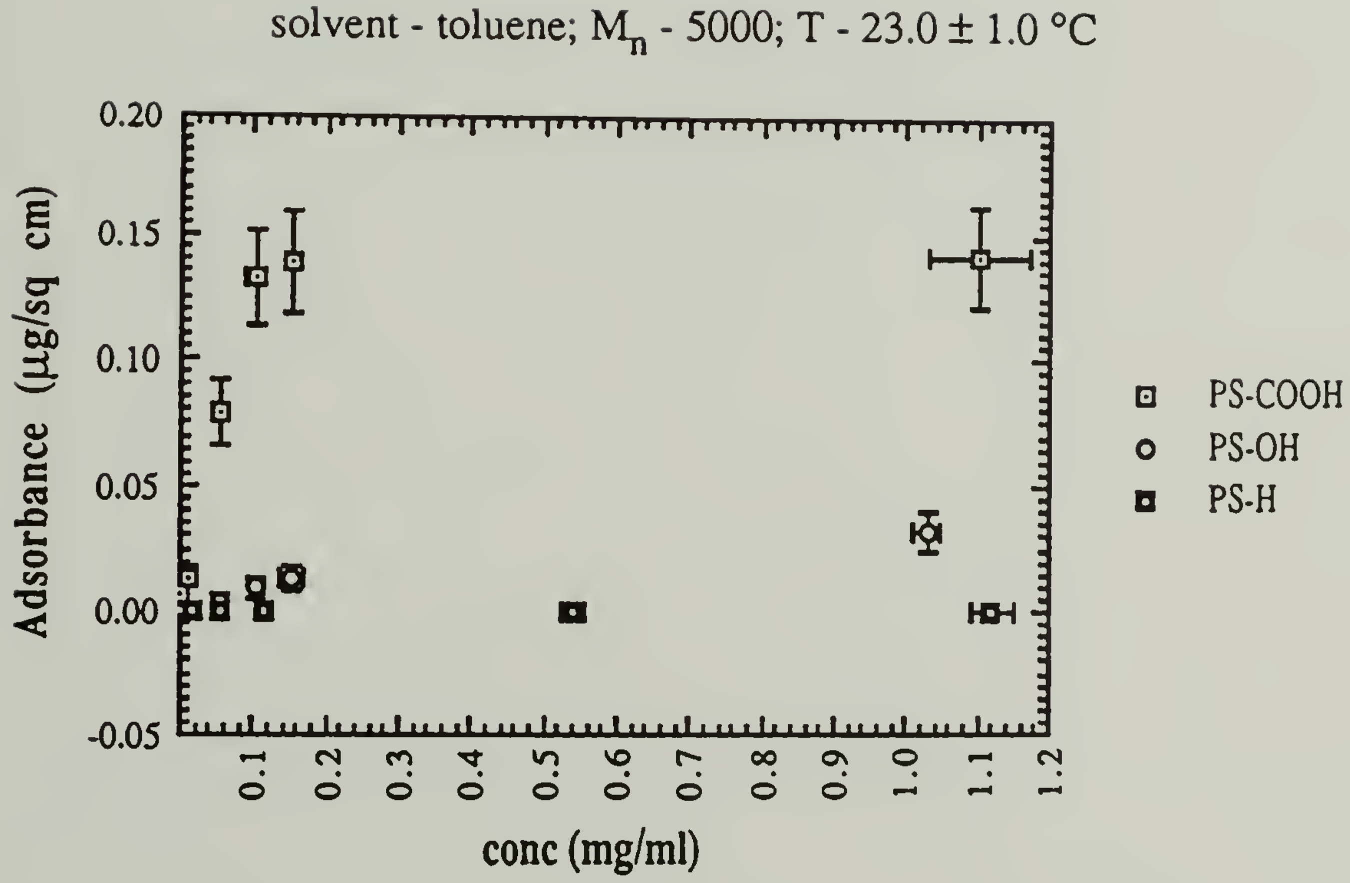


Figure 4.8 Adsorption Isotherms

solvent - toluene; M_n - 10000; T - 23.0 ± 1.0 °C; top - 1SF; bottom - 2SF

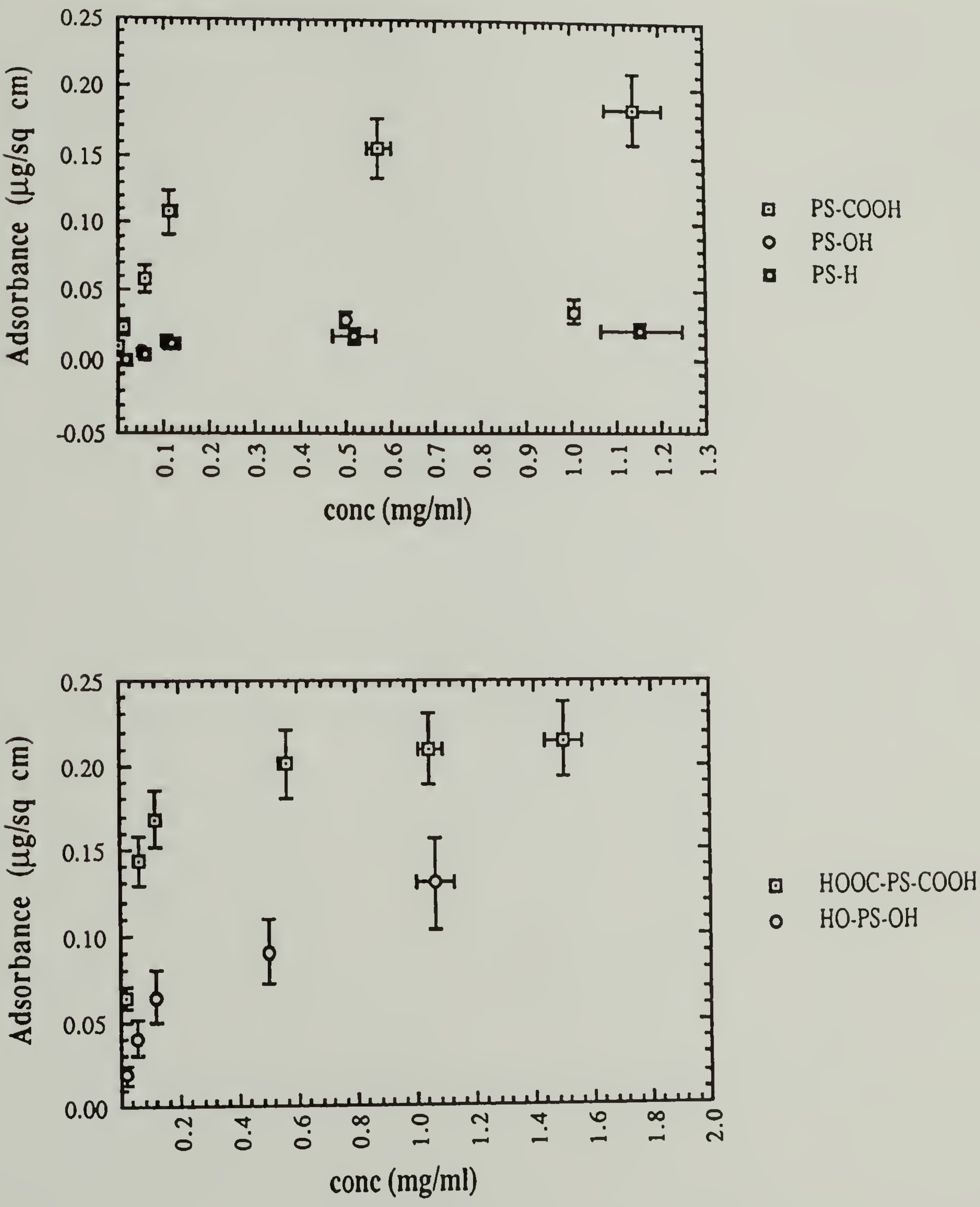


Figure 4.9 Adsorption Isotherms

solvent - toluene; M_n - 30000; T - 23.0 ± 1.0 °C; top - 1SF; bottom - 2SF

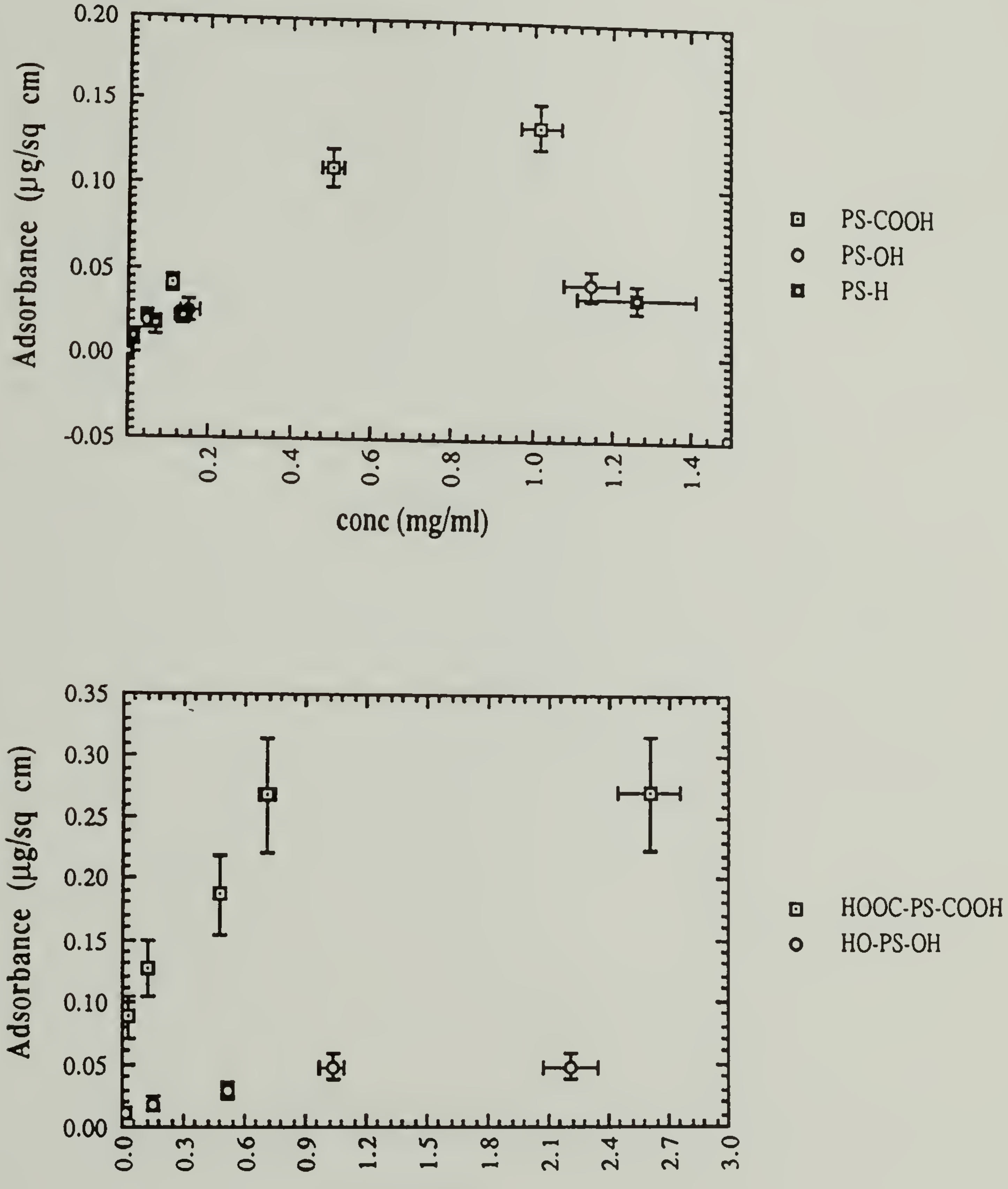


Figure 4.10 Adsorption Isotherms

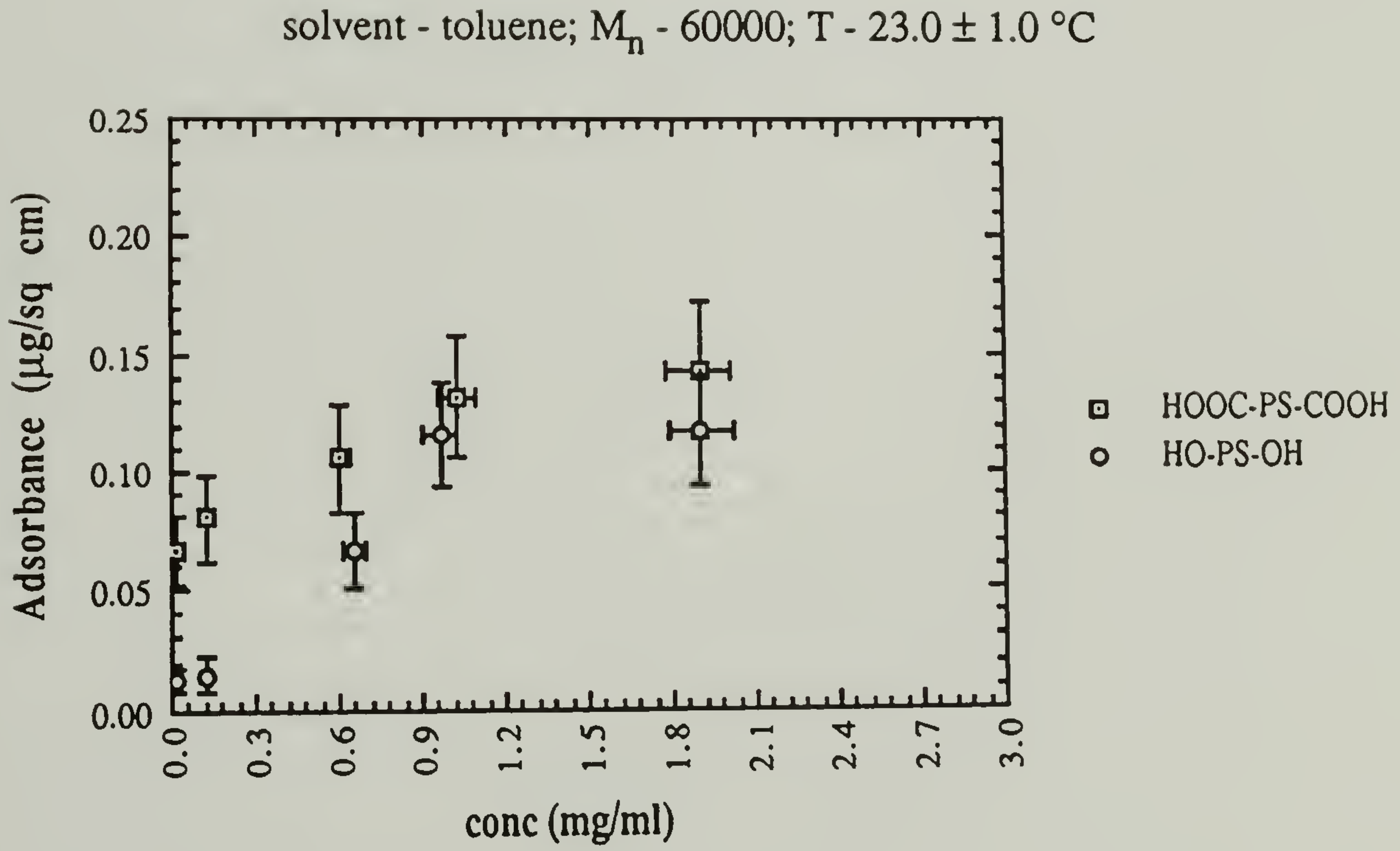


Figure 4.11 Adsorption Isotherms

solvent - toluene; M_n - 140000; T - 23.0 ± 1.0 °C; top - 1SF; bottom - 2SF

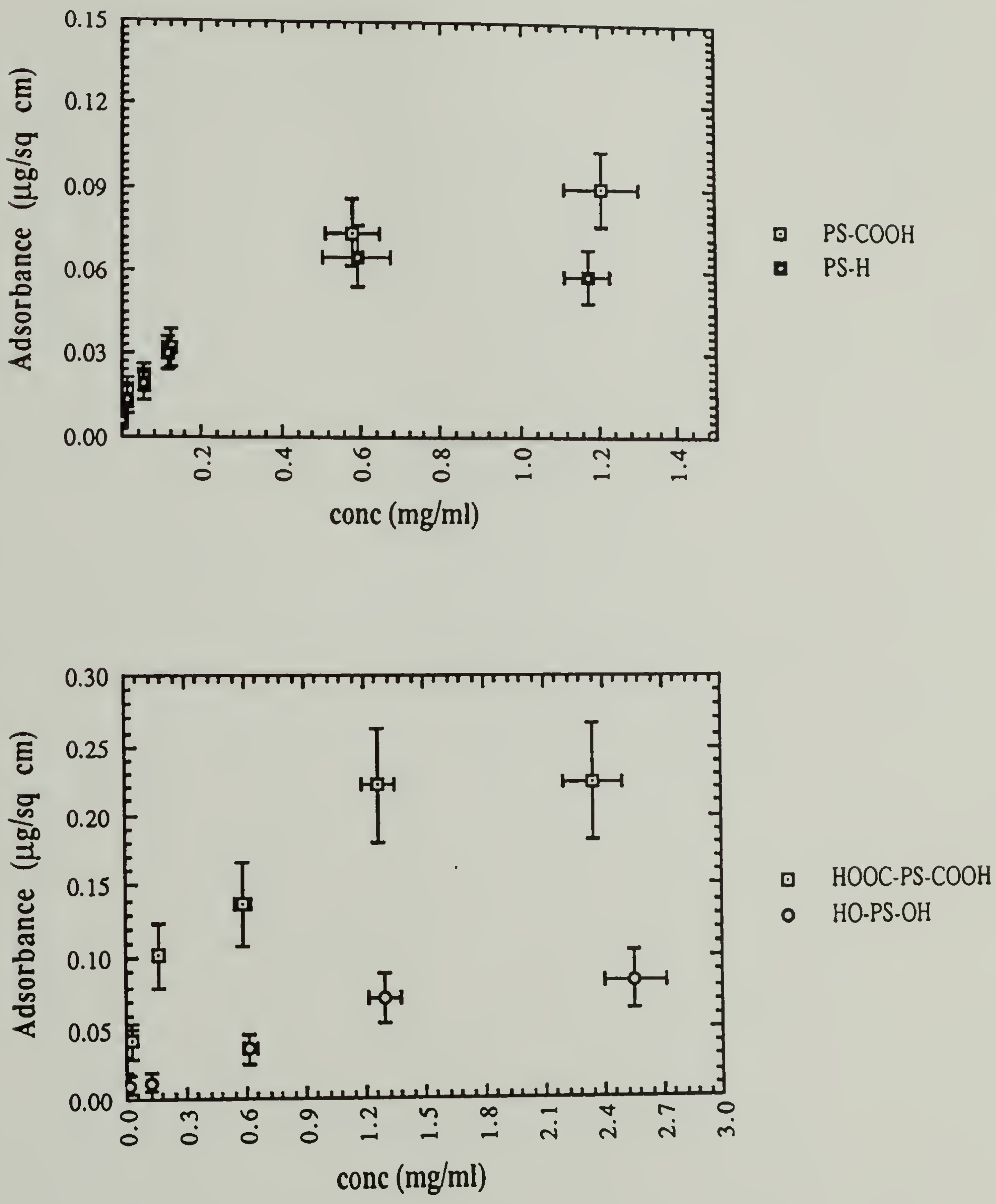


Figure 4.12 Adsorption Isotherms

An inspection of the isotherms reveal the same facts and trends as observed and explained for in cyclohexane. However the absolute magnitude of the adsorbances remain to be explained. The adsorbances of polystyrenes with a carboxylic acid end-group in toluene is always lower than that in cyclohexane (samples with a hydroxyl end-group function have the same adsorbance as polystyrene within experimental error). The radius of gyration of a polystyrene coil in toluene is greater than its radius in cyclohexane as the segments prefer toluene over other segments (often referred as the osmotic interaction of the solvent). In addition the solvent swollen segments within a coil and among coils avoid each other (self-avoidancy) and this repulsive interaction is referred to as excluded volume interaction. Because of the above two factors individual chains occupy more surface area and its difficult to compress them in the volume above the surface and hence lower adsorbances.

Absorbances of polystyrenes with two end groups follows the above pattern at high molecular weights and solution concentrations. However at low concentrations peculiar behavior is observed. This is explained in detail by comparing the adsorbances of 10K samples in toluene.

Concentration (mg/ml)	$A_{\text{PS-COOH}} / A_{\text{PS-H}}$	$A_{\text{HOOC-PS-COOH}} / A_{\text{PS-H}}$	$A_{\text{HOOC-PS-COOH}} / A_{\text{PS-COOH}}$
1.00	8.41	9.55	1.14
0.50	9.12	11.82	1.30
0.10	9.00	14.0	1.56
0.06	11.6	28.8	2.48
0.02	-	-	2.83

Concentration (mg/ml)	$A_{PS\text{-}OH} / A_{PS\text{-}H}$	$A_{HO\text{-}PS\text{-}OH} / A_{PS\text{-}H}$	$A_{HO\text{-}PS\text{-}OH} / A_{PS\text{-}OH}$
1.00	1.64	5.91	3.61
0.50	1.71	5.35	3.14
0.10	1.17	5.42	4.64
0.06	1.20	8.20	6.83

The role of carboxylic acid end group in increasing the adsorbance is particularly relevant if the increase in the ratio with decreasing solution concentration (within a column) and by the presence of a second carboxylic acid end group (among columns)is noticed. A similar effect is seen for the HO-PS-OH. In cyclohexane the ratio of the adsorbances of di-functionally-terminated polystyrenes to polystyrene was less than one at low concentrations and surpassed one as the concentration in solution was increased revealing interesting conformation changes from that dominated by trains (at low concentrations) to that dominated by loops and tails (at high concentration). In toluene the segments do not compete effectively for surface sites as their differential enthalpy of interaction with the surface is marginal and are not relevant unless the number of segments per chain is large (high molecular weights). Therefore polystyrenes with two functional end-groups must adsorb with an average conformation consisting mainly of loops. The size of the loop probably depends on the enthalpy of interaction of the end-group with the surface (the higher the enthalpy the larger the loops). Based on these arguments the size of the loops in an adsorbed HO-PS-OH molecules is much smaller than that of HOOC-PS-COOH.

Even though hydroxyl end-group is not an effective sticky foot under most of the solution conditions, it is clear that it is if the concentration of the hydroxyl end-group is high enough as evident from the adsorbance of HO-PS-OH (1 mg/ml; 10K). Lower molecular weights and higher solution concentrations result in higher end-group concentration and these result in higher adsorbances (in the absence of significant competition from the segments of the backbone) and this is illustrated by the $A_{HOOC\text{-}PS\text{-}COOH}/A_{PS\text{-}COOH}$ ratios of 10K (and 30K sample as well). Similar arguments apply for samples of higher molecular weight as well.

It is interesting to note that a plot of the differences in the adsorption of carboxylic acid-terminated polystyrene and un-functionalized polystyrene versus the end-group concentration is a straight line independent of molecular weight, in a certain regime of end-group concentration. This is shown in figure 4.13.

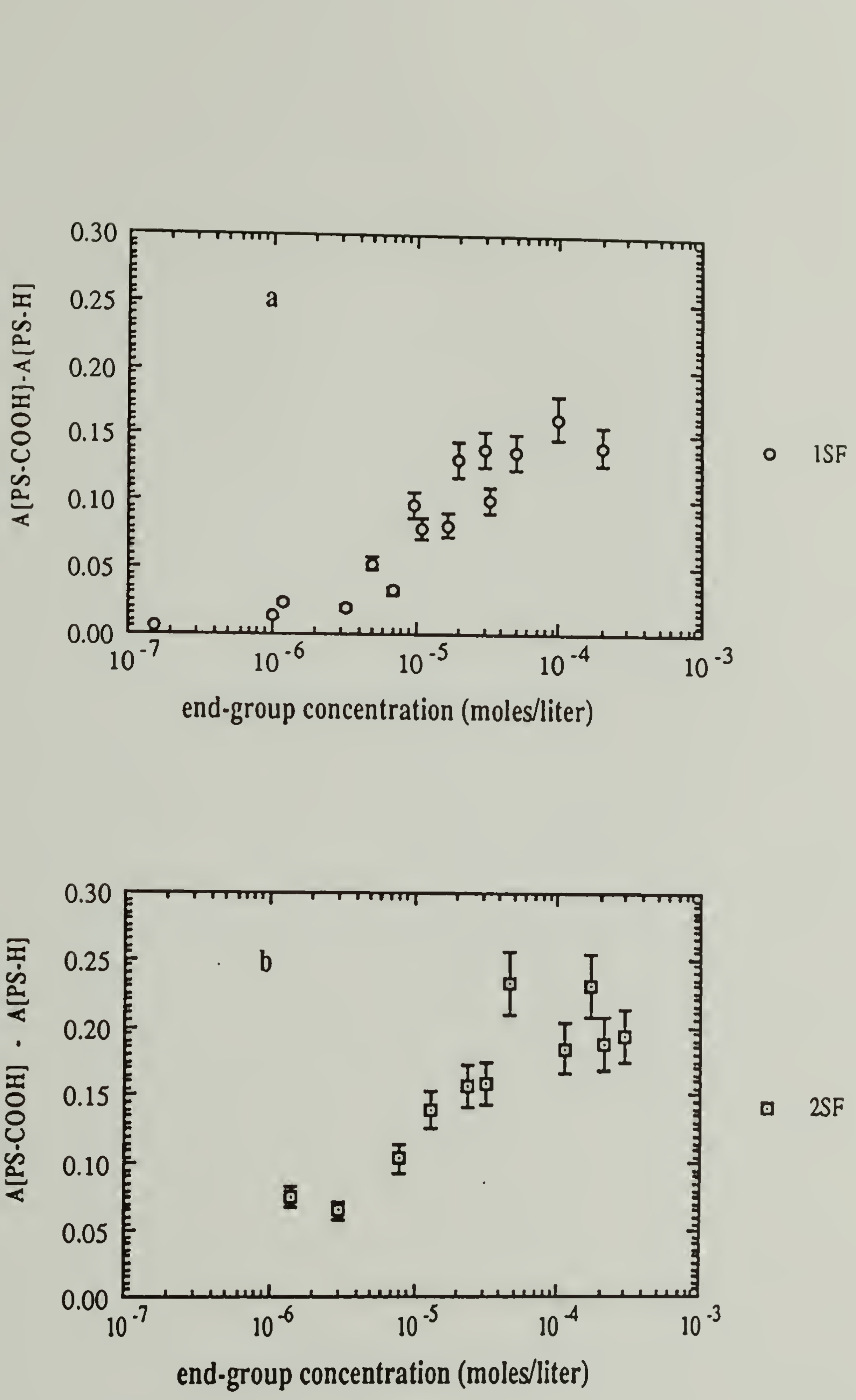


Figure 4.13 a) Adsorbance Differences [PS-COOH - PS-H] versus Molar Concentration of the End-Group in Toluene. b) Analogous one for [HOOC-PS-COOH - PS-H].

4.4.5 Molecular Weight Effects

The effect of chain length or molecular weight on the adsorbance at a solution concentration of 1 mg/ml is shown in figures 4.14a (cyclohexane) and 4.14b (toluene). Adsorbance increases with molecular weight as M^{α} where $\alpha = 0.42 \pm 0.02$ in cyclohexane and 0.33 ± 0.03 in toluene. Adsorbance is predicted to increase with molecular weight as $A = KM^{\alpha}$ by Koral where K is a constant.[21] The reason behind the increasing adsorbance is that many more segments are present in loops and tails for the same surface coverage as the molecular weight increases. However adsorbance does reach a plateau at very high molecular weights. This is because the dimension of the chain increases with molecular weight and these chains in view of a small fraction of segments being required to overcome the critical adsorption energy, adsorb undistorted from their conformation in solution and therefore the surface area occupied per chain increases. At some high molecular weight the increase in adsorbance owing to the presence of a larger number of segments in loops and tails is compensated by the increasing surface area per molecule and adsorbance reaches a plateau value.

The variation of the adsorbances of carboxylic acid-terminated polystyrene as a function of molecular weight at two different solution concentrations in cyclohexane and toluene are shown in figures 4.15 and 4.16.

From the adsorption isotherms we recognize that the adsorbance is governed by two contributions. The first and major contribution is from the concentration of the end-groups which is inversely proportion to the molecular weight (in addition to the absolute concentration in solution) and the second is from the concentration of the segments and the number of segments per molecule or the molecular weight. Therefore adsorbance is given by the empirical equation shown below.

$$A = KM^{\alpha} + J\,[\text{end-group}]^{\beta}$$

where K and J are arbitrary constants, α is the power law index for polystyrene and the value of β is not known (positive and greater than zero). The molar concentration of the

concentration = 1 mg/ml; a) cyclohexane; b) toluene

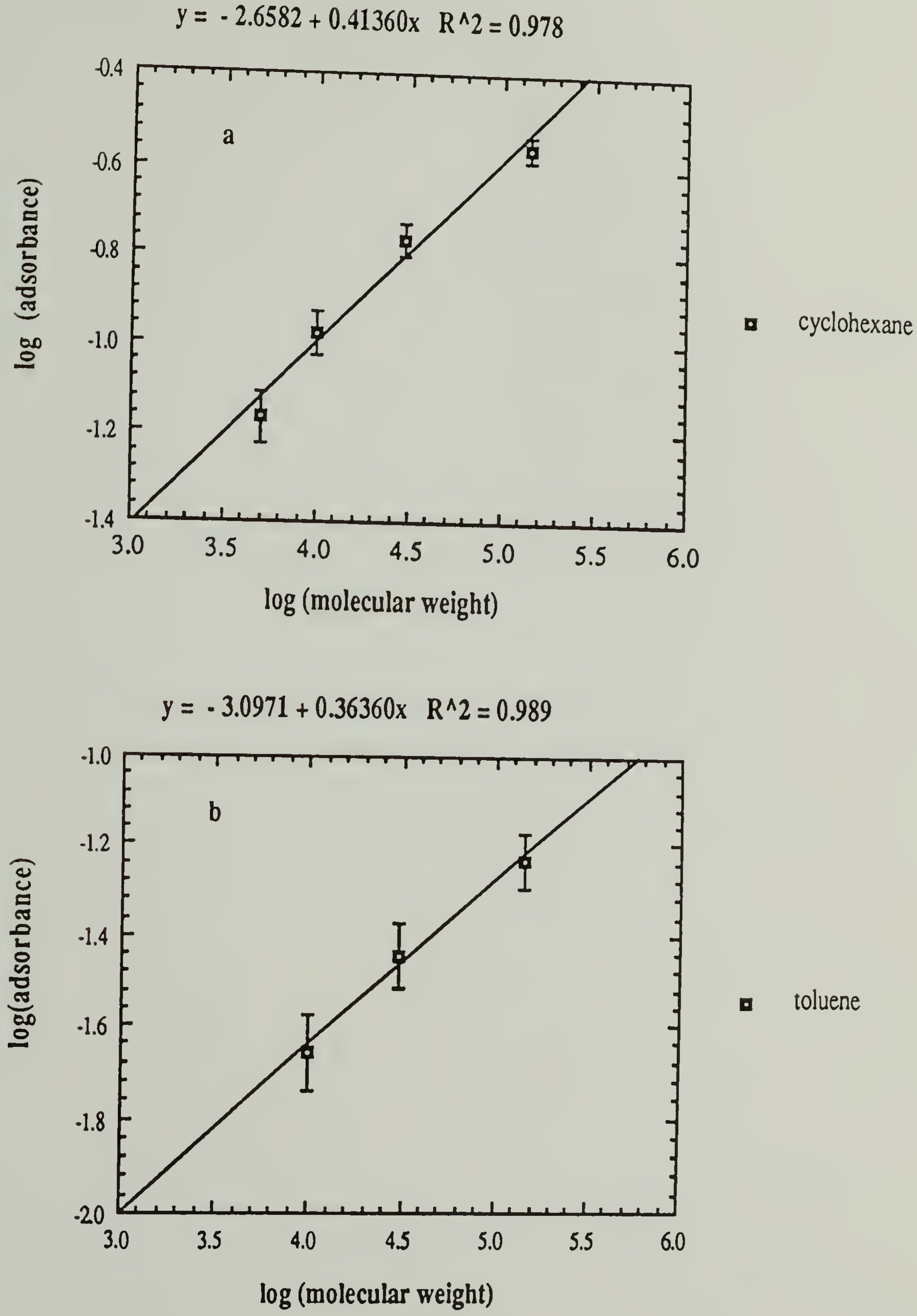


Figure 4.14 Adsorbance versus Molecular Weight of Polystyrene

concentration = 1 mg/ml; a) cyclohexane; b) toluene

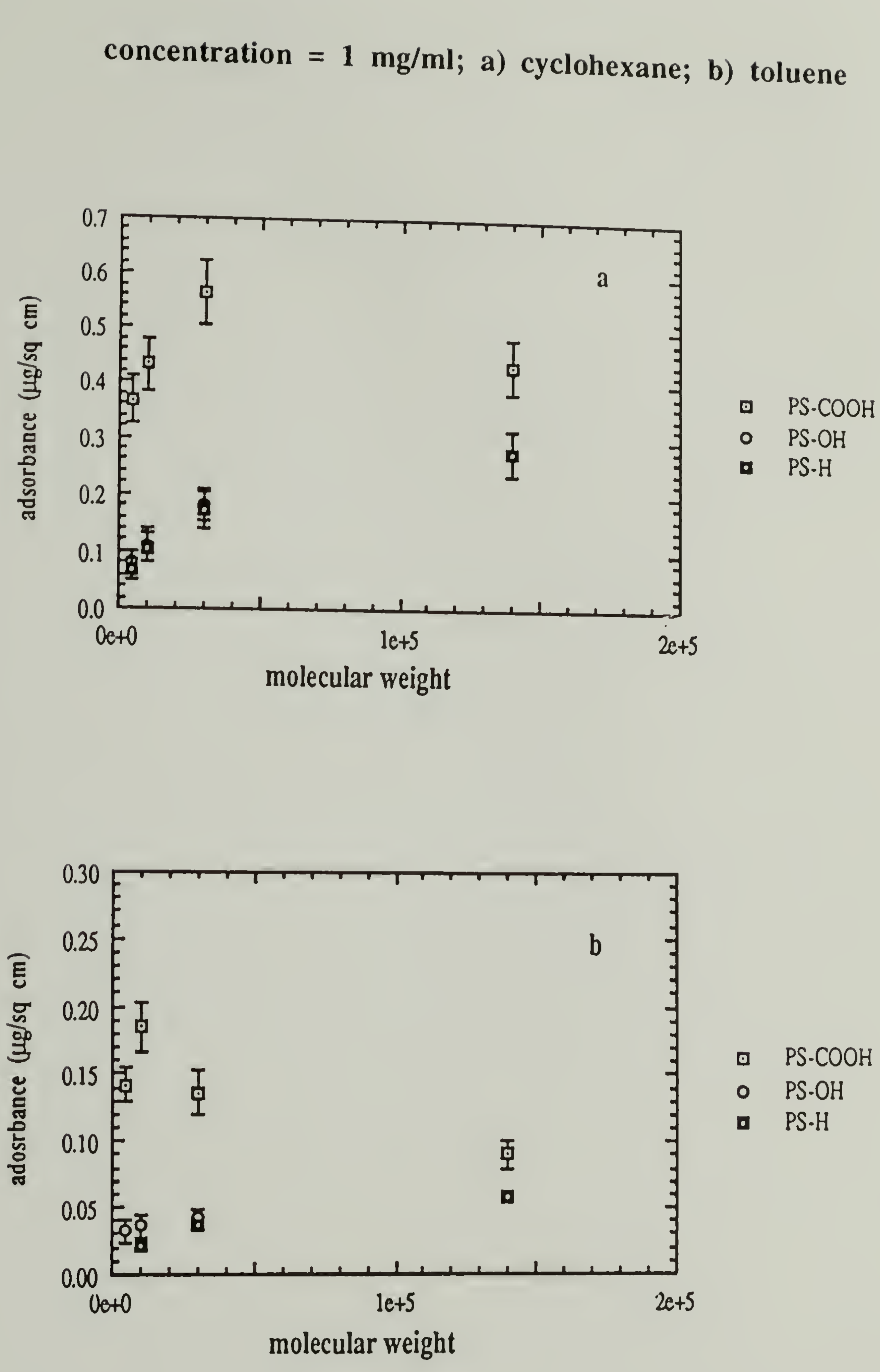


Figure 4.15 Adsorbance versus Molecular Weight of Carboxylic Acid-Terminated Polystyrenes

concentration = 0.01 mg/ml; a) cyclohexane; b) toluene

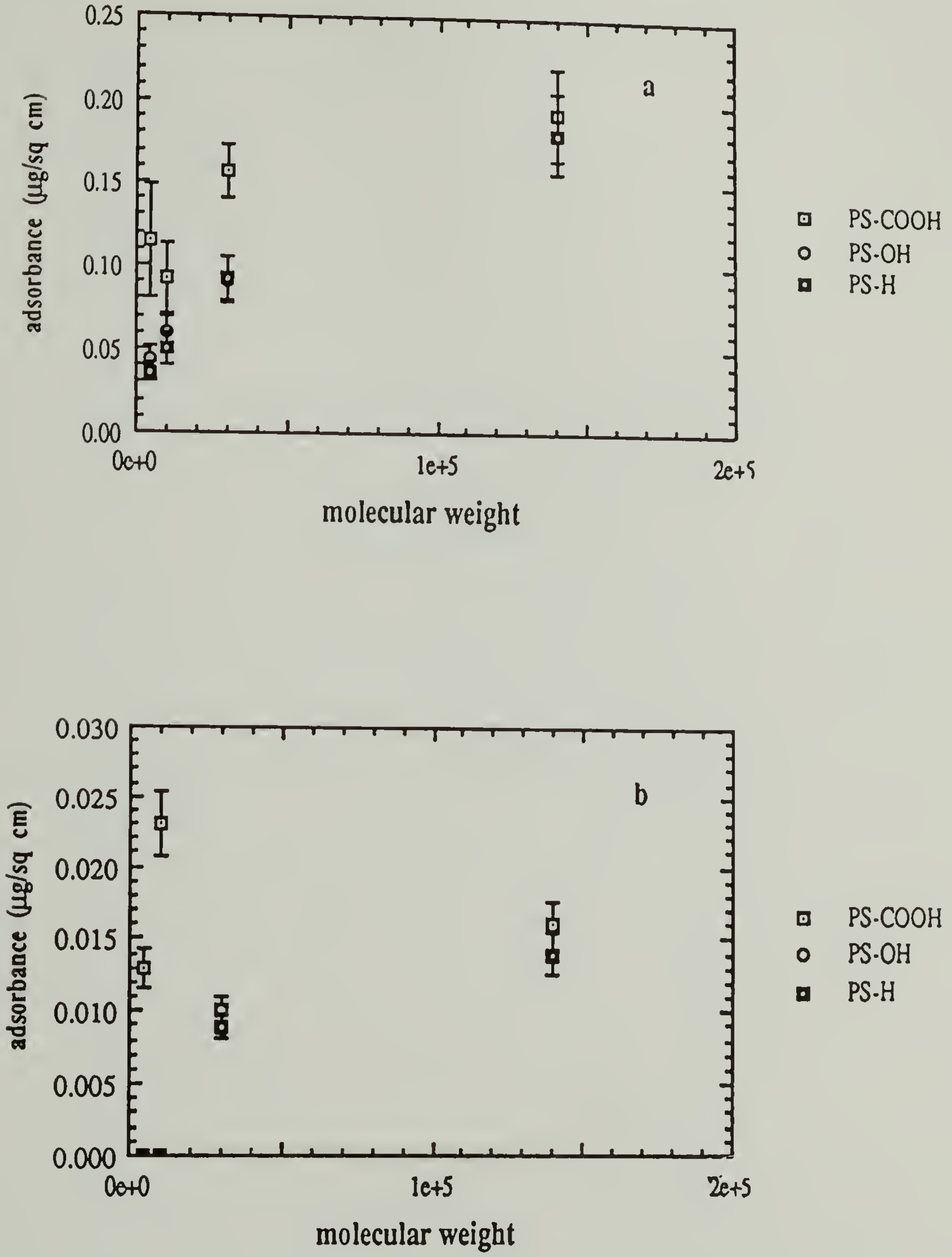


Figure 4.16 Adsorbance versus Molecular Weight of Carboxylic Acid-Terminated Polystyrenes

end-group is given by c/M where c is the concentration of the solution is mg/ml or g/l and M is the number average molecular weight. The first term is from the adsorption of segments alone (as in the case of un-functionalized polystyrenes or very dilute solutions of PS-COOH when $A_{PS\text{-}COOH} = A_{PS\text{-}H}$). The second term is from the increasing adsorbance that takes place above a certain threshold concentration of the carboxylic acid end-group, independent of the molecular weight. However it applies only to a limited range of end-group concentration (10^{-4} moles/liter for carboxylic acid end-group). The significance of this term is reduced at very low solution concentrations or higher molecular weights. There is an additional term involving the probability of a functional end-group being present at the periphery of the coil for attachment on contact with the surface (it can be shown to be proportional to $M^{-0.4}$) and its effect is particularly relevant at high molecular weights. The importance of the term is recognized but it is ignored in the present discussions as most of the samples studied were of low molecular weight. The following discussions are based on the above equation.

The adsorbance of PS-COOH increases with molecular weight and after a certain critical molecular weight decreases towards that of un-functionalized polystyrene. This initial increase is due to the increase in the number of segments with molecular weight (note that the concentration of the carboxylic acid end-group is still above the threshold and therefore they compete for surface sites and pack effectively). Above the critical molecular weight the concentration of carboxylic acid end-group is below the threshold value and hence the contribution from the second term for the adsorbance is negligible. At high enough molecular weights adsorbances are due to the term KM^{α} alone and therefore PS-COOH samples at this molecular weight behave as though they contain no end-group. This argument is applicable at low end-group concentration as well and therefore at low solution concentrations adsorbance should monotonically increase with molecular weight and reach a plateau value at some high molecular weight just as in un-functionalized polystyrene and that this is the case is shown in figure 4.16a. In toluene similar trends are observed for PS-

COOH samples but the critical molecular weight above which adsorbance starts to decrease is lower. This is because of an additional osmotic repulsion term that minimizes the effect of the end-group and is not discussed in detail.

The variation of the adsorbances of di-functionally-terminated polystyrenes as a function of molecular weight at two different solution concentrations in cyclohexane and toluene are shown in figures 4.17 and 4.18. In cyclohexane adsorbance increases with molecular weight at low solution concentrations, an effect attributed to the increasing number of segments in loops with the majority still being present in trains with both the ends at the surface. At higher solution concentrations the end-group concentration is well above the threshold and therefore adsorbance increases with molecular weight. A decrease from the plateau value at these concentrations is expected at very high molecular weights (much above 140 K). In toluene the trends are similar to that observed with polystyrenes with a carboxylic acid end-group, within experimental error.

The amount of carboxylic acid-terminated polystyrene adsorbed from cyclohexane increases with increasing molecular weight up to a molecular weight of 30000. The amount adsorbed at 140K is lower than that of the 30K sample but is still higher than that of the un-functionalized polystyrene of molecular weight 140K. This result indicates that at this molecular weight the effect of end-group is small.

concentration = 1 mg/ml; a) cyclohexane; b) toluene

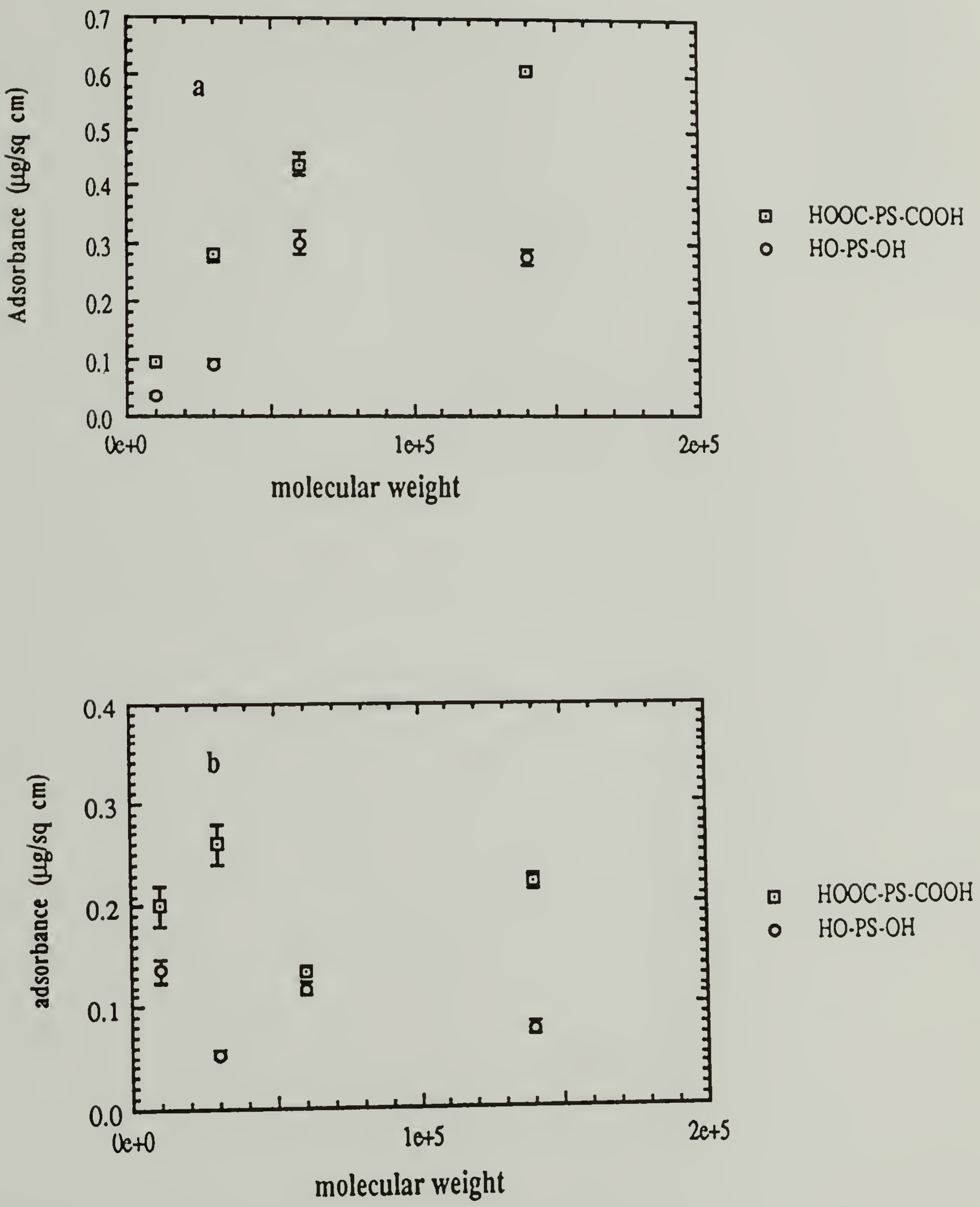
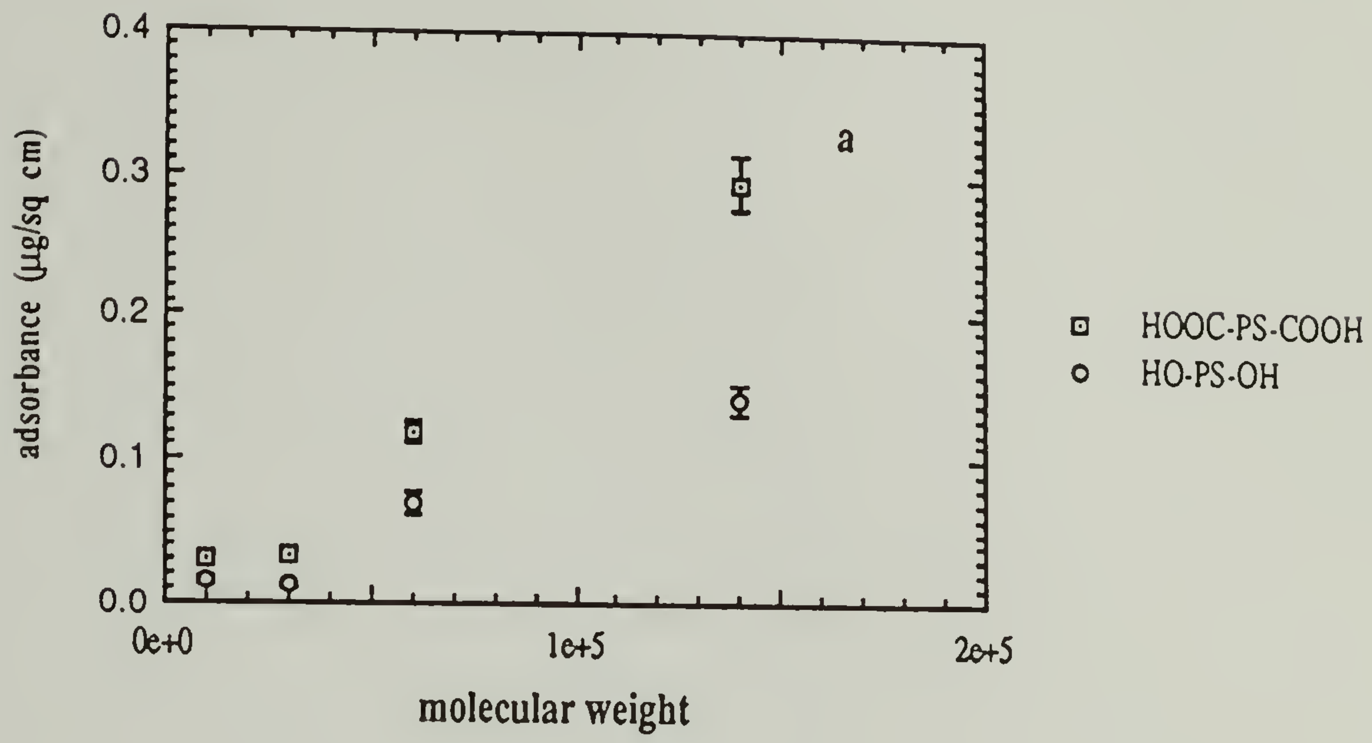


Figure 4.17 Adsorbance versus Molecular Weight of Di-Functionally-Terminated Polystyrenes

concentration = 0.01 mg/ml; a) cyclohexane; b) toluene



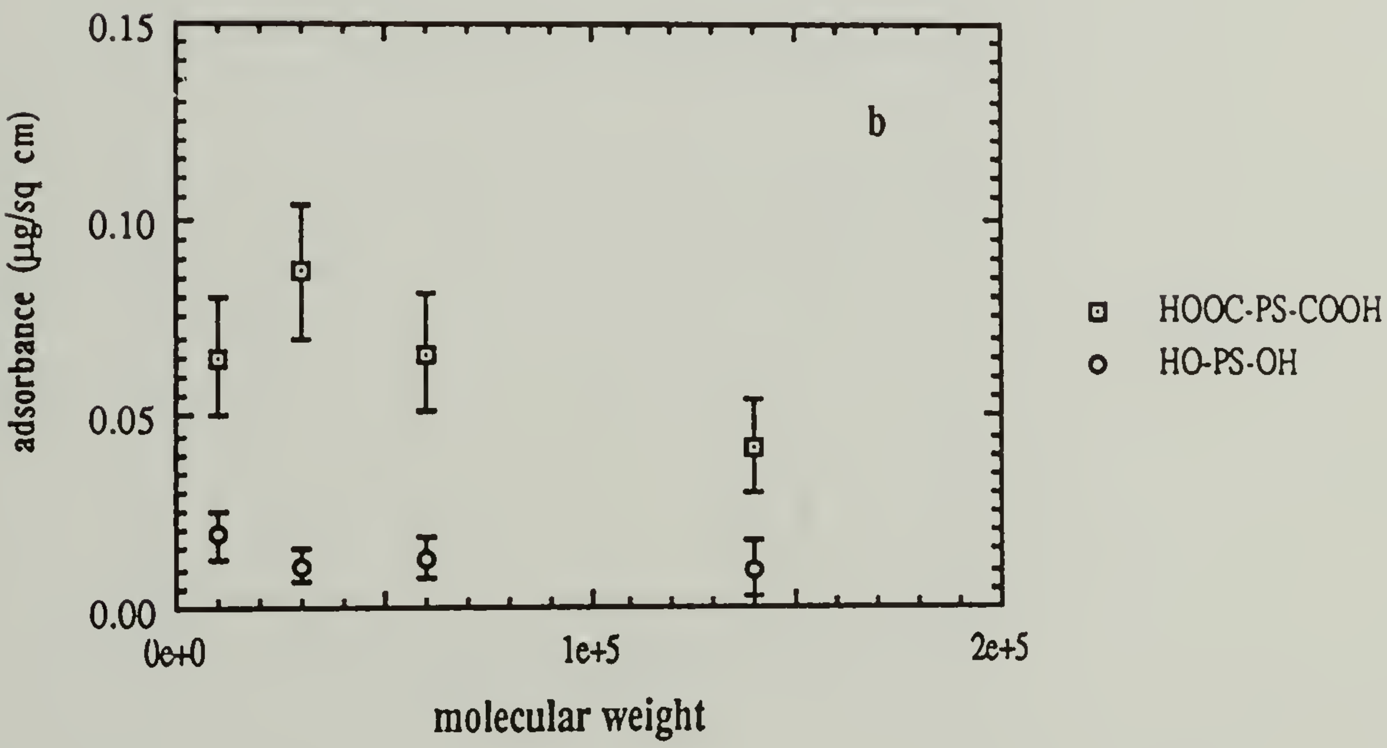


Figure 4.18 **Adsorbance versus Molecular Weight of Di-Functionally-Terminated Polystyrenes**

4.4.6 Graft Density Calculations

The normalized graft density (σ) as defined by de Gennes [22] was calculated in an effort to interpret chain stretching as a function of end-group concentration uniformly. It is defined as the ratio between the area occupied by a segment (usually the monomer or the repeat unit that is considered to make up a segment) to that of an adsorbed chain and is calculated as follows:

$$(A\ (\mu g) \times 10^{-6} \times N) / M_n \qquad = S \quad .....(1)$$

where S is the surface density [22]

$$1 / 4\pi R^2 \qquad = S_0 \quad ....(2)$$

and S_0 is the number of coils per square centimeter of the surface if there were no interaction with the surface and between the coils and they just pack the surface. R^2 is the radius of gyration squared.

$S^{0.5}$ is the number of coils per cm of the surface and therefore D the distance between the grafting sites is the inverse of this quantity. σ is the normalized grafting density defined as a^2 / D^2 where a is the monomer (styrene) segment length and was taken to be 5.7 Å.[23]

All the above mentioned parameters for the adsorbed chains were calculated and the numbers for the 10K sample in cyclohexane and toluene are shown in Table 4.6 and 4.7. The plots of normalized graft density versus end-group concentration in moles/liter in cyclohexane is shown in figure 4.19 and that in toluene in figure 4.20 for the 10K samples. The plot shows three distinct regions; a) in the first region (at low concentration) the graft density increase is very small with concentration. b) in the second region graft density increases linearly with concentration and c) in the third region it is invariant to concentration changes. The slope of the second region is a function of the molecular weight and decreases with increasing molecular weight (not shown here). In addition to a high affinity pattern the following trends are observed. 1) grafting density decreases with decreasing end-group concentration and increasing goodness of the solvent (consistent with increasing coil size and osmotic repulsions) for the single sticky foot samples. 2) In the case of the polymer with two sticky feet grafting density decrease with decreasing concentration in cyclohexane is more than that in toluene. At low concentrations some unique solution behavior in cyclohexane enables both the chain ends to bind resulting in the graft density being lower than that in toluene. The parameters calculated for samples of other molecular weight are shown in Appendix B.

Table 4.6 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Cyclohexane

Number averaged Molecular weight - 10000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. $\times 10^6$ (moles/l)	E.C. $\times 10^6$ (moles/l)	$S \times 10^{-13}$ (cm^{-2})	D (Å)	σ
PS-COOH							
28.5	0.39	0.0011	10.6	0.11	0.34	54.0	0.020
		0.010	96.0	1.0	0.55	42.5	0.032
		0.095	912.1	9.5	1.53	25.6	0.087
		0.480	4608.7	48.0	2.37	20.6	0.135
		1.150	11041.8	115.0	2.60	19.6	0.148
PS-OH							
28.5	0.39	0.0014	13.4	0.14	0.30	58.2	0.017
		0.013	124.8	1.3	0.36	53.0	0.020
		0.105	1008.2	10.5	0.40	50.2	0.023
		0.550	5280.8	55.0	0.54	43.2	0.031
		1.085	10417.7	108.5	0.66	38.9	0.038
PS-H							
28.5	0.39	0.0010	9.6		0.28	60.1	0.016
		0.011	105.6		0.30	57.6	0.017
		0.118	1133.0		0.44	47.7	0.025
		0.520	4992.8		0.49	45.3	0.028
		1.155	11089.8		0.63	39.8	0.036
HOOC-PS-COOH							
28.5	0.39	0.015	144.0	3.0	0.19	73.2	0.011
		0.150	1440.2	30.0	0.28	60.1	0.016
		0.938	9006.2	187.6	0.57	41.8	0.033
		1.510	14498.3	302.0	1.91	22.9	0.109

Continued, next page

Table 4.6 Continued

Number averaged Molecular weight - 10000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	S x 10^{-13} (cm^{-2})	D (Å)	σ
HO-PS-OH							
28.5	0.39	0.019	182.4	3.8	0.09	105.2	0.005
		0.190	1824.3	38.0	0.14	85.0	0.008
		0.935	8977.4	187.0	0.22	67.9	0.012
		1.450	13922.2	290.0	0.41	49.4	0.023

Note: R_g is the radius of gyration of the above polystyrenes at 34.5°C in cyclohexane from reference 24. S_0 is the number of coils per square centimeter of the surface if there were no interaction with the surface and the coils just pack the surface. S is the number of coils per square centimeter after adsorption at equilibrium and is called the surface density [6]. If $S > S_0$ then the polystyrene buoys will overlap. Conc stands for the concentration of the solution in mg/ml. S.C. stands for the concentration of the polystyrene segments in moles/liter while E.C. stands for the concentration of the end group (-COOH or -OH) in moles/liter. D is the distance in angstrom between grafted chains and s is the normalized grafting density (unit less) as defined by de Gennes [22].

Table 4.7 Surface Density, Distance between Graft sites, Graft Density and Solution Characteristics in Toluene

Number averaged Molecular weight - 10000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. $\times 10^6$ (moles/l)	E.C. $\times 10^6$ (moles/l)	$S \times 10^{-13}$ (cm^{-2})	D (Å)	σ
PS-COOH							
33.0	0.29	0.0012	11.5	0.12	0.06	128.9	0.003
		0.012	115.0	1.2	0.14	85.0	0.008
		0.058	556.9	5.8	0.35	53.5	0.020
		0.115	1104.2	11.5	0.65	39.2	0.037
		0.575	5520.9	57.5	0.93	32.7	0.053
		1.142	10965.0	114.2	1.11	30.0	0.064
PS-OH							
33.0	0.29	0.0011	10.6	0.11			
		0.010	96.0	1.0			
		0.051	489.7	5.1	0.04	166.3	0.002
		0.104	998.6	10.4	0.08	108.9	0.005
		0.500	480.1	50.0	0.18	75.7	0.010
		1.002	9620.7	100.2	0.22	67.9	0.012
PS-H							
33.0	0.29	0.0014	13.4				
		0.017	163.2				
		0.058	556.9		0.03	182.2	0.002
		0.118	1133.0		0.07	117.6	0.004
		0.520	4992.8		0.10	98.8	0.006
		1.155	11089.8		0.13	86.9	0.008
HOOC-PS-COOH							
33.0	0.29	0.015	144.0	3.0	0.39	50.5	0.022
		0.067	643.3	13.4	0.87	34.0	0.049
		0.120	1152.2	24.0	1.01	31.4	0.058
		0.560	5376.9	112.0	1.21	28.7	0.069
		1.050	10081.6	210.0	1.26	28.1	0.072
		1.500	14402.3	300.0	1.29	27.8	0.074

Continued, next page

Table 4.7 Continued

Number averaged Molecular weight - 10000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	$S \times 10^{-13}$ (cm^{-2})	D (Å)	σ
HO-PS-OH							
33.0	0.29	0.019	182.4	3.8	0.11	93.5	0.007
		0.056	537.7	11.2	0.25	63.6	0.014
		0.120	1152.2	24.0	0.39	50.5	0.022
		0.497	4772.0	99.4	0.55	42.7	0.031
		1.060	10177.6	212.0	0.78	35.7	0.045

Note: R_g is the radius of gyration of the above polystyrenes at 23 °C in toluene from reference 24. S_0 is the number of coils per square centimeter of the surface if there were no interaction with the surface and the coils just pack the surface. S is the number of coils per square centimeter after adsorption at equilibrium and is called the surface density [6]. If $S > S_0$ then the polystyrene buoys will overlap. Conc stands for the concentration of the solution in mg/ml. S.C. stands for the concentration of the polystyrene segments in moles/liter while E.C. stands for the concentration of the end group (-COOH or -OH) in moles/liter. D is the distance in angstrom between grafted chains and s is the normalized grafting density (unit less) as defined by de Gennes [22].

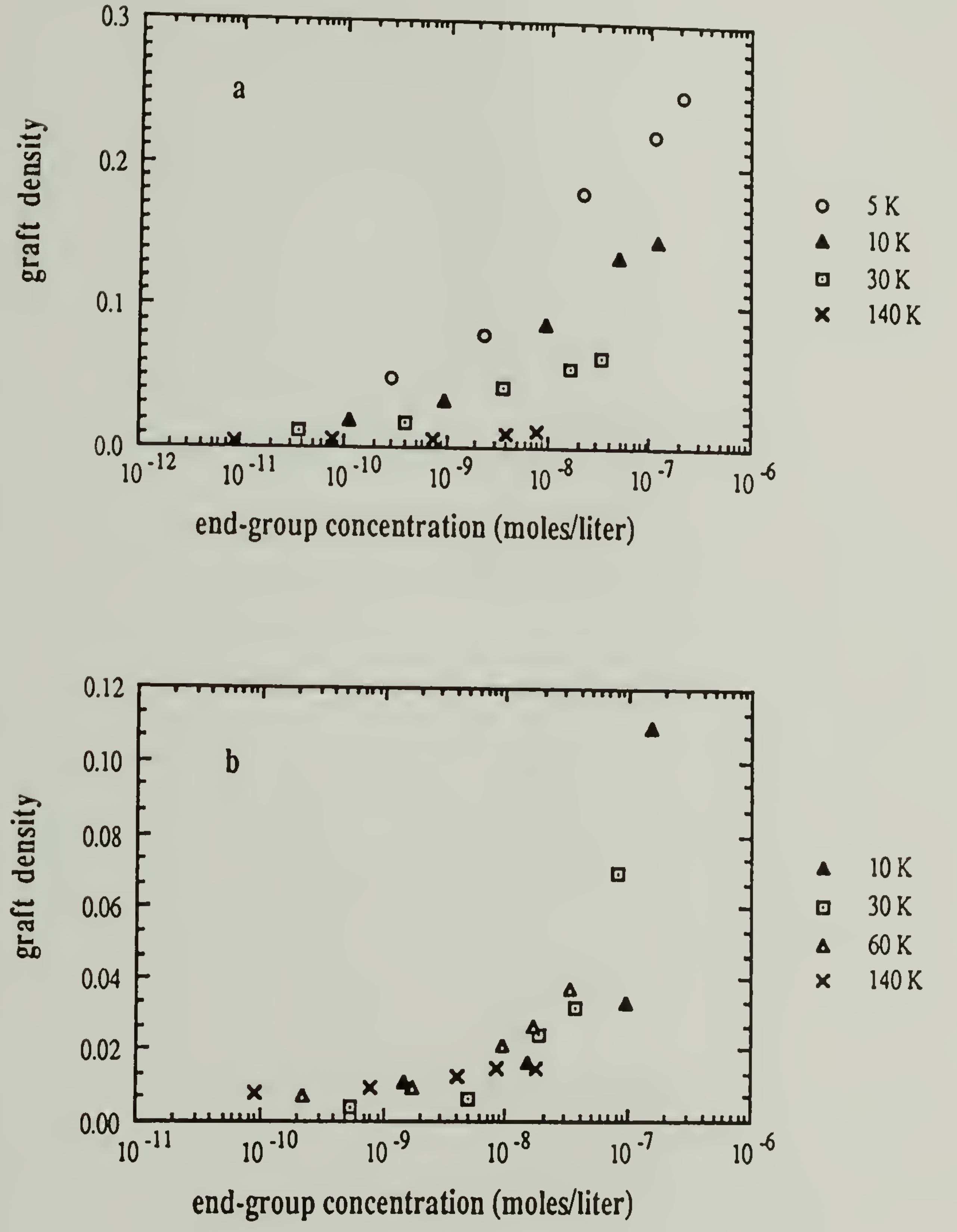


Figure 4.19 a) Graft Density versus End-Group Concentration for PS-COOH in Cyclohexane. b) Analogous data for HOOC-PS-COOH

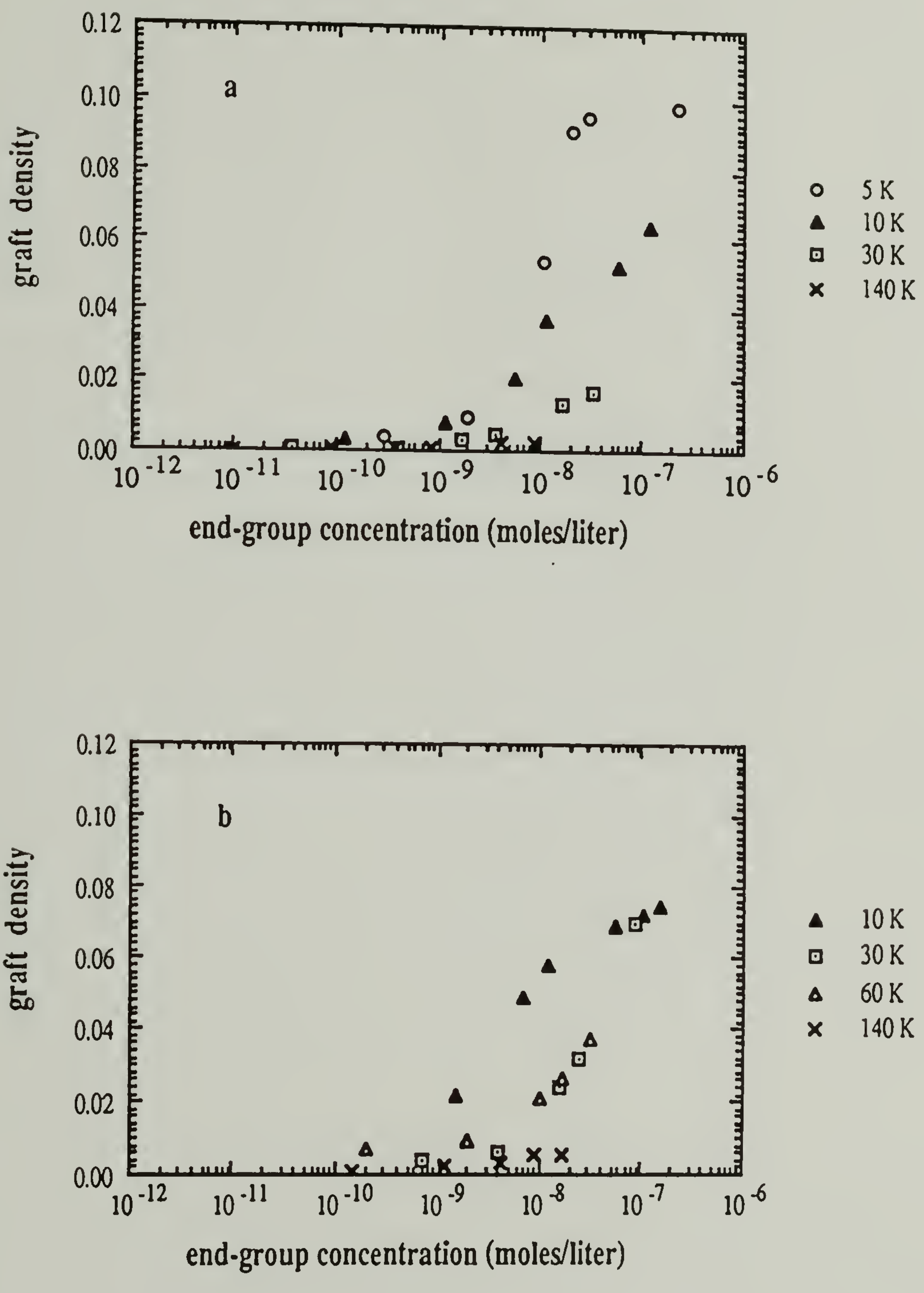


Figure 4.20 a) Graft Density versus End-Group Concentration for PS-COOH in Toluene. b) Analogous data for HOOC-PS-COOH

4.4.7 Surface Excess Calculations

The ratio of the number of polymer molecules present in an imaginary surface of unit area immediately above the glass surface after adsorption to that present before adsorption ($t = 0$ min) in solution in the same area is defined as the surface excess. It was calculated from the adsorbance (A μg/sq cm) and the solution concentration (c mg/ml) as follows:

surface concentration of the polymer (molecules/sq cm) = $A \times 10^{-6} \times N / M_n$

solution concentration of the polymer (molecules/sq cm) = $(c \times 10^{-3} \times N / M_n)^{2/3}$

surface excess = surface concentration / solution concentration

This ratio gives a good idea about the compactness of the adsorbed layer and the relative viscosity of the polymer chains at the interface. This also enables us to know as to how close the system is to c^* (overlap concentration region) so that appropriate theories can be applied to interpret the results in the future. The compactness of the adsorbed layer can be best understood if the number of chains per unit area of the amorphous solid polymer is calculated assuming a bulk density of 1 g/cm^3 (reported values are between 1.04 and 1.07 for the amorphous polymer and around 1.11 for the crystalline polymer)

As examples the calculated values for surface concentration, solution concentration and surface excess for functionalized polystyrenes of number average molecular weight 140K are shown in Tables 4.8 (cyclohexane) and 4.9 (toluene). The number of molecules per square centimeter of an imaginary surface in amorphous polystyrene of number average molecular weight 140K turns out to be 2.65×10^{12}. The surface concentration of carboxylic acid-terminated polystyrene on glass increases with concentration of the polymer in solution and reaches that of the amorphous polymer at very high concentration of the end-group. This indicates that the viscosity of the polymer in the adsorbed layer must be extremely high (particularly in a poor solvent) that any approach to true equilibrium from the quasi steady state adsorbance would take a long time (as $\tau = A \exp(\eta_1/\eta_2)$).

Table 4.8 Surface Excess Results in Cyclohexane

PS-COOH and PS-H; Number average molecular weight - 140K

solution concentration (mg/ml)	solution concentration (molecules/sq. cm)	surface concentration PS-COOH	surface concentration PS-H	surface excess PS-COOH	surface excess PS-H
0.001	2.66 e+8	6.80 e+11	6.54 e+11	2560	2459
0.01	1.23 e+9	8.30 e+11	7.79 e+11	674	632
0.1	5.71 e+9	1.11 e+12	8.95 e+11	194	157
0.5	1.67 e+10	1.63 e+12	1.08 e+12	98	65
1.0	2.65 e+10	1.87 e+12	1.19 e+12	71	45

HOOC-PS-COOH and HO-PS-OH; Number average molecular weight - 140K

solution concentration HOOC-PS-COOH (mg/ml)	solution concentration HOOC-PS-COOH (mol/cm^2)	solution concentration HO-PS-OH (mg/ml)	solution concentration HO-PS-OH (mol/cm^2)	surface concentration acid (mol/cm^2)	surface concentration alcohol (mol/cm^2)	surface excess acid	surface excess alcohol
0.013	1.39 e+9	0.015	1.53 e+9	1.27 e+12	6.11 e+11	916	401
0.109	5.76 e+9	0.126	6.35 e+9	1.61 e+12	7.49 e+11	280	118
0.570	1.75 e+10	0.620	1.85 e+10	2.07 e+12	9.03 e+11	118	49
1.147	2.79 e+10	1.294	3.02 e+10	2.62 e+12	1.18 e+12	94	39
2.41	4.58 e+10	2.553	4.76 e+10	2.58 e+12	1.39 e+12	56	29

Note: mol/cm^2 stands for molecules/square centimeter on an imaginary plane above the surface. In solution at t = 0 min it is the number of molecules per cubic centimeter to the power two thirds. Surface concentration was obtained from the adsorbance.

Table 4.9 Surface Excess Results in Toluene

PS-COOH and PS-H; Number average molecular weight - 140K

solution concentration (mg/ml)	(molecules/sq. cm)	surface concentration PS-COOH	PS-H	surface excess PS-COOH	PS-H
0.001	2.69 e+8	3.01 e+10	2.58 e+10	112	96
0.01	1.25 e+9	6.88 e+10	6.02 e+10	55	48
0.05	3.59 e+9	9.03 e+10	8.17 e+10	25	22
0.1	5.70 e+9	1.38 e+11	1.29 e+11	24	22
0.15	7.57 e+9	3.18 e+11	2.80 e+11	42	37
1.0	2.65 e+10	3.87 e+11	2.50 e+11	15	9

HOOC-PS-COOH and HO-PS-OH; Number average molecular weight - 140K

solution concentration HOOC-PS-COOH (mg/ml)	(mol/cm^2)	solution concentration HO-PS-OH (mg/ml)	(mol/cm^2)	surface concentration acid (mol/cm^2)	alcohol (mol/cm^2)	surface excess acid	alcohol
0.021	1.91 e+9	0.017	1.66 e+9	6.02 e+11	6.11 e+11	1324	363
0.164	7.57 e+9	0.136	6.68 e+9	5.72 e+12	7.23 e+11	756	108
0.586	1.78 e+10	0.551	1.71 e+10	1.99 e+12	9.03 e+11	451	117
1.269	2.98 e+10	1.195	2.87 e+10	1.34 e+13	4.58 e+12	448	160
2.342	4.50 e+10	2.254	4.38 e+10	1.32 e+13	4.82 e+12	293	110

Note: mol/cm^2 stands for molecules per square centimeter.

The surface excess ratio on an imaginary layer of unit area in typical polystyrene solutions on going from a solution concentration of 1 mg/ml to the overlap concentration (150 mg/ml or 7.47 x 10^{11} molecules/ sq cm) is 28. In cyclohexane it is clear that the coils overlap in the adsorbed layer when adsorbed from a solution of concentration 1 mg/ml. In toluene, PS-COOH and PS-H coils clearly do not overlap in the adsorbed layer while HOOC-PS-COOH and HO-PS-OH coils do under the same solution conditions.

4.4.8 Summary of the Results

Incorporation of a carboxylic acid group at one end of the polystyrene chain increases the number of polymer chains adsorbed to glass surface. The effect is more pronounced at end-group concentrations between 10^{-5} to 10^{-4} moles/liter. The adsorbance increases with molecular weight up to 30K. The adsorbance of PS-COOH of number average molecular weight 140K suggests that the effect of carboxylic acid end-group at this molecular weight is diminished and that in all probability chains of higher molecular weight containing a -COOH end-group will behave as though they do not have an end group. The kinetics of adsorption of PS-COOH in toluene shows an initial maximum in the amount adsorbed followed by a decline to an equilibrium value. The report of Klein, et al.,[25] mentions that PS-COOH did not adsorb to mica from toluene as monitored by force - distance studies. It is possible that they tried their experiment at low concentrations and their technique may not be sensitive enough to detect weakly stretched brushes. They also mention that PS-H did not adsorb to mica from toluene while we observe that it does to glass above a molecular weight of 10K (at 1 mg/ml; for the specific activity of our polymers we detect adsorption from 10K). At low molecular weights it is possible that polystyrene is adsorbed in a flat conformation (displaceable by solvent molecules) in toluene and the their technique is not sensitive enough to detect that. We have also detected adsorbed PS-COOH on glass slides by XPS (5K; 1 mg/ml; 24 h; three washes with pure solvent and dried under vacuum) and contact angle analysis. This leaves us with no doubt about our result and leads us to believe that the information provided by Klein, et al., whose methodology is limited, is not relevant to the studies reported here. A hydroxyl group at one end of the chain is not an effective sticky foot for all the molecular weights and concentrations studied.

Incorporation of a carboxylic acid group at both the ends of the polystyrene chain increases the number of polymer chains adsorbed relative to the single sticky foot analog at high concentrations in cyclohexane. However the amount adsorbed is lower than that of the single sticky foot analog at lower concentrations. The adsorbance of HOOC-PS-COOH, 10K increases gradually with concentration up to 0.8 - 1 mg/ml beyond which it increases steeply. This effect is less pronounced as the molecular weight increases. The adsorbance increases with molecular weight. HO-PS-OH of number average molecular weight 10K and at a solution concentration range of 0.5 to 1 mg/ml has higher adsorbance values than PS-H. At all other molecular weights and concentrations the adsorbance of HO-PS-OH is lower than or equal to that of PS-H. The amount of di-carboxylic acid-terminated polystyrene increases with concentration and molecular weight for all the polymers. The amount of polymer adsorbed is greater than the single sticky foot analog at all concentrations and this difference is particularly prominent at low concentrations. Hydroxyl end-groups in toluene do not have a pronounced effect on the adsorbance.

4.4.9 Conclusions

To conclude, incorporating a -COOH group at the end of a polystyrene chain results in the formation of weakly stretched brushes. In cyclohexane the segments of the polystyrene chains interact with an enthalpy of interaction of 1.9 kT [17] with the surface and are present in large concentrations. Therefore they compete with the end-group and so some trains and loops are formed as well. In toluene the segment-surface interaction is much smaller than in cyclohexane [17]. Therefore in the absence of a carboxylic acid end-group polystyrene does not adsorb to glass at low molecular weights. At high molecular weight the cumulative effect of many weak segmental interactions results in adsorption. A single carboxylic acid end-group enables the adsorption of low molecular weight polystyrenes. The surface concentration of PS-COOH adsorbed to glass from toluene is below the overlap concentration suggesting the formation of mushrooms. The presence of a hydroxyl end-group does not seem to have any significant effect on the amount adsorbed or on the rate of adsorption.

A polymer with two end groups adsorbed to a substrate from a solution probably consists of two types of primary chain architecture, namely those held by one end group and those held by both (this is an ideal picture and the segments definitely adsorb competitively to the surface, the competition being dependent on such factors as the solvent quality and nature, the number of segments per chain and their concentration. With chains containing larger number of segments, cooperativity associated with their low probability of desorption and therefore the area that they will occupy on the surface can not be ignored). The number of chains present in each of these form is a function of the solution concentration of the end groups, the concentration of the segments, the number of segments per chain, the enthalpy of interaction of the end group with the surface and the solvent nature and quality.

Chains with two sticky feet at the ends adsorb in a flatter conformation compared to those with one sticky foot at an end from cyclohexane solutions of low concentrations. The di-hydroxyl-terminated polymer is adsorbed in a flatter conformation than the di-carboxylic acid-terminated polymer. This suggests that the contribution of the un-functionalized-end present as a long tail in single sticky foot polymers is absent in the di-functionalized polymers and both the ends are probably present at the ends of loops or in combination with the near end segments form long trains. The increasing adsorbance with concentration is probably due to the formation of mixed monolayer structures consisting of chains bound by both the ends to the surface and chains bound just by one end. At very low solution concentrations (up to 0.05 mg/ml) adsorbances lower than that of polystyrenes are encountered. At low concentrations both the chains ends are bound to the surface, effectively reducing tails whose contribution is significant in the adsorbance of un-functionalized polymer. Interesting conformational transitions involving large tails at high concentrations, increasing loop size with increasing molecular weight and large trains at low concentrations are hypothesized.

The incorporation of two -COOH groups at both the chain ends enhances the adsorption of polystyrene molecules to glass from toluene. This is probably due to the increased chain end concentration and therefore greater enthalpy of interaction per chain. The adsorbance increases with molecular weight at all the concentrations. The enthalpy of interaction of polystyrene segments with glass in cyclohexane is 1.9 kT while that in toluene is a fraction of a kT. Since the segments do not interact strongly with the surface loop formation is favored at low molecular weights. At higher molecular weights contribution of unbound segments in loops and tails (as in un-functionalized polystyrene) become important and adsorbance increases with molecular weight.

The incorporation of two -OH groups at both the chain ends of the 10K sample results in the chains being weakly oriented at high concentrations (0.5 to 1 mg/ml) and are adsorbed in a flatter conformation at lower concentrations. The amount adsorbed decreases with increasing molecular weight as the hydroxyl group is a weak sticky foot and therefore if both the hydroxyl groups were involved in adsorption it is easier to bring the whole chain to the interface. At high molecular weights the samples behave as though they do not have the sticky feet.

The graft density data indicates that carboxylic acid-terminated polystyrenes (PS-COOH and HOOC-PS-COOH) form weakly stretched brushes when adsorbed from a theta or a good solvent. The extent of stretching is governed primarily by the concentration of the end group(s), solvent nature and size of the polymer (molecular weight), being higher at higher concentrations of the end-group(s), and lower in a better solvent and with increasing molecular weight. The di-hydroxyl-terminated polystyrene forms a weakly stretched brush at higher concentrations and lower molecular weights with the stretching being lower than the carboxylic acid analog. The nature of adsorption is competitive; i.e. the segments from the backbone compete with the end group for surface sites the competition being more prominent in cyclohexane.

The increasing graft density with concentration tempts us to compare this with the increasing orientation of small molecules (with a polar terminus) observed in a Langmuir - Blodgett trough with increasing pressure. Though the orientations achieved in our experiments are much less (weakly stretched brush) we do achieve increasing orientation with increasing concentration. With polymer chains it would be difficult to achieve complete orientation because, beyond the first layer i.e. a layer of the size of the polar end-group and containing the end-group, the segments of each of the chain would be in a random walk configuration. This random walk of segments takes place because there is no effective dispersive force operating in atactic polystyrene to induce lateral orientation unlike stearic acid which can crystallize by such such lateral dispersive interaction. Even with a weak dispersive interaction the viscosity of the molecules at the interface (as shown in surface excess calculations) which is 100 to 3000 fold that of the corresponding bulk solution would prevent an effective orientation in the time scale of several months. We therefore believe that the carboxylic acid group is a mild enthalpic perturbation to the adsorption process resulting in weakly stretched brushes. It might be possible to increase the orientation by increasing the enthalpy of interaction of the end-group with the surface (by selecting another end-group which would have an enthalpy of interaction with the surface of the order of 20 to 40 kT), but it would be beyond experiments to attain the type of orientation idealized in scaling theories even with the enthalpy of interaction of the order of a chemical bond for the reasons (osmotic forces that repel close packing and excluded volume effects that eliminate certain conformations) and experimental facts stated above.

Extension of polymer chains with an end anchored to the surface is in all probability entropy limited. As much as the chains would try to get one end to the surface, the number of chain-ends grafted to the surface would be limited by the following factors: (1)

Geometric constraint imposed by the first monomer (attached to the chain end) and subsequent monomers (excluded volume effect). (2) Tendency of the segments to adsorb to the surface particularly in poor or theta solvents Ideal extensions are therefore achieved with small molecules containing a polar terminus. If we are to look for conditions under which segments will not adsorb and only end-terminated groups will adsorb, still there is no doubt in my mind that a fully extended layer would not be possible because beyond the length of the end group the segments of the chains can still do a random walk. So I think that perfect orientation is possible if and only if structural design allows lateral overlap of segments (tacticity match) resulting in enthalpic gain significantly greater than the entropy loss accompanying orientation perpendicular to the surface. However the solubility of a such a polymer would be limited to very few solvents and solution conditions.

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CHAPTER 5

SEGMENT DENSITY DISTRIBUTION DETERMINATIONS BY NEUTRON REFLECTION EXPERIMENTS AND CHARACTERIZATION OF DRY ADSORBED FILMS BY X-RAY PHOTOELECTRONS SPECTROSCOPY AND WATER CONTACT ANGLE MEASUREMENTS

5.1 Introduction

The segment density distribution in the direction perpendicular to the surface was determined by neutron reflection experiments. This work was performed in collaboration with Professor Stein's research group at the University of Massachusetts and the neutron reflection group at the National Institute for Standards and Technology (NIST), Maryland.[1] The segment density distribution, $\phi(z)$, is one of the key theoretical predictions that differentiates the two major theories discussed in Chapter 1. Earlier other research groups outside the United States have used this technique to determine segment density distribution in adsorbed polymer layers[2, 3] and within the United States to study the volume fraction profile near the surface of homo polymers, diblock polymer films (spin cast) and adsorbed diblock polymer.[4-6] A recent review summarizes most of the reported work on neutron reflectivity.[7]

The thickness of dry polymer films on glass after adsorption was evaluated by angle resolved x-ray photoelectron spectroscopy and the wetting behavior were assessed by water contact angle analysis.

The chapter is organized as follows. A brief introduction to each of the techniques mentioned in the above paragraphs is given in the following paragraphs. The experimental section follows the introduction. The results from each of the techniques is presented and discussed in the next section and the conclusions are presented in the final section.

Several techniques have emerged recently which enable the study of segment density distribution of polymers at interfaces. They fall in to two broad categories, the ion beam techniques and the reflectivity techniques.[7] The ion beam techniques involve the use of ions and are destructive in nature as the ions interact with the polymer and degrade it. Examples of ion beam techniques are Rutherford backscattering spectrometry, forward recoil spectrometry and secondary ion mass spectrometry. The spatial resolution of these techniques is ~ 100 Å. The reflectivity techniques that are currently used to study the segment density distribution of polymers away from the surface are neutron and x-ray reflectivities.[8, 9] The spatial resolution of the two techniques is ~ 10 Å and the penetration depth is ~ 1000 Å. Neutron reflectivity detects the variation in scattering length density as a function of depth while x-ray reflectivity detects the variation in electron density. Reflectivity techniques are non-destructive and samples can be studied in situ (in solution while an adsorption is being performed and under atmospheric conditions).

Neutrons incident at an interface undergo reflection and refraction as the refractive indices of the constituents of the interface are usually different. The refractive index of a material (non-magnetic) for neutrons is given by,

$$n = 1 - [N_A (\lambda^2/2\pi) \Sigma_i (\rho_i b_i/A_i)]$$

where N_A is the Avagadro number, λ is the wave length of the neutron, ρ_i is the density, b_i is the neutron scattering length and A_i the atomic weight of component i. The extent to which the neutrons are reflected depends on the differences in the momentum transfer on either side of the interface (represented by the differences in the wave vector of the incident and reflected neutrons). In vacuum the component of the wave vector normal to the surface is given by,

$$k_{z,0} = 2\pi \text{ x } \sin\theta/\lambda$$

where θ is the angle of incidence (usually measured as the angle from the plane of the sample to the neutron beam unlike conventional definition) and λ is the wavelength of the neutrons (the geometry of the reflectivity measurements is maintained such that the angle of incidence and the detection angle are equal and therefore components of the wave vector other than that normal to the surface can be ignored). In a medium i of density ρ_i the wave vector is given by,

$$k_{z,\, i} = [(k_{z,\, 0})^2 - (k_{c,\, i})^2]^{0.5}$$

where $k_{c,\, i}$ is the critical value of $k_{z,\, i}$ below which total reflection occurs. For a given scattering length density the condition of total reflection can be achieved by varying the angle of incidence at a constant wave length.

In the case of an air-polymer interface the reflection coefficient $r_{0,\, 1}$ is given by the following equation:

$$r_{0,\, 1} = [(k_{z,\, 0}) - (k_{z,\, 1})] / [(k_{z,\, 0}) + (k_{z,\, 1})]$$

The reflectivity R is the square of the reflection coefficient. For an interface with a continuous variation in the scattering length density it is the usual practice to model it as a multiple layer of discrete thicknesses so that a recursive relationship can be used to describe the reflectivity. This in turn simplifies the calculation of the theoretical reflectivity for that particular model (matrix solution).[7]

In real neutron reflection experiments the reflectivity profile (the square of the reflection amplitude) is measured and phase information is lost due to the nature of the measurements. The loss of phase information implies that the direct calculation of the scattering length density or the segment density distribution is not possible. Therefore the theoretical reflectivity profile for previously predicted segment density distribution is calculated and compared with the experimentally obtained profile. The theoretical model that describes the experimental result is taken to be the correct one. It follows immediately from such arguments that there might be other mathematical descriptions of the segment density distribution which might lead to the same experimentally observed reflectivity profile. This is one of the serious draw backs of the reflectivity measurements. In the absence of any other sophisticated technology to measure the finer properties of adsorbed polymers, the reflectivity measurements definitely enable a better understanding.

The thicknesses of some dry polymer films were determined by x-ray photoelectron spectroscopy (XPS).[10, 11] XPS enables the direct and non-destructive evaluation of the thickness using the angle resolved method (ARXPS).[12] XPS or electron spectroscopy for chemical analysis (ESCA) is a well established surface characterization technique. It involves the bombardment of x-rays of characteristic energy on the specimen of interest under ultra high vacuum (10^{-9} to 10^{-10} Torr) and the measurement of the number of ejected electrons of a particular kinetic energy throughout the characteristic energy range. The result is a spectrum indicating the number of electrons of particular kinetic energies versus the kinetic energies of the electrons. Since electron of a particular kinetic energy have to come from specific orbitals of the various elements of the periodic table and since they possess discrete binding energies the spectrum also represents the number of atoms responsible for a peak of a particular kinetic energy versus the binding energy of the electron in that particular orbital. XPS is extremely sensitive to the chemical composition of the top 0 - 100 Å of a surface. This sensitivity is the result of the limited distance that the electrons ejected out of the atoms of the specimen being examined can travel within the solid before suffering an inelastic collision and losing their characteristic energy and thus their chemical identity. Most of the contribution (67%) to the intensity of the characteristic energy peak (for any particular element) is from the atoms lying within a characteristic distance from the surface called the mean free path (MFP). Several research groups have worked on the determination of the MFP of the electrons from the different orbitals.[13-18] A survey indicated that the literature is plagued with inconsistencies and theoretically non-acceptable values suggesting that this is a difficult problem. The thickness of thin polymer films can be determined by ARXPS. This method relates the thickness to the relative angular dependence of the signals from the overlayer to that from the substrate. The intensities of the characteristic ESCA signals emitted from the atoms beneath the overlayer of a material are attenuated by the overlayer. By rotating the sample under investigation about an axis on its surface the signals originating from the atoms beneath the surface can be enhanced or attenuated relative to those coming from the atoms on or near the surface.

The contact angle made by a water drop at the surface-air interface (say glass-air interface) is very sensitive to the physical and and chemical structure in the outer few angstroms of the surface. Our technique involves the measurement of the dynamic contact angle made by a water drop at the surface-air interface. The contact angle made by a water (θ) drop under equilibrium conditions is governed by Young's equation. It involves the balance of the forces at the point where the surface-water-air phases are in equilibrium. Application of the triangle law of forces at this point leads to the following equation:

$$\gamma_{sa} - \gamma_{sw} = \gamma_{wa} \cos\theta$$

where the subscripts s, a, w stand for surface, air and water and the γs are the respective interfacial tensions. The immediate result that follows from this equation is that if the surface in question is a hydrophilic substance such as glass, the surface modification of glass to form a hydrophobic surface by the adsorption of functionalized polystyrenes should result in large contact angle changes. This has been well exploited by several research groups in the past to monitor surface modification and we follow the path of others and take advantage of the surface sensitivity of water contact angle values.[19-21]

5.2. Experimental

5.2.1 Materials

Perdeuterated polystyrene and carboxylic acid-terminated polystyrene of degree of polymerization (DP) 121 and poly dispersity index 1.05 was prepared from perdeuterated styrene (Aldrich) by methods discussed in detail in chapter 2. Protonated analogs of degree of polymerization 134 and polydispersity index 1.05 were prepared in parallel. Fully protonated, carboxylic acid-terminated, and hydroxyl terminated polystyrenes of number average molecular weight 5K, 10K, 30K, 60K, and 140K prepared and characterized as reported in Chapter 2 were used in the thickness determinations by XPS. Perdeuterated cyclohexane and fully protonated cyclohexane (NIST) were used without further purification. Fully protonated cyclohexane and toluene (Fisher) dried over calcium hydride were distilled and used in adsorption experiments in which thicknesses were determined by XPS. The silicon single crystal and the quartz cell used in the reflectivity measurements were optically polished to $\lambda/20$. They were immersed in sulfuric acid-potassium perchlorate solution for 1 to 2 h to remove any surface impurity and were washed thoroughly in distilled water before adsorption. The glass slides (2 cm x 1 cm) used in XPS were cleaned before adsorption using nochromix and sulfuric acid mixture as detailed in Chapter 4.

5.2.2 Neutron Reflectivity Measurements

The concentration of the functionalized polystyrenes used was 2 mg/ml. The experiments were performed with the BT-7 reflectometer in the reactor hall at the National Institute for Standards and Technology, Maryland. The experimental set up as designed by NIST is shown in figure 5.1[22, 23] The incident monochromatic neutron beam (after passing through a Be filter and a graphite monochromator) of wavelength 0.2367 nm ($\delta\lambda/\lambda = 0.01$) incident on the silicon single crystal passes through it and is reflected from the silicon-polymer solution interface on the other side of the crystal. The reflected beam passes through the crystal and is detected by a ^{3}He detector placed on a goniometer. The silicon crystal is also mounted on a goniometer so that it can be placed at any angle of incidence θ with respect to incident beam. The detector located at 2θ collects the specularly reflected neutrons The polymer solution along with the silicon crystal is placed in a fused quartz cell with two 0.5 mm thick windows for the incident and reflected beams as shown in figure 5.1b. The thickness of the polymer solution is usually kept low to minimize incoherent scattering (depth of the quartz cell 0.5 mm)[6].

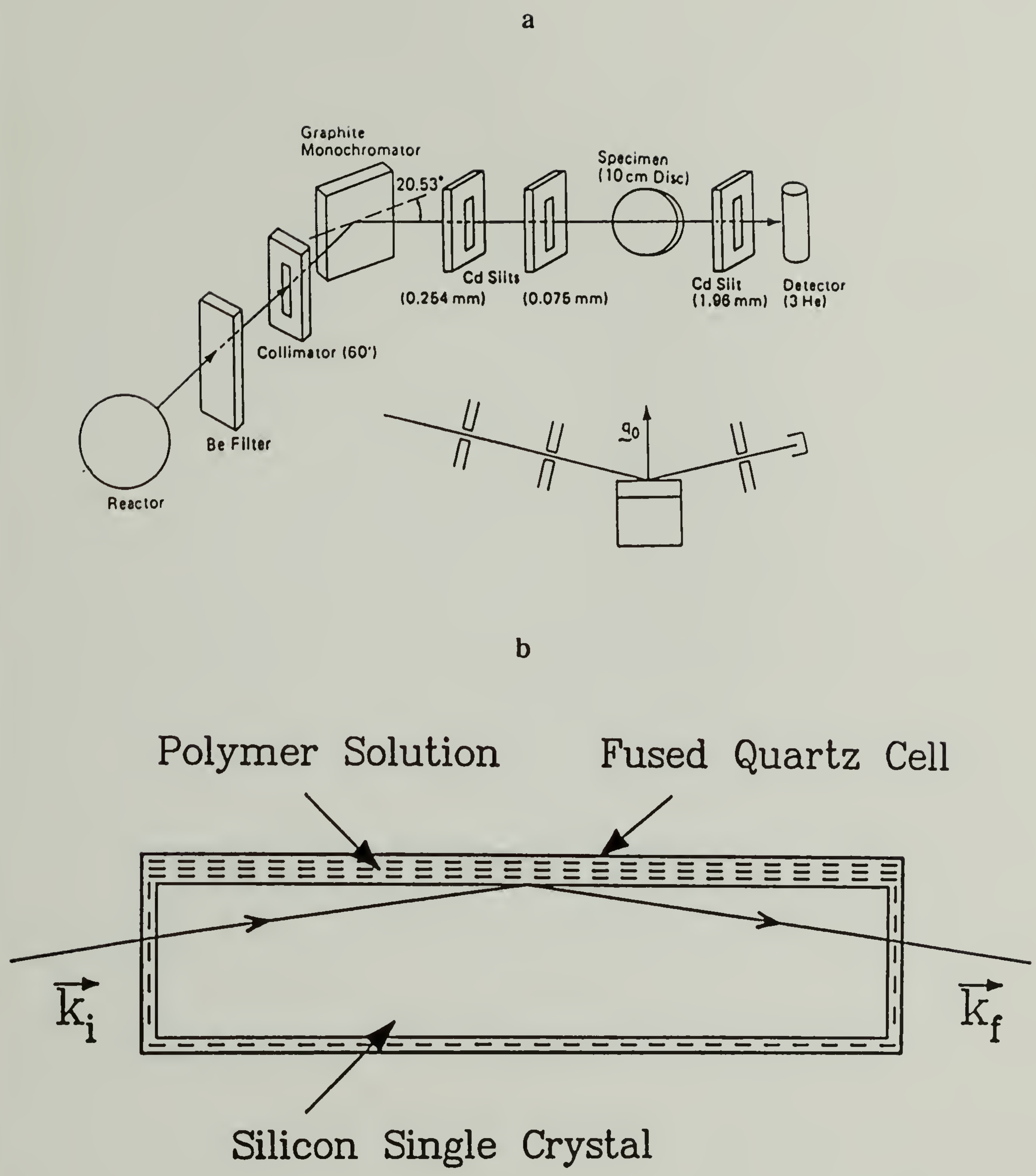

Figure 5.1 a) Diagram of the Fixed Wavelength Neutron Reflectometer at the National Institute of Standards and Technology (from Anastasiadis, et al) and b) the Reflection Geometry (from Composto, et al).

After injecting the polymer solution into the cell the system was allowed to equilibriate for an hour before reflectivity measurements (this time is sufficient for equilibriation as evident from the results in Chapter 4). Typical data collection times were 12 h and the experiments were performed by Todd Mansfield and Dr. Russel Composto working with the NIST researchers. The neutron reflectivity as a function of $Q = 2k = 4\pi\ (\mathrm{Sin}\theta/\lambda)$ were evaluated for the pure solvents and after polymer adsorption from the solvents. Deuterated polymers were used with protonated solvents and vice versa as this combination provides the best scattering length density contrast and results in the technique being more sensitive. The experimental reflectivity data were fitted using two types of segment density distribution profiles (other types were ignored as the pronounced minimum in the observed reflectivity cannot be obtained from these models): parabolic and a simple step-function polymer film with a gaussian rounding at the polymer solution interface. The calculations were performed using well established methods.[24]

5.2.3 X-ray Photoelectron Spectroscopy

XPS spectra of dry polymer films were obtained using a Perkin-Elmer-Physical Electronics 5100 spectrometer using Mg K_α excitation (400 W, 15.0 kV). Survey spectra (pass energy = 89.45 eV) and multiplex spectra (pass energy = 35.75 eV) of the individual elemental regions constituting the sample (from the survey) were recorded at three takeoff angles, 15°, 30° and 75° (measured between the plane of the glass surface and the vertical line to the entrance lens of the detector optics). The integrated intensities of the Si_{2p}, Si_{2s}, O_{1s} (all from glass) and C_{1s} (from the polystyrene on the glass) regions were measured. The integrated intensities of the Si_{2p}, Si_{2s}, O_{1s} regions from a clean glass surface (previously sputter cleaned using helium ions in the XPS ultra high vacuum chamber; 25 mA emission current and 3 kV beam voltage) was measured as well. The integrated intensities from different glass slides cleaned under identical sputtering conditions result in integrated intensities were within ± 5% of each other.

The thickness of the polymer overlayer (d) on a given glass slide was determined from the integrated intensities for the Si_{2p} peak using the equation shown below.

$$d = - \ln (Si_{2p,\, \theta,\, f} \,/\, Si_{2p,\, \theta,\, g}) \times \lambda \, \mathrm{Sin}\theta$$

where the term within the bracket is the ratio of the integrated intensities of the Si_{2p} peaks from glass covered with a overlayer of thickness d at a takeoff angle of θ and sputter cleaned glass at the same takeoff angle. λ is the mean free path of Si_{2p} electrons through glass and it is assumed that it is the same through the polystyrene overlayer (even though the density of glass is 2.34 and that of polystyrene ~ 1) as this assumption considerably simplifies the calculations. A mean free path value of 22.0 ± 1.0 Å was used in the thickness calculations as this value is in between the experimental value of 21 Å reported by Clark[16] and the theoretical prediction[25] of 23 Å, for Si_{2p} electrons through an organic material of density 1. The simplifications associated with the equation used in the thickness calculation are, 1) uniformly thick overlayer and no patches, 2) the distribution of the roughness associated with the glass surface used in adsorption and the one that was sputter cleaned are the same.

5.2.4 Water Contact Angle Measurements

Dynamic advancing (θ_A) and receding (θ_R) water contact angles were measured with a Rame-Hart telescopic goniometer and a Gilmont syringe with a flat tipped 24-gauge needle as water was added (θ_A) or withdrawn (θ_R) from the drop. The water used was house distilled water that was redistilled with a Gilmont still.

5.3 Results and Discussion

5.3.1 Segment Density Distribution Profiles from Neutron Reflectivity Measurements

The reflectivity profile as a function of neutron momentum transfer (or the angle of incidence; 0 to 2°) for pure protonated cyclohexane is shown in figure 5.2 as a log(reflectivity) versus Q (nm^{-1}) plot. Total reflection is observed up to Q ~ 0.14 nm^{-1} beyond which reflectivity decreases monotonically suggesting the increasing transfer of neutron momentum with increasing angle of incidence (the angle of incidence is defined as the angle between the plane of the silicon single crystal and the neutron beam) as more and more scattering centers are involved. The observed reflectivity profile in the presence of adsorbed perdeuterated polystyrene in the same solvent (not shown in the figure) is different only at higher angles of incidence (> 0.43°) (suggesting that it might be adsorbed with a diffuse layer structure). The profile for perdeuterated carboxylic acid-terminated polystyrene from the same solvent is also shown in the same figure. It follows that of the solvent up to an angle of incidence of 0.18° above which the reflectivity starts to decrease rapidly reaching a minimum at 0.27°. Above this angle reflectivity increases again up to an angle of incidence of 0.36 (still less than that of pure solvent at this angle) and starts to decrease above this angle. This pattern is characteristic of the presence of a thin polymer film as observed first by Stamm.[4]

The theoretical reflectivity profiles were evaluated for the system Si/SiO_2/cyclohexane and Si/SiO_2/deuteriopolystyrene with an acid end-group, using the well known scattering length densities of the different samples for a native oxide layer of 12 Å thickness and 3.4 Å roughness.[26] These are shown as continuous lines along with the experimental data points in figure 5.2. The segment density distribution assumed for the deuterio PS-COOH away from the silicon dioxide-cyclohexane interface is shown in the inset of figure 5.2.

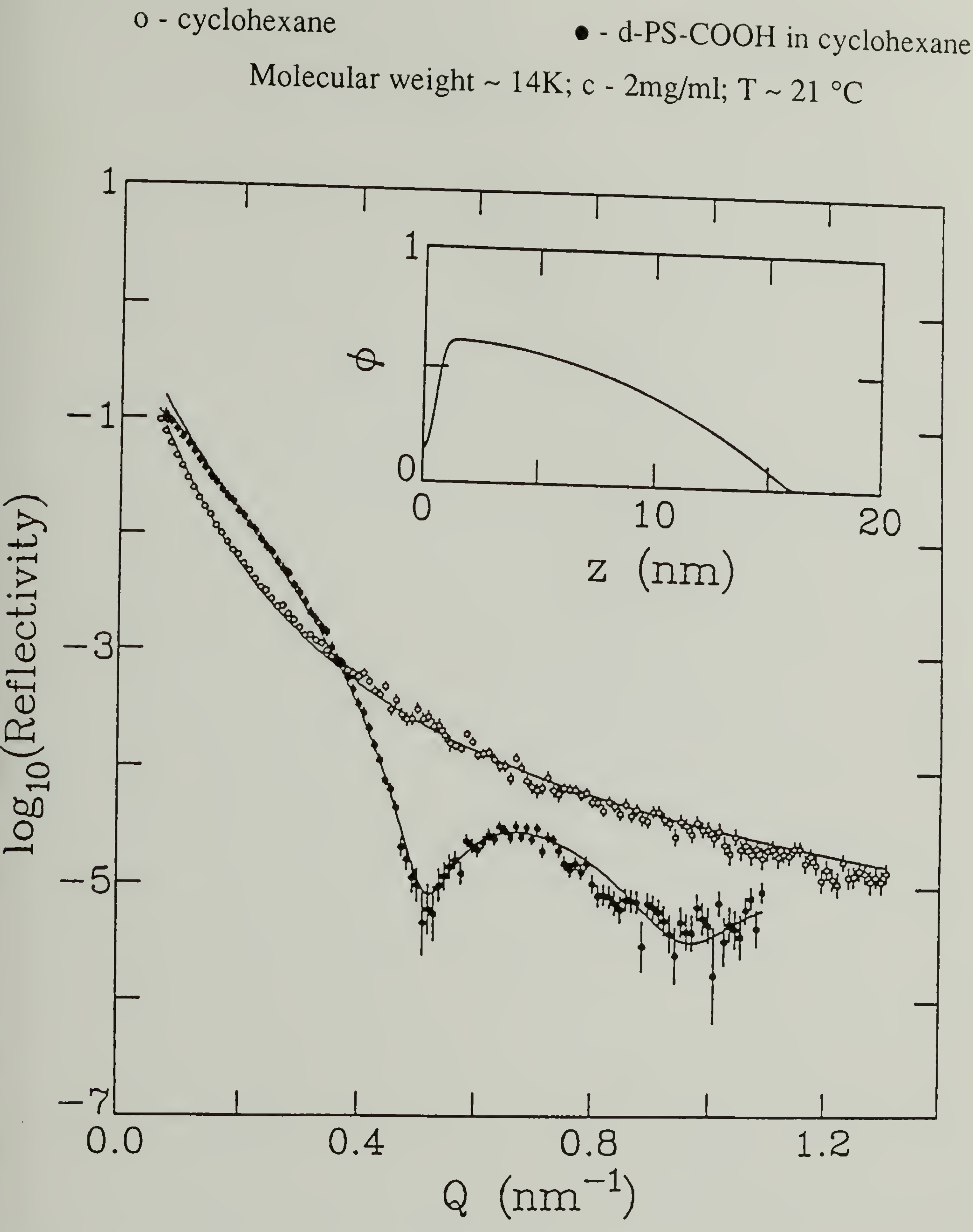

Figure 5.2 Experimental and Calculated (–) Neutron Reflectivity versus Neutron Momentum Transfer for Perdeuterated PS-COOH Adsorbed from Fully Protonated Cyclohexane Solution. Inset: Theoretical Reflectivity Profile Assumed in the Reflectivity Calculation

It can be seen that the theoretical reflectivity data from the assumed parabolic segment density distribution fits the experimental data very well.

The research interest of this thesis concerns functionalized polystyrenes and as such the results pertaining to PS-COOH alone are discussed. In the theoretical calculation of the reflectivity profile only two segment density distribution profiles were considered as exponential or power law types of profiles will not result in a minimum as observed in the reflectivity results. The parabolic and a step-function profile with a gaussian rounding were considered as they were relevant to the experimental result. The theoretical profile that best fits the experimental reflectivity data for perdeuterio-carboxylic acid-terminated polystyrene is shown below.

$$\phi(z) = \phi(z = 0)\ (h^2 - z^2) / h^2 \text{ for all } z \leq h, \text{ where } h = 155\ \text{Å}.$$

The fit to the data is better if a slight rounding (s = 3 Å) in the vicinity of z=h is considered and considerably better if a depletion layer of 12 Å is considered. The step-function distribution profile fails to describe the data well. Similar results for protonated PS-COOH in perdeuterio cyclohexane and perdeuterio toluene were obtained. These reflectivity profiles (experimental and theoretical) are shown in figures 5.3 and 5.4.

The theoretical segment density distribution profiles that best fit the experimental data are shown as insets in figure 5.3 and 5.4. A modified parabolic segment density distribution profile fits the data well. We believe that the difference between the segment density distribution profiles of deuterio PS-COOH in cyclohexane and PS-COOH in deuterio cyclohexane is due to lower χ_s value in the case of the former.

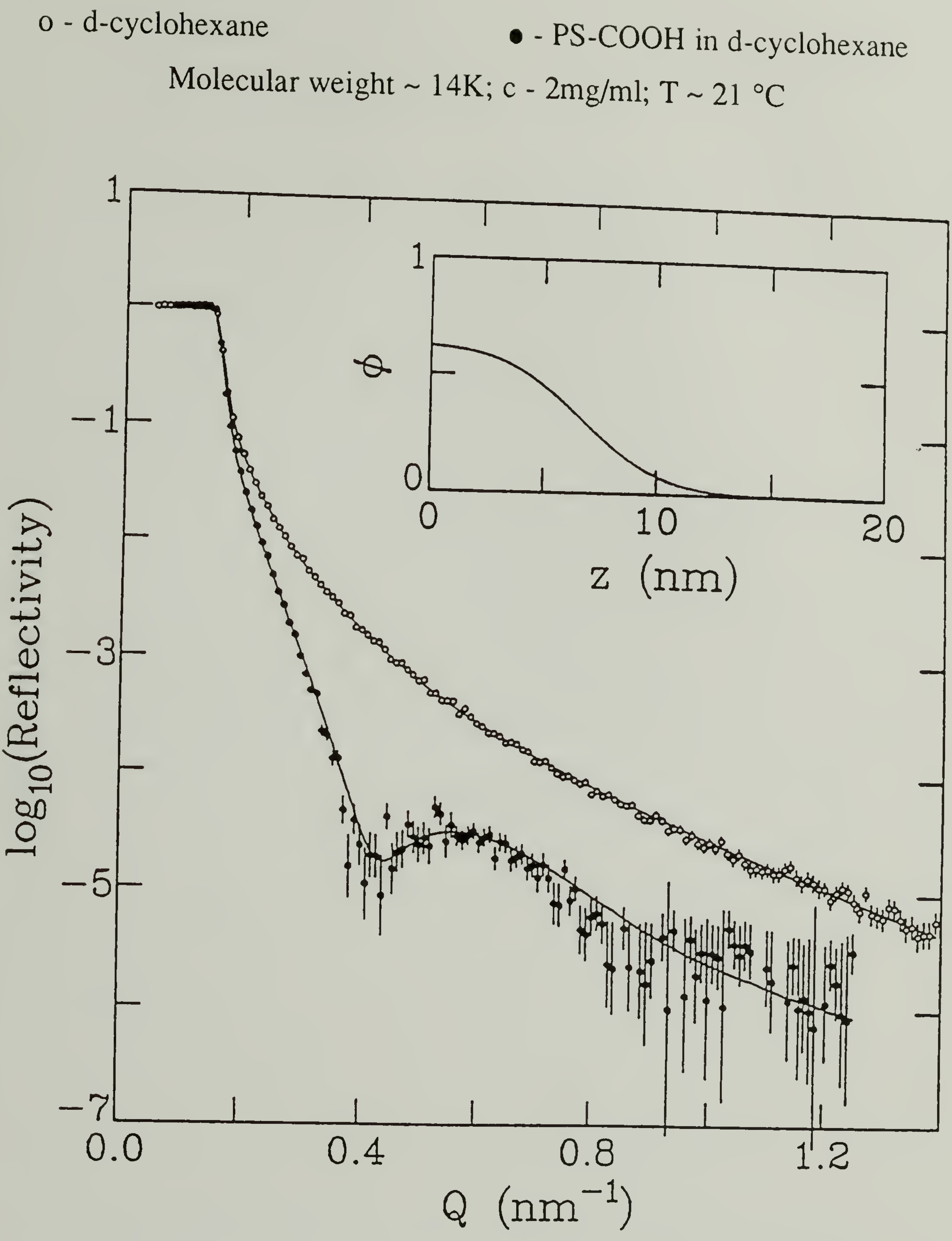

Figure 5.3 Experimental and Calculated (–) Neutron Reflectivity versus Neutron Momentum Transfer for Fully Protonated PS-COOH Adsorbed from Perdeuterated Cyclohexane Solution. Inset: Theoretical Reflectivity Profile Assumed in the Reflectivity Calculation

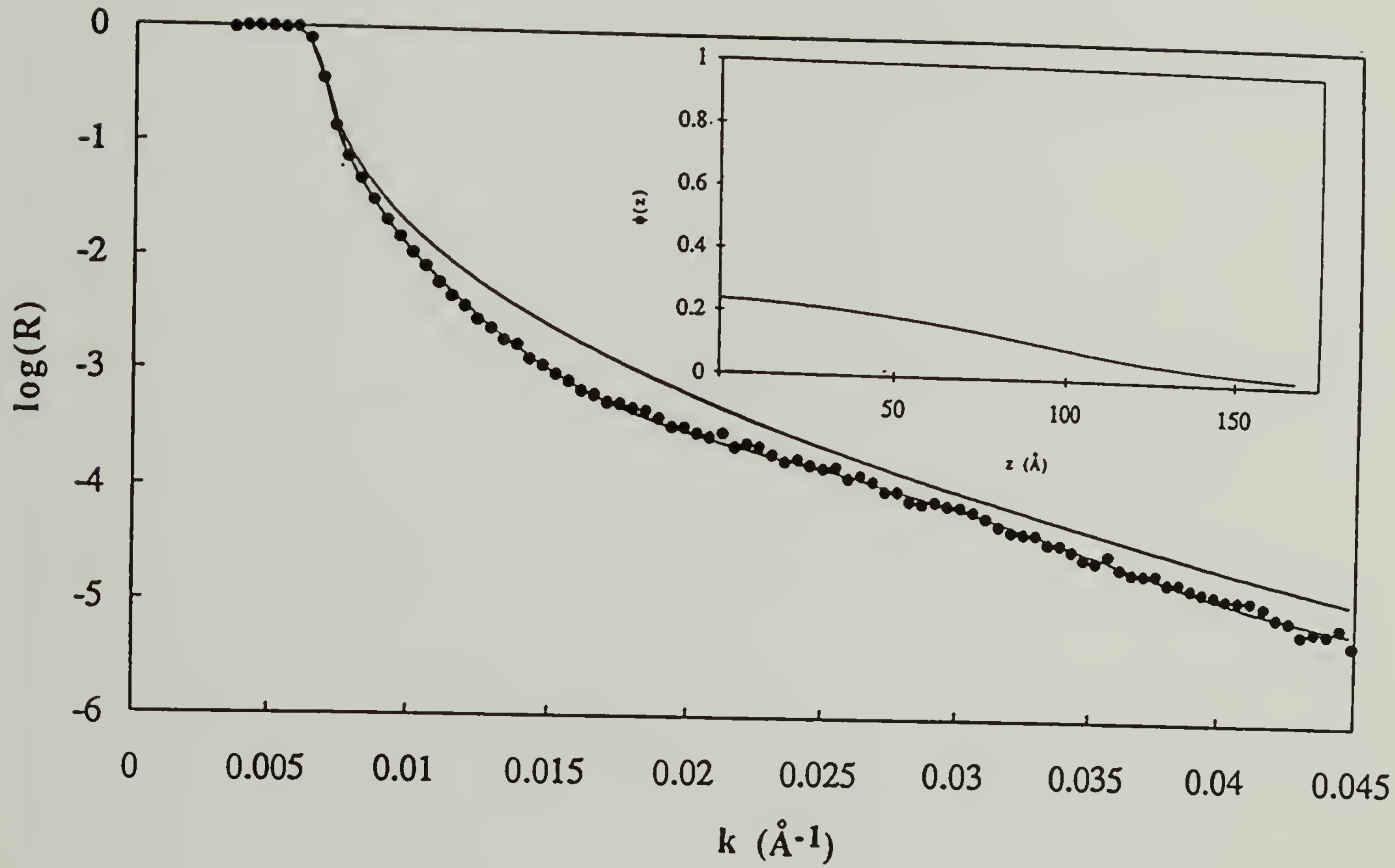

Figure 5.4 Experimental and Calculated (–) Neutron Reflectivity versus Neutron Momentum Transfer for Fully Protonated PS-COOH (DP = 134) Adsorbed from Perdeuterated Toluene Solution. Inset: Theoretical Reflectivity Profile Assumed in the Reflectivity Calculation

Earlier the mean field theories of Scheutjens and Fleer have predicted 1) a monotonically decreasing segment density distribution profile for polymer segment-surface interaction parameter of 0.5 (χ_s) and a polymer-solvent interaction parameter of 0.5 (χ) and 2) a segment density profile with a pronounced maximum at some distance away from the surface for $\chi_s = 0$ and $\chi = 0.5$.[27] A parabolic segment density distribution for polymer segments anchored to the surface by one of their end-group has been predicted for an isolated chain by Hesselink[28] and for strongly stretched chains by Milner[29] as well. The scaling theory of de Gennes[30] predicts a uniform concentration profile up to a certain distance from the surface for strongly stretched brushes and a power law decay for mushrooms ($\phi(z) \sim z^{2/3}$) provided several assumptions are made (flexible chains, large molecular weight, segments do not adsorb by themselves, etc. See Chapter 1 for a critical review of the different models).

Before comparing our results to the results of the theoretical models we have to ensure that the assumptions made in deriving the models reflect our experimental conditions well (even though some assumptions such as very high grafting density and strongly stretched chains cannot be incorporated in an experiment before hand). The results from chapter 4 indicate that weakly stretched brushes had formed in cyclohexane (from the low graft densities) while mushrooms are formed in toluene. This eliminates the comparison with Miner and de Gennes predictions for highly grafted brushes. However the flexibility of the mean field theories of Scheutjen and Fleer, and the fact that mushrooms are formed in toluene (de Gennes assumptions hold good for adsorptions from toluene) enable some comparisons to be made.

In cyclohexane the mean field theory of Scheutjens and Fleer predicts a monotonically decreasing segment density profile for ($\theta = 1$) polymer segment-surface interaction parameter of 0.5 (χ_s) and above and a polymer-solvent interaction parameter of 0.5 (χ). The TLC displacement experimental results of Cohen Stuart[31] indicates that the segment-surface interaction parameter for the polystyrene-silica system is 1.5. The polystyrene segment -solvent interaction parameter is 0.5 as our experiments were performed just above the theta condition. However the experimental segment density profile is very different from the monotonically decreasing profile predicted by the SF theory suggesting that it does not describe our system accurately. The theory that best predicts the segment density distribution profile of PS-COOH in cyclohexane is the one due to Hesselink for isolated polymer chains grafted to a surface. Clearly we do not have isolated chains at the surface.

In toluene, a good solvent, the segment density distribution is completely different from the scaling predictions of de Gennes which predicts a uniform concentration profile up to a certain distance from the surface for strongly stretched brushes and a power law decay for mushrooms ($\phi(z) \sim z^{2/3}$; Chapter 1). From our adsorbance data for PS-COOH in toluene we infer that it is present in the form of mushrooms on the surface. The observed reflectivity profile clearly indicates that the scaling theory does not describe the segment density distribution of PS-COOH mushrooms in toluene while a parabolic segment density distribution with appropriate fitting parameter will fit the experimental data. The mean field theory of Scheutjen and Fleer predict a maximum in the segment density distribution profile under the conditions of our experiment and it is clear from figure 5.4 that it's prediction is close to what we observe.

5.3.2 X-ray Photoelectron Spectroscopic and Water Contact Angle Characterization of Adsorbed Polymer in the Form of Dried Films

The survey spectrum of a glass surface after chemical cleaning and drying, after argon sputtering and after adsorption at a takeoff angle of 15° are shown in figure 5.5. The chemical composition of glass is SiO_2 primarily with trace amounts of metal ions such as sodium and potassium. The surface composition of chemically cleaned glass indicates that in addition to Si, O, very small amount of sodium (a small peak is observed at ~ 1074 eV) and carbon are present as well. Carbon is seen in the XPS spectrum of almost all high energy solids and is due to the adsorption of small molecules such as carbon monoxide, carbon dioxide, methane and other hydrocarbons from the ambient atmosphere. These contaminants known as adventitious carbon can be removed from the surface in the ultra high vacuum chamber of the spectrometer by argon ion sputtering as shown by the absence of carbon peak in figure 5.5b. However they are always present on glass slides under ambient conditions and are easily displaced by polymers.

The XPS spectrum of glass after the adsorption of PS-COOH (30 K, 1 mg/ml, T = 36.7 ± 0.1 °C) is shown in figures 5.5c and 5.5d (c - cyclohexane and d - toluene). The appearance of the carbon peak of high intensity and the attenuation of the intensities of the Si peaks (2p and 2s) and the oxygen peak from the substrate suggests the formation of a overlayer. The multiplex spectrum of the C_{1s} peak is shown in figure 5.6. The appearance of the π-π^* shakeup peak confirms the presence of polystyrene.

X-ray photoelectron spectra of dry films were recorded at three takeoff angles of 15°, 30° and 75°. From the attenuation of the integrated intensity of the Si_{2p} peak the thicknesses of the films were calculated using the formula shown in the experimental section. The mean free path of Si_{2p} electrons was assumed to be 22.0 ± 1.0 Å (see experimental section). The results of the calculations are presented in Tables 5.1 and 5.2 (Adsorption experiments notebook #1, p 79 -103).

The thickness values were also determined from the corresponding adsorbances (from the LSC data) assuming that the density of polystyrene in the adsorbed layer is 1 g/cm^3). On comparing the XPS and the LSC thickness it can be seen that the XPS thickness values are smaller than that obtained by LSC. For example consider the case of the thickness values for PS-COOH of number average molecular weight 140K from a cyclohexane solution of concentration 1 mg/ml. The LSC thickness is 43.4 ± 5.7 Å while that from ARXPS is 31.4 ± 10.2 Å. The surface excess calculations show that the number of chains in the adsorbed layer per unit area (1.87 e+12) is less than that present in an amorphous solid of polystyrene (2.65 e+12) of the same area. This indicates that the density of the polymer in the adsorbed layer is less than that assumed and suggests that part of the

Number average molecular weight - 30 K; c = 1 mg/ml; T = 36.7 ± 0.1 °C

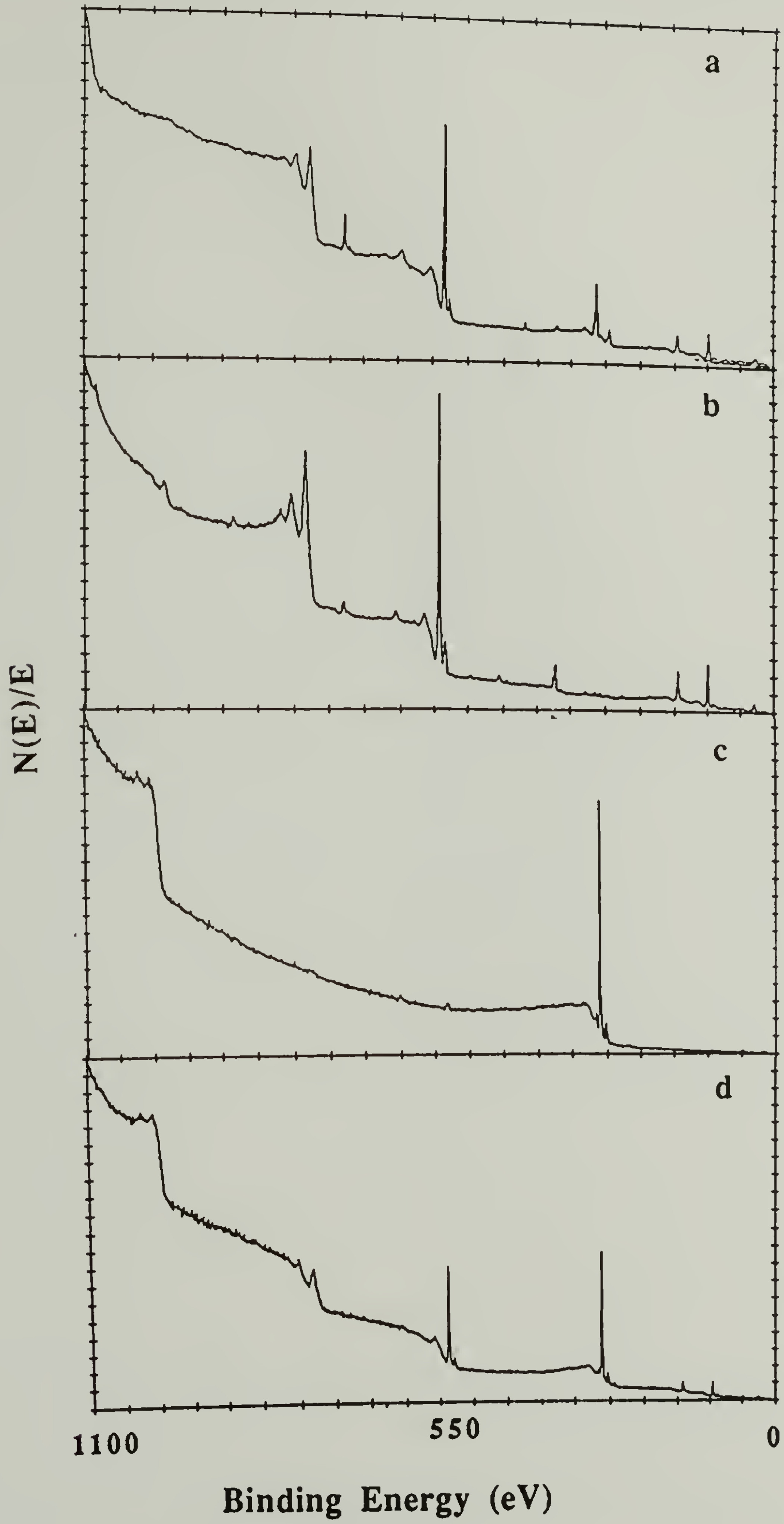

Figure 5.5 XPS Survey Spectra of Different Glass Surfaces.
a) after chemical cleaning; b) after sputter cleaning; after the adsorption of PS-COOH from c) cyclohexane and d) toluene

Number average molecular weight - 30 K; c = 1 mg/ml; T = 36.7 ± 0.1 °C

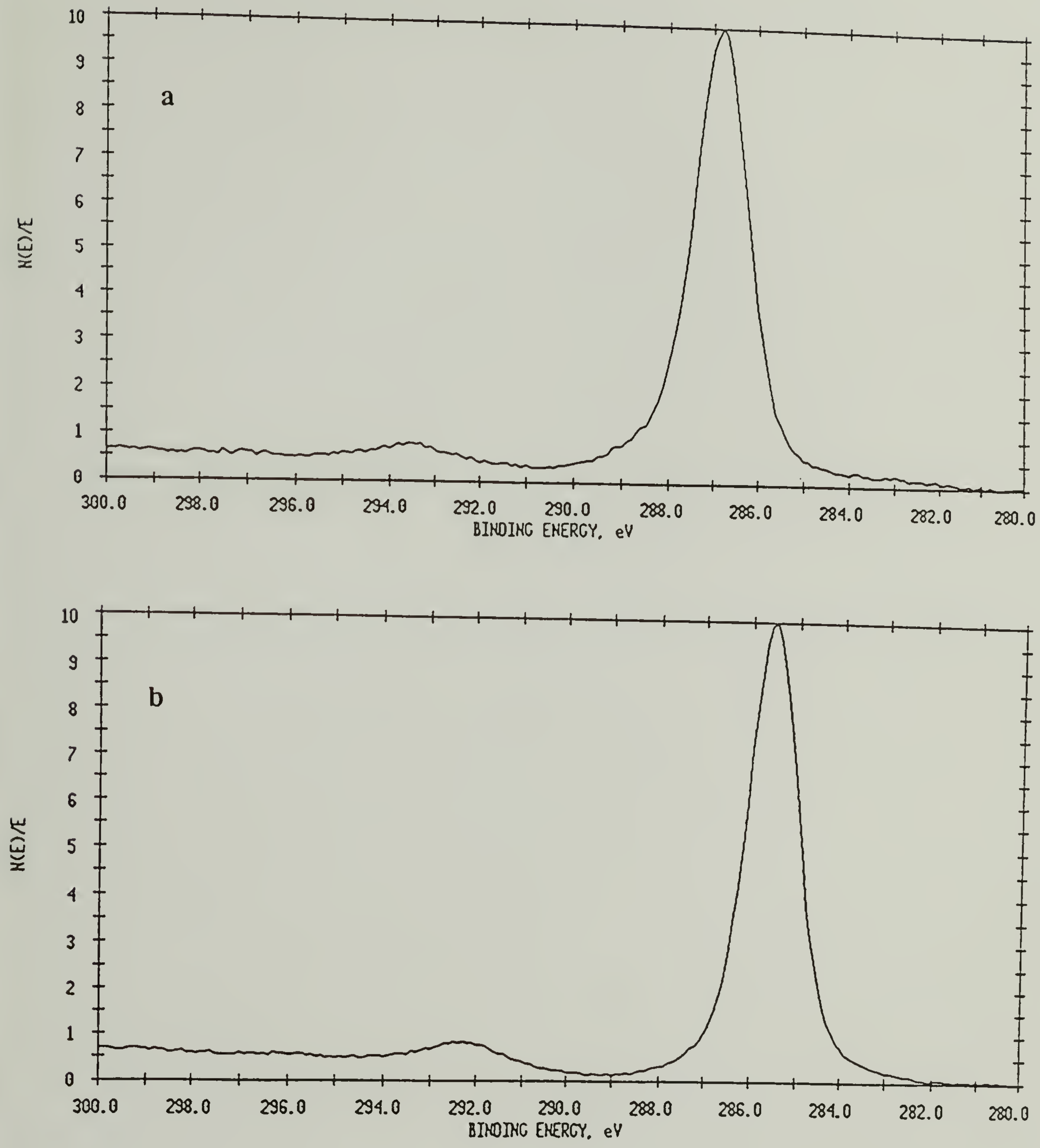

Figure 5.6 XPS Multiplex Spectrum of the C_{1s} Region. After the Adsorption of PS-COOH from a) cyclohexane and b) toluene

Table 5.1 Dry Film Thickness From XPS Data and Contact Angle Data

Samples adsorbed from cyclohexane at 36.7 ± 0.1 °C

Sample	M_n.	c	θ	d (Å)	t (Å)	θ_A / θ_R
PS-COOH	5000	1.0	15	12.0	36.6 ± 4.8	90/70
			30	13.7		
			75	10.7		
PS-COOH	10000	1.0	15	21.1	43.2 ± 4.8	90/74
			30	30.2		
			75	31.5		
PS-COOH	30000	1.0	15	23.1	56.3 ± 7.3	89/76
			30	37.9		
			75	39.3		
PS-COOH	140000	1.0	15	23.0	43.3 ± 5.7	90/78
			30	28.6		
			75	42.7		
PS-COOH	5000	0.1	15	12.1	25.9 ± 3.5	85/68
			30	13.2		
			75	8.30		
PS-COOH	10000	0.1	15	14.2	25.4 ± 3.5	88/64
			30	15.7		
			75	12.3		
PS-COOH	30000	0.1	15	11.2	37.2 ± 5.0	89/70
			30	18.5		
			75	25.1		
PS-COOH	140000	0.1	15	7.90	25.7 ± 3.5	88/57
			30	9.30		
			75	8.00		

Continued, next page

Table 5.1 Continued

Samples adsorbed from cyclohexane at 36.7 ± 0.1 °C

Sample	M_n.	c	θ	d (Å)	t (Å)	θ_A / θ_R
PS-H	5000	1.0	15 30 75	6.5 6.1 3.8	6.8 ± 1.1	89/50
PS-H	10000	1.0	15 30 75	6.7 6.5 4.6	10.5 ± 1.6	89/53
PS-H	30000	1.0	15 30 75	8.1 9.1 6.7	17.2 ± 2.5	89/56
PS-H	140000	1.0	15 30 75	7.9 7.0 4.5	27.7 ± 3.7	88/54
PS-H	5000	0.1	15 30 75	3.2 2.8 1.5	4.4 ± 0.8	87/48
PS-H	10000	0.1	15 30 75	3.8 3.3 1.7	7.3 ± 1.2	89/54
PS-H	30000	0.1	15 30 75	3.8 3.2 1.8	10.3 ± 1.6	87/47
PS-H	140000	0.1	15 30 75	3.4 3.1 1.4	20.8 ± 2.9	86/47

Note: M_n stands for the number average molecular weight determined by Gel Permeation Chromatography, c (mg/ml) for the concentration in mg/ml, θ for the takeoff angle (measured as the angle between the analyzer normal and the sample plane), d (Å) for the dry film thickness in angstroms from ARXPS, t (Å) for the thickness from LSC data and θ_A / θ_R for the advancing and receding water contact angles (LSC NB#2 p 28 to 32).

Table 5.2 Dry Film Thickness From XPS Data and Contact Angle Data

Samples adsorbed from toluene at 23.0 ± 1.0 °C

Sample	M_n.	c	θ	d (Å)	t (Å)	θ_A / θ_R
PS-COOH	5000	1.0	15	5.0	14.2 ± 2.1	76/24
			30	5.9		
			75	5.9		
PS-COOH	10000	1.0	15	7.4	18.5 ± 2.6	85/41
			30	8.3		
			75	7.3		
PS-COOH	30000	1.0	15	6.5	13.6 ± 2.0	86/50
			30	8.4		
			75	8.2		
PS-COOH	140000	1.0	15	4.4	9.0 ± 1.4	77/29
			30	5.6		
			75	6.0		
PS-OH	5000	1.0	15	3.9	3.2 ± 0.8	74/33
			30	4.8		
			75	4.7		
PS-OH	10000	1.0	15	3.4	3.6 ± 0.9	76/32
			30	4.3		
			75	3.9		
PS-OH	30000	1.0	15	3.8	4.3 ± 0.9	77/30
			30	5.8		
			75	6.1		
PS-OH	140000	1.0	15	2.9		62/16
			30	3.7		
			75	3.9		

Continued, next page

Table 5.2 Continued

Samples adsorbed from toluene at 23.0 ± 1.0 °C

Sample	M_n.	c	θ	d (Å)	t (Å)	θ_A / θ_R
PS-H	5000	1.0	15 30 75	3.5 4.1 4.2	-	49/0
PS-H	10000	1.0	15 30 75	2.9 3.1 2.8	2.2 ± 0.5	65/0
PS-H	30000	1.0	15 30 75	3.2 3.9 3.7	3.6 ± 0.8	73/0
PS-H	140000	1.0	15 30 75	3.1 4.0 3.6	5.8 ± 1.0	67/0

Note: The symbols have the same abbreviation as given in Table 5.1. The contact angle data are from LSC NB#2, p 22.

discrepancy between the LSC and the XPS results may be from the higher densities (a flat 1 g/cm^3 is used for all the samples) used in converting the LSC adsorbances to thickness values (a smaller density in the LSC calculation would lead to smaller film thickness). At lower molecular weights and very high solution concentrations the adsorbances of PS-COOH correspond to almost the same number of molecules per unit area as in amorphous polystyrene indicating that the role of surface roughness cannot be neglected either. Our adsorbance values for polystyrenes and a protonated PS-COOH (~ 12 K) in protonated cyclohexane agree well with those on optically smooth surfaces reported by Granick[32] (for polystyrenes) and Composto[23] (for PS-COOH of DP = 134 from perdeuterated cyclohexane) and this consistency leads us to believe that the effect of surface roughness is minimal.

The contact angle of a water drop on glass immediately after chemical cleaning ranges from 12-14°/0° (θ_A/θ_R). The contact angle increases with storage time under ambient conditions and typical values range from 19-24°/0°. The contact angle of glass on adsorption increases due to the presence of a hydrophobic layer. The value of the advancing angle ranges from 49 to 90° while that for the receding angle from 0 to 78°. The reported contact angle of water on pure polystyrene film from the literature is 89 to 90°/77 to 78° (θ_A/θ_R).[21] The contact angle values obtained after the adsorptions from cyclohexane suggests that we have modified a hydrophilic surface of very good water wettability to a hydrophobic and water repelling surface. Most of the contact angle data after adsorption from toluene indicate that we have prepared surfaces with very little to moderately high hydrophobicity. The water wettability after adsorption depends on the functionallity on the polymer with very little wettability changes recorded for un-functionalized and hydroxyl end-functionalized polystyrenes and significant changes for polystyrenes with a carboxylic acid end-group. These changes can be best understood by comparing the adsorbances and XPS thickness values of PS-H, PS-OH and PS-COOH. PS-H and PS-OH adsorb with very few chains (just above the detection limit) and form very thin films (probably patchy too). Therefore they exhibit intermediate contact angles. The receding contact angle value of 0° recorded for the polystyrenes adsorbed from toluene and the positive adsorbance values confirms that patchy films are formed.

5.4 Conclusions

We conclude from the neutron reflection studies that the segment density distribution of polystyrene with a carboxylic acid end-group is parabolic away from the glass-polymer interface. The mean field theory of Scheutjens and Fleer predicts a monotonically decreasing profile in cyclohexane and a profile with a maximum close to the surface (similar to a parabola) in toluene. Therefore the SF predictions are partly correct. The scaling predictions of de Gennes is not valid for carboxylic acid end-terminated polystyrenes grafted to silicon/glass as evident from the observed neutron reflectivity profiles in toluene and mushrooms are formed at the interface (evident from the graft density and surface excess data). Other theories such as the strong stretching theory of Milner and that of Hesselink predict parabolic profiles. However the assumptions under which the predictions were made are not applicable under our experimental conditions and therefore cannot be compared with the observed results.

The dry film thicknesses calculated from the ARXPS data are lower than that obtained from adsorbance values. Therefore adsorbance values cannot be simply converted to thickness values assuming the same density (1 g/cm) for all the adsorbed layers. In addition it also points out that the roughness of the surface not taken into account in adsorbance determination might explain the lower thicknesses observed by ARXPS measurements.

The water contact angle values suggest that we have modified the surface of glass with a high degree of water wettability to one with a very low degree of water wettability by the adsorption of carboxylic acid-terminated polystyrenes.

5.5 References and Notes

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APPENDICES

APPENDIX A

ADSORPTION OF END-FUNCTIONALIZED POLYSTYRENES BY THIN LAYER CHROMATOGRAPHY

A.1 R_f as a Measure of the Probability of Adsorption

By definition the probability of adsorption "P" is given by,

$$P = \varepsilon^{-\Delta G/kT} = \varepsilon^{\Delta S/k} * \varepsilon^{-\Delta H/kT} \quad ....(1)$$

$$= \exp(\Delta S/k) * \exp\{ -\Delta P * r * (\varepsilon_{23} + \varepsilon_{11} - \varepsilon_{12} - \varepsilon_{13}),$$

where ΔS is the total entropy change of the dilute polymer solution upon adsorption; ΔP is the degree of polymerization; r is the fraction of segments adsorbed; ε_{23} is the enthalpy of each polymer segment-surface contact; ε_{11} is the enthalpy of solvent-solvent contact; ε_{12} is the enthalpy associated with every segment-solvent contact; and ε_{13} is the enthalpy associated with every solvent-surface contact.

By definition R_f = Rate of polymer movement/rate of solvent movement........(2)

Also, $(1-P) = n_1 / (n_1+n_2)$ .... (3) ,

where (1-P) is the probability of residency of the macromolecule in the mobile phase, n_1 is the # of macromolecules in the mobile phase and n_2 is the # of macromolecules in the stationary phase.

From Snyder[11], $R_f = 1/ \{ 1 + (W/V_0) * (n_2/n_1) \}$ ....(4),

where W is the weight of the adsorbent and V_0 is the pore volume accessible to the solvent. W/V_0 is a constant for identical thin layers, and when it is equal to 1,

$$R_f = 1/ \{ 1 + (n_2/n_1) \} = n_1 /(n_1 + n_2) \quad ....(5)$$

Comparing (3) and (5) it can be seen that R_f is a measure of the probability of residency of the macromolecule in the mobile phase.

This can be derived more rigorously, for small probabilities of adsorption,from the Second law of Thermodynamics. From the Second law of Thermodynamics, the distribution coefficient "K" is given by, $K = (n_2/n_1) = \exp(-\Delta G/kT)$ ....(6)

Substituting eq (6) in eq (5), and knowing that the right hand side of eq (6) is "P" (from eq (1)), it follows that for small P's $R_f = (1-P)$.

A.2 TLC in Understanding Thin Film Architecture

Upon end-functionalization of polystyrene its R_f value changes from 1 to 0 suggesting that the end-group is at the interface. That thin film architecture can be understood based on the changing R_f values is illustrated below. Consider the probability of adsorption vs log(mol. Wt)) curve shown in figure 3.10 of Chapter 3. Let P_n be a macromolecule (with a small but finite adsorption potential), where n is the degree of polymerization. Let P_n have a R_f value of 1 in a given good solvent, on a given surface, up to a certain "n". This "n" is represented as Point A in fig. 3.10. Upon suitable organic synthesis let P_n have a end group X for all "n". Let P_n-X have a $R_f = 0$, up to a certain value of "n" say "m", where $m < n$. This "m" is represented as Point "B" in fig. 3.10. An $R_f = 0$ up to "m" implies that the X group is at the interface. This is illustrated for -COOH end-group in polystyrene, from different good solvents, on alumina and silica in this work.

For some $n > m$, say p let $R_f > 0$. Now let P_n have -X group at both the ends by some suitable organic synthesis. If X-P_n-X has an $R_f = 0$, for $n = p$, it follows from the above argument that both the "X" groups are at the interface and hence the desired thin film architecture. Similarly let $R_f > 0$, for X-P_n-X for some $n = q$. If an additional "X" group is designed on a suitable location along the backbone of "P" and if the R_f for such a design is 0, it follows that the polymer is held to the surface by all the three "X" groups. Extending such arguments one can prove that below the molecular weight regime where the polymer spontaneously adsorbs sheerly by the number of contacts it can make with the surface, TLC can be used to show whether a polymer is bound to the surface by a functional group on its backbone, designed to do that job. The region between “A” and “B” in figure 3.10 (Chapter 3) is therefore named as the "Polymer Architecture Region".

A.3 Free Energy Change of a Single Polymer Chain on Adsorption

Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Fleer, G. J. restrict their polymer solution to a lattice consisting of polymer segments (p), and solvent molecules(o) (for details see Chapter 1). Their simplified expression of equation 2 is given as equation 3.

$$\Delta G_{po} / kT = \ln (\phi_1 / (\phi_*) - pr \ln \{(\phi_1)^0 / (\phi_*)^0 \} + (pr-1) \chi_{sc} - pr \{(\chi_s)^{po} - \Delta H_{po} /kT\} \quad ...(3)$$

$\Delta H_{po} /kT$ is the mixing energy per chain and $(\chi_s)^{po}$ is the adsorption energy from the solvent and the rest of the symbols have the same meaning as defined in chapter 1. This equation again, is complicated, and therefore they simplify it cleverly by involving a third component which acts as a displacer (d) by specifically binding to the adsorbent and at equilibrium or critical displacer concentration, polymer segments are displaced to the bulk, i.e $\Delta G_{po} / kT = \Delta G_{do} / kT = 0$. Invoking a series of approximations such as i) the surface excess is a monotonic function of the volume fraction of the segments in the first layer (one-layer approximation), ii) dilute polymer solution (simplified expressions for volume fractions of displacer and solvent), iii) displacer molecules replace polymer segments as well as solvent molecules so that $(\phi_1)^d = 1$ at critical conditions and iv) mathematical simplifications to retain just the exponential terms, they arrive at an expression for the adsorption energy as given in equation 4.

$$(\chi_s)^{po} = (\chi_s)^{do} + \ln (\phi_{crit}) + \chi_{sc} - \lambda_1 \chi^{pd} - (1- \phi_{crit}) (1- \lambda_1) (\chi^{po} - \chi^{pd} - \chi^{do}) \quad ...(4)$$

where the χ^{ij} terms represent the interaction between component i and j, χ_{sc} is the critical adsorption energy given by $-\ln (1- \lambda_1)$ in lattice theories and λ_1 is the fraction of sites in layer i+1 to which a polymer segment in layer i is bound. Cohen Stuart, et al., arrive at reasonably accurate values for the adsorption energy ($(\chi_s)^{po}$) of a polystyrene segment from cyclohexane and carbon tetrachloride using displacers such as benzene and toluene from the solvent strength values that Snyder had derived for small molecular mixtures and the χ^{ij} values available in literature for a given pair i-j.

APPENDIX B

LIQUID SCINTILLATION COUNTING DATA

B.1 Determination of the Efficiency of the Cocktail

The efficiency of the cocktail was determined by the internal standard method.[9, 10] The background radioactivity [cpm(b)] was determined by counting 10 ml each of the cocktail in 20 vials for 10 minutes. 100 µl each of tritiated toluene supplied by New England Nuclear (1 µCi/ml as on 01.02.90) was added to the scintillation vials after the background counting. The counting of each of the vial was performed for 10 minutes [cpm(s)]. The efficiency of the cocktail was determined using equation 1:

{cpm(s) - cpm(b)}/actual disintegrations per min of 100 µl of the standard (1)

The efficiency of the cocktail was determined to be 47.5 ± 1.5 %. The data obtained are presented in Table B.1.

In a typical adsorbance determination a glass slide after adsorption is immersed in the cocktail overnight to ensure complete desorption of the polymer. This can alter the adsorbance calculated from the cpm vs. mass of polystyrene standard curves in two ways. The first one is that different samples (PS-H, PS-OH, PS-COOH, HO-PS-OH, HOOC-PS-COOH) may affect the efficiency of the cocktail by quenching it to different degrees. The second one is concerned with the different degrees of desorption of the samples into the cocktail. A thorough investigation of both the problems were conducted. It was concluded that small amounts (up to several µg's) of polystyrene or carboxylic acid-terminated polystyrenes did not alter the efficiency of the cocktail and that the components of the designed cocktail ensured complete desorption of all the polymers studied. The results of such studies are presented in detail in the following sections.

Table B.1 Determination of the Efficiency of the Cocktail

$V_{standard}$	$dpm_{standard}$	V_c	cpm + r.e	$cpm(s-b)_{ave}$ + r.e + s.e	efficiency %
100µl	201000 ± 5000	10	100689 ±196.7		
100µl	201000 ± 5000	10	101051 ± 197.0		
100µl	201000 ± 5000	10	100211 ± 196.2		
100µl	201000 ± 5000	10	100226 ± 196.2	100417.1 ± 808.8	50 ± 1.5
25µl	50250 ± 1250	10	24427.5 ± 96.9		
25µl	50250 ± 1250	10	24269.5 ± 96.6		
25µl	50250 ± 1250	10	24404.0 ± 96.8		
25µl	50250 ± 1250	10	24099.5 ± 96.2	24233.0 ± 136.4	48 ± 1.0
10µl	20100 ± 500	10	9444.3 ± 60.2		
10µl	20100 ± 500	10	9650.7 ± 60.9		
10µl	20100 ± 500	10	9616.6 ± 60.8		
10µl	20100 ± 500	10	9583.3 ± 60.7	9525.4 ± 181.4	47.5 ± 2

Note: V_c stands for the volume of the cocktail, r.e for the random error and s.e for the systematic error. The data is from LSC notebook #1, p 10 - 11.

B.2 Efficiency of the Cocktail in the Presence of Polystyrene

The efficiency in the presence of a small amount of polystyrene in the cocktail was calculated as follows: A solution of cold (non radioactive) polystyrene (Mn = 4300, 0.105 mg/ml) in toluene was prepared by dissolving 5.25 mg of polystyrene in 50 ml of toluene. A small amount of polystyrene (5 to 200 μl) from the solution was added to each of the vials containing 20 ml of the cocktail and 100 μl of tritiated toluene and they were counted again for 10 min [cpm(s1)]. Each experiment was performed in duplicate. The data are shown in Table B.2. The efficiency of the cocktail in the presence of polystyrene was calculated using equation 2:

$$\{\mathrm{cpm(s1)} - \mathrm{cpm(b)}\} / \text{actual disintegrations per min of 100 μl of the standard} \qquad (2)$$

A plot of the values of the efficiency versus the amount of polystyrene is shown in figure B.1. From this figure it can be inferred that a small amount of polystyrene in the cocktail, has little effect on its efficiency.

B.3 Efficiency of the Cocktail in the Presence of Carboxylic Acid-Terminated Polystyrene

The above experiment was also performed with a radioactive polymer solution of a carboxylic acid-terminated polystyrene (PS-COOH, Mn = 5000) as follows. A solution in toluene was prepared by dissolving 7.7 mg of the polymer in 50 ml of toluene (0.154 mg/ml). This solution (solution 1) was diluted to 0.006 mg/ml by appropriate dilution procedure (solution 2). After a 10 min count for background in 40 scintillation vials, 25 μl of the tritiated toluene standard was added to each of the vials and a 10 min count was performed. Then 5 to 100 μl of solution 2 was added to the above vials. Each addition was performed in quadruplicate. Four blank runs were performed with 10 ml of cocktail and 25 μl of tritiated toluene standard. The efficiency of the cocktail in the presence of the radioactive polymer was determined as in equation 2 and the results are shown in Table B.3.

Table B.2 Efficiency of the Cocktail in the Presence of Polystyrene

No	PS-H (μg)	cpm(s-b) + r.e	cpm$_{avg}$ + r.e + s.e.	efficiency
1	0.525 ± 0.026	98722.5 ± 194.7	101052.0 ± 6622.0	50.3 ± 4.7 %
2	0.525 ± 0.026	103381.4 ± 199.4		
3	1.050 ± 0.053	101130.4 ± 197.1	100994.2 ± 377.7	50.3 ± 0.3 %
4	1.050 ± 0.053	100857.9 ± 197.0		
5	2.100 ± 0.105	101306.4 ± 197.3	101007.7 ± 828.1	50.3 ± 1.7 %
6	2.100 ± 0.105	100708.9 ± 196.7		
7	4.200 ± 0.210	100529.9 ± 196.5	100392.7 ± 380.4	49.9 ± 0.5 %
8	4.200 ± 0.210	100255.4 ± 196.3		
9	6.300 ± 0.315	99441.9 ± 195.5	99651.2 ± 580.0	49.6 ± 0.5 %
10	6.300 ± 0.315	99860.4 ± 195.9		
11	8.400 ± 0.420	99412.9 ± 195.5	99368.2 ± 195.4	49.4 ± 0.4 %
12	8.400 ± 0.420	99323.4 ± 195.3		
13	12.60 ± 0.630	99257.4 ± 195.3	99887.7 ± 1747.0	49.7 ± 2.2 %
14	12.60 ± 0.630	100517.9 ± 196.5		
15	21.0 ± 1.050	100025.9 ± 196.0	99158.9 ± 2403.2	49.3 ± 2.5%
16	21.0 ± 1.050	98291.9 ± 194.3		

Note: The data is from LSC notebook #1, p 12 - 13.

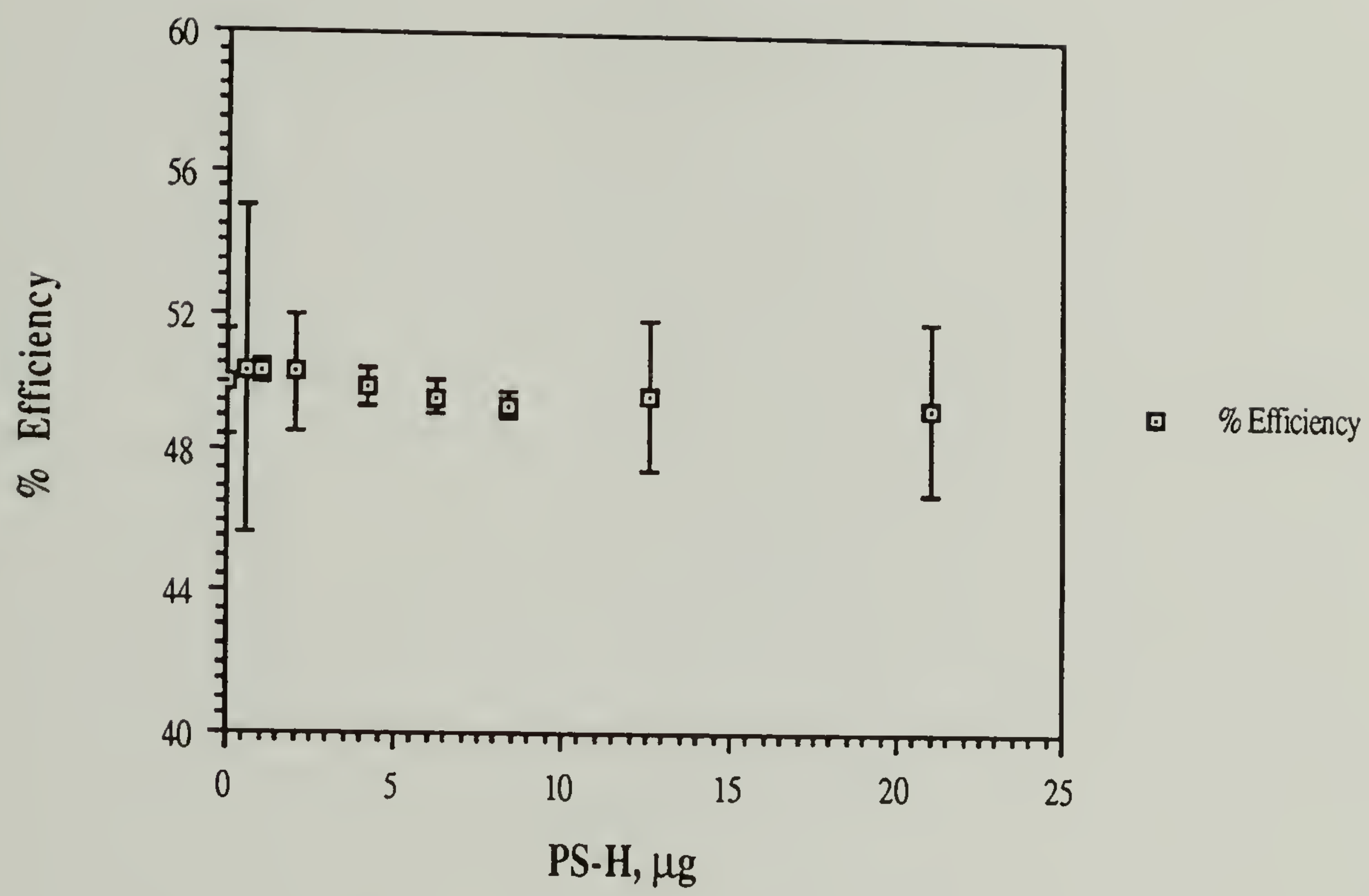

Figure B.1 Efficiency of the Cocktail versus the Amount of Polystyrene in Solution

Table B.3 Efficiency of the Cocktail in the Presence of Carboxylic Acid-Terminated Polystyrene

No	PS-COOH, µg	cpm(s-b) + r.e	Col 3 + 10µl std	efficiency
0	0.0	117.0 ± 6.7	24183.1 ± 295.5	48.1 ± 1.9 %
1	0.077 ± 0.004	83.0 ± 15.5	24085.0 ± 103.1	
2	0.077 ± 0.004	83.0 ± 15.5	24209.5 ± 103.4	
3	0.077 ± 0.004	60.0 ±14.9	24116.5 ± 103.2	
4	0.077 ± 0.004	52.5 ± 14.8	24386.5 ± 103.7	
	avg+ r.e + s.e	69.6 ± 30.9	24199.4 ± 265.5	48.0 ± 1.5 %
5	0.154 ± 0.007	133.5 ± 16.5	24293.5 ± 103.5	
6	0.154 ± 0.007	138.5 ± 16.6	24293.0 ± 103.5	
7	0.154 ± 0.007	127.0 ± 16.4	24122.0 ± 103.2	
8	0.154 ± 0.007	143.0 ± 16.7	24175.5 ± 103.3	
	avg+ r.e + s.e	135.5 ± 16.6	24221.0 ± 175.7	47.9 ± 1.6 %
9	0.308 ± 0.014	278.5 ± 19.0	24579.5 ± 104.1	
10	0.308 ± 0.014	284.5 ± 19.1	24292.0 ± 103.5	
11	0.308 ± 0.014	281.0 ± 19.1	24482.5 ± 103.9	
12	0.308 ± 0.014	287.5 ± 19.2	24550.0 ± 103.8	
		282.9 ± 19.1	24476.0 ± 260.0	48.1 ± 1.8 %
13	0.462 ± 0.021	399.5 ± 20.8	24456.5 ± 103.9	
14	0.462 ± 0.021	410.5 ± 20.9	24665.5 ± 104.3	
15	0.462 ± 0.021	422.5 ± 21.1	24661.5 ± 104.3	
16	0.462 ± 0.021	401.0 ± 20.8	24744.5 ± 104.4	
	avg+ r.e + s.e	408.4 ± 20.8	24632.0 ± 241.2	48.2 ± 1.8 %
17	0.770 ± 0.039	555.0 ± 22.8	24656.0 ± 104.3	
18	0.770 ± 0.039	582.0 ± 23.1	24927.0 ±104.8	
19	0.770 ± 0.039	610.0 ± 23.4	24912.0 ± 104.8	
20	0.770 ± 0.039	606.0 ± 23.4	24932.0 ± 104.8	
	avg+ r.e + s.e	588.3 ± 49.7	24856.8 ± 262.8	48.3 ± 1.9 %
21	1.540 ± 0.070	1151.0 ± 28.8	25414.0 ± 105.7	
22	1.540 ± 0.070	1176.0 ± 29.0	25471.0 ± 105.8	
23	1.540 ± 0.070	1105.0 ± 28.4	25446.5 ± 105.8	
24	1.540 ± 0.070	1163.5 ± 28.9	25475.0 ± 105.9	
	avg+ r.e + s.e	1148.9 ± 60.7	25451.6 ± 105.8	48.4 ± 1.5%
25	3.080 ± 0.140	2574.5 ± 38.9	26735.5 ± 108.3	
26	3.080 ± 0.140	2567.0 ± 38.8	26853.0 ± 108.5	
27	3.080 ± 0.140	2555.0 ± 38.7	26724.0 ± 108.2	
28	3.080 ± 0.140	2760.0 ± 39.9	26957.0 ± 108.7	
	avg+ r.e + s.e	2614.1 ± 191.3	26817.4 ± 222.0	48.2 ± 2.0 %

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Table B.3 Continued

No	PS-COOH, μg	cpm(s-b) + r.e	Col 3 + 10μl std	efficiency
29	4.620 ± 0.210	3713.0 ± 45.1	27843.5 ± 110.3	
30	4.620 ± 0.210	3726.0 ± 45.1	28293.5 ± 111.2	
31	4.620 ± 0.210	3803.0 ± 45.5	27780.5 ± 110.2	
32	4.620 ± 0.210	3695.5 ± 45.0	27757.0 ± 110.2	
	avg+ r.e + s.e	3634.4 ± 93.0	27918.6 ± 501.7	48.1 ± 2.5 %
33	6.160 ± 0.280	5029.5 ± 51.2	28997.0 ± 112.5	
34	6.160 ± 0.280	5088.5 ± 51.4	29418.5 ± 113.2	
35	6.160 ± 0.280	5094.5 ± 51.4	28989.5 ± 112.4	
36	6.160 ± 0.280	5097.0 ± 51.5	29308.0 ± 113.0	
	avg+ r.e + s.e	5077.4 ± 69.7	29178.3 ± 428.0	48.0 ± 2.2 %

Note: The data is from LSC notebook #1, p 14 - 26.

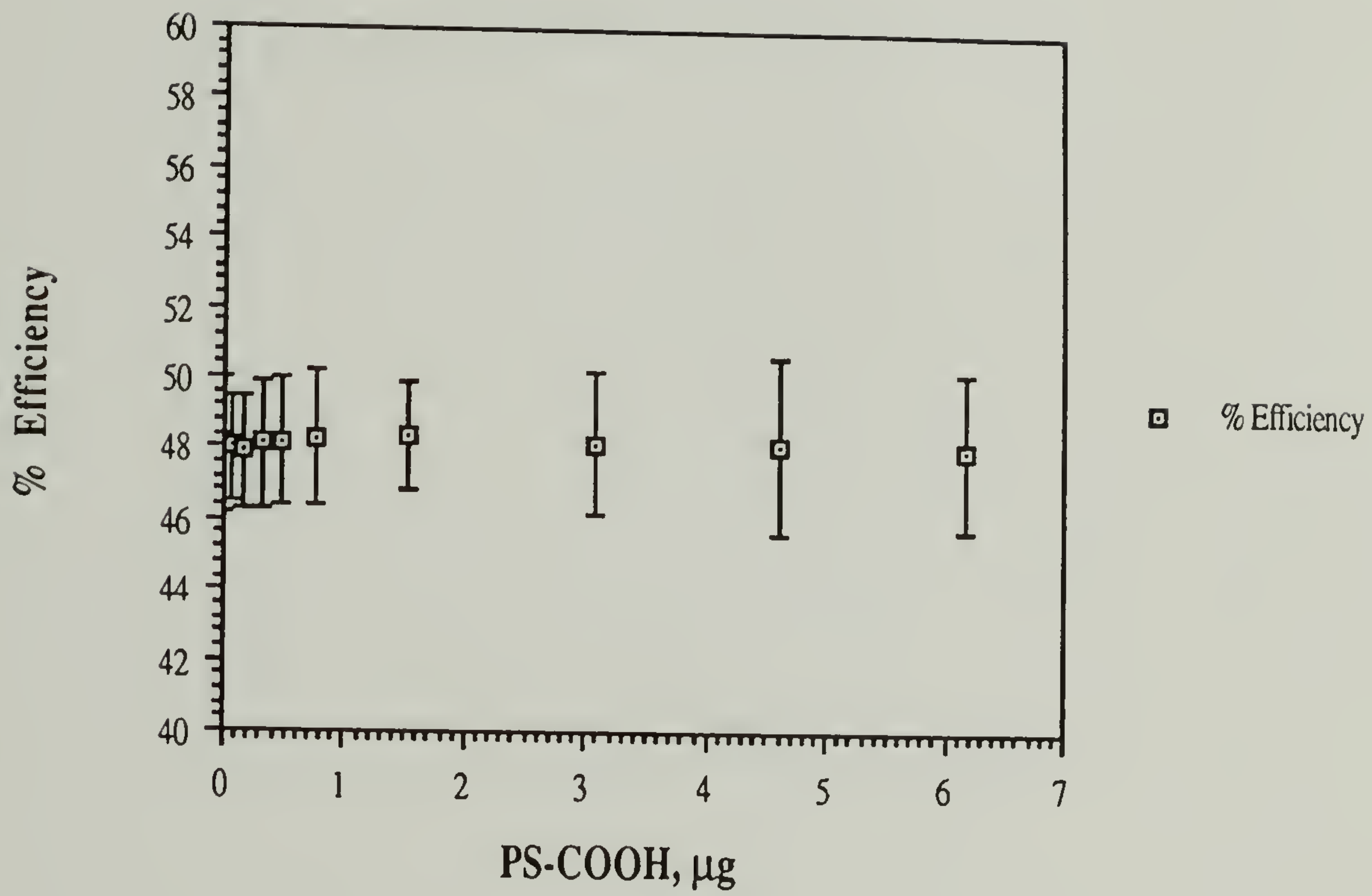


Figure B.2 Efficiency of the Cocktail versus Amount of Tritium-Labeled Carboxylic Acid-Terminated Polystyrene in Solution

A plot of the values of the efficiency versus the amount of carboxylic acid-terminated polystyrene is shown in figure B.2. From this figure it can be inferred that a small amount of carboxylic acid-terminated polystyrene in the cocktail, has little effect on its efficiency.

B.4 Efficiency of the Cocktail in the Presence of a Thin Film of Carboxylic Acid-Terminated Polystyrene on a surface (AgO/Ag/glass)

The experiments were performed as follows: two to three drops of methylene chloride was placed on silver/glass slides, (1.5 cm x 1.3 cm) lying on a relatively flat surface, using a 2 ml Pasteur pipette. 5 to 25 µl of a dilute polymer solution (0.1 and 0.01 mg/ml, 5K) was spotted on to the glass slides carefully. The solvent was allowed to evaporate over a period of 24 h after which the slides were immersed in 10 ml of the cocktail and were counted after 24 h.

The samples were counted for ten minutes [cpm(s)]. The data are shown in Table B.4. A plot of the efficiency versus the amount of radioactive polymer on a silver coated glass slide is shown in figure B.3. From the data and the figure it can be inferred that neither a small amount of polystyrene on a surface nor the physical presence of a glass slide affects the efficiency of the cocktail.

Table B.4 Efficiency of the Cocktail in the Presence of a Thin Film of Tritium-Labeled Carboxylic Acid-Terminated Polystyrene on AgO/Ag/Glass

No	PS-COOH, µg	cpm(s-b) + r.e [PS-COOH (µg) + 10 µl std]	efficiency
0	0.0	9566.1 ± 177.7	
1	0.0308 ± 0.0015	9406.9 ± 67.7	47.6 ± 2.1 %
2	0.0308 ± 0.0015	9325.3 ± 67.5	
3	0.0308 ± 0.0015	9593.9 ± 68.3	
4	0.0308 ± 0.0015	9722.2 ± 67.7	
	avg + r.e + s.e	9512.1 ± 352.1	
5	0.0616 ± 0.003	9506.4 ± 66.7	47.3 ± 3.0 %
6	0.0616 ± 0.003	9642.2 ± 67.3	
7	0.0616 ± 0.003	9232.2 ± 66.5	
8	0.0616 ± 0.003	9690.3 ± 67.2	
	avg + r.e + s.e	9517.8 ± 403.2	
9	0.0924 ± 0.0045	9254.7 ± 66.3	47.4 ± 3.2
10	0.0924 ± 0.0045	9709.7 ± 68.1	
11	0.0924 ± 0.0045	9373.5 ± 67.0	
12	0.0924 ± 0.0045	9601.9 ± 67.9	
	avg + r.e + s.e	9485.0 ± 407.4	
13	0.1232 ± 0.006	9306.8 ± 68.3	47.2 ± 3.3
14	0.1232 ± 0.006	9539.4 ± 68.5	
15	0.1232 ± 0.006	9364.2± 67.9	
16	0.1232 ± 0.006	9731.8 ± 69.1	
	avg + r.e + s.e	9485.6 ± 375.7	
17	0.1848 ± 0.009	9267.5 ± 69.0	47.2 ± 3.1
18	0.1848 ± 0.009	9749.7 ± 69.0	
19	0.1848 ± 0.009	9487.4 ± 69.2	
20	0.1848 ± 0.009	9575.0 ± 70.0	
	avg + r.e + s.e	9519.9 ± 393.0	
21	0.2464 ± 0.012	9467.2 ± 70.9	47.4 ± 3.2
22	0.2464 ± 0.012	8807.6 ± 68.3	
23	0.2464 ± 0.012	8929.3± 68.6	
24	0.2464 ± 0.012	9154.8 ± 69.8	
	avg + r.e + s.e	9089.7 ± 568.1	
25	0.3080 ± 0.015	9314.2 ± 71.5	45.2 ± 4.1 %
26	0.3080 ± 0.015	9689.1 ± 72.4	
27	0.3080 ± 0.015	10005.2 ± 73.4	
28	0.3080 ± 0.015	9127.4 ± 70.6	
	avg + r.e + s.e	9534.0 ± 767.3	
29	0.4928 ± 0.024	9388.4 ± 74.8	47.4 ± 5.2 %
30	0.4928 ± 0.024	9600.2 ± 75.4	
31	0.4928 ± 0.024	9514.0 ± 74.7	
32	0.4928 ± 0.024	9711.8 ± 75.7	
	avg + r.e + s.e	9553.6 ± 267.9	47.5 ± 2.6 %

Note: The data is from LSC notebook #1, p 27 - 28.

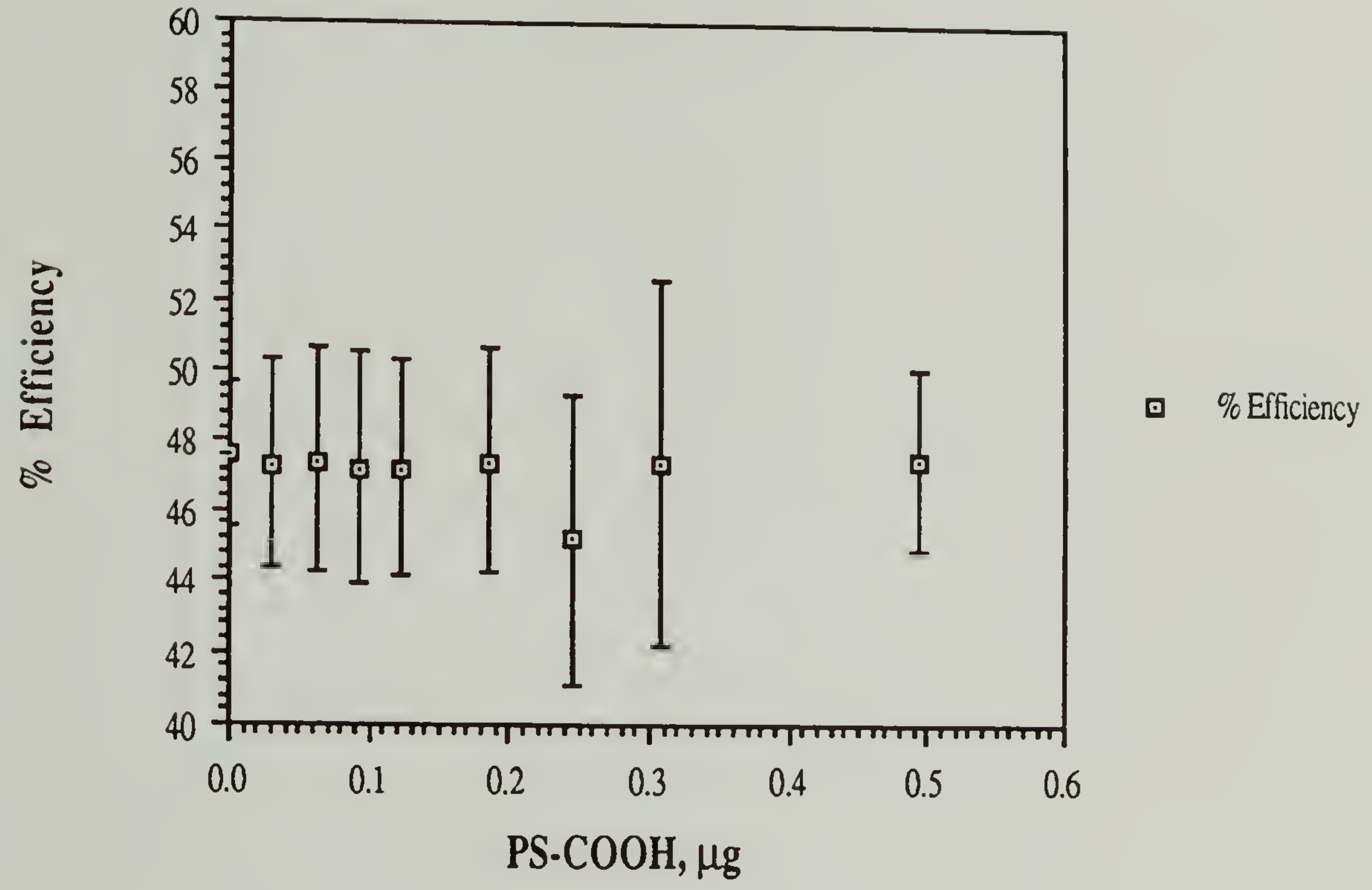


Figure B.3 Efficiency of the Cocktail versus Amount of Tritium-labeled Carboxylic Acid-Terminated Polystyrene on AgO/Ag/glass

B.5 Calibration Curves (cpm vs amount of radiolabeled polymer)

The desorption of the adsorbed polystyrenes from the glass and silver coated glass slides by the cocktail was evaluated as follows. A small amount of radioactive polymer was added to ten ml of the cocktail in one experiment. A similar amount of radioactive polymer was cast on glass/silver slides from a dilute solution in an another experiment. The cpm obtained from the above two samples in the presence of 10 ml of cocktail, 24 h after the addition of the cocktail were compared . The inherent assumption in this evaluation is that polymers adsorb in a flat conformation when cast as a film from a dilute solution and therefore if the cocktail was not effective in the complete desorption of the adsorbed chains one would expect that to show up as a significant difference in the cpms obtained. All the experiments were performed in quadruplicate with radio-labelled polymers of different molecular weights.

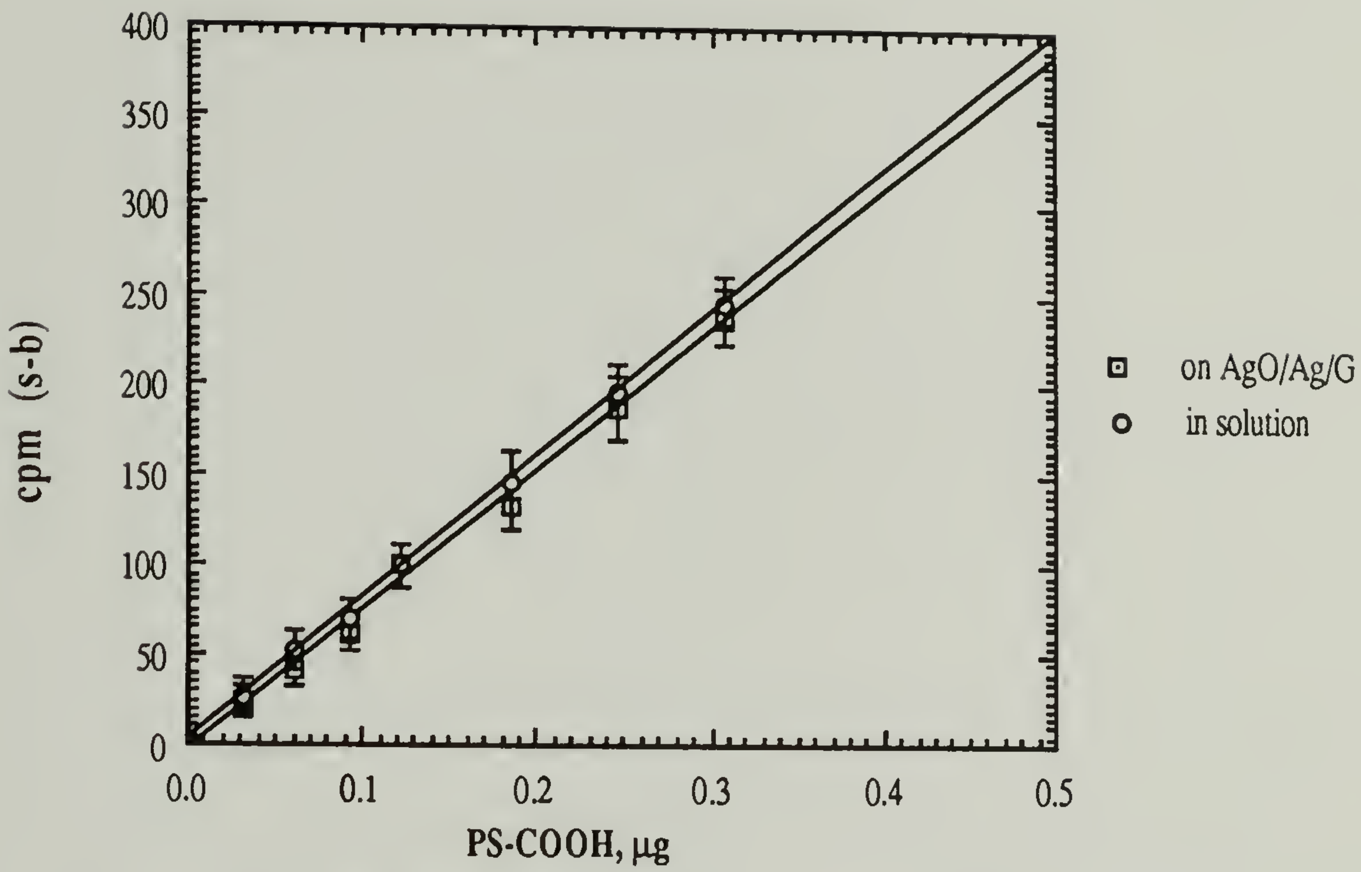
The results are shown in Tables B.5 to B.12. The plots of cpm(s-b) vs the amount of a polymer (different molecular weights) in solution as well as on silver/glass substrates are shown in figures B.4 to B.11. A linear curve fit analysis was performed using cricket graph software (Microsoft Corp.). The resulting equations obtained for the eight polymers used, on glass (silver) surface are shown in Table B.13.

These data illustrate that more than 95% of the polymer, cast as a film, is extracted in to the cocktail. The equations in Table B.5.9, were used in calculating the amount adsorbed, from the cpm obtained from a given glass slide.

Table B.5 Counts Per Minute Obtained from Different Amounts of Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on AgO/Ag/Glass; M_n = 5000

No	PS-COOH, µg	cpm(s-b)$_{\text{Ago/Ag/G}}$ + r.e	cpm(s-b)$_{\text{solution}}$ + r.e
1	0.0308 ± 0.0015	24.3 ± 9.3	23.0 ± 9.3
2	0.0308 ± 0.0015	23.0 ± 9.3	29.6 ± 9.9
3	0.0308 ± 0.0015	23.6 ± 9.3	28.0 ± 9.6
4	0.0308 ± 0.0015		28.6 ± 9.6
	cpm$_{avg}$ + r.e + s.e	24.0 ± 9.3	27.3 ± 9.6
5	0.0616 ± 0.003	44.1 ± 9.9	55.7 ± 10.3
6	0.0616 ± 0.003	43.1 ± 9.9	55.2 ± 10.3
7	0.0616 ± 0.003	39.2 ± 9.8	49.8 ± 10.1
8	0.0616 ± 0.003	42.0 ± 9.8	50.2 ± 10.1
	cpm$_{avg}$ + r.e + s.e	42.1 ± 9.8	52.7 ± 10.2
9	0.0924 ± 0.0045	62.0 ± 10.5	62.0 ± 10.5
10	0.0924 ± 0.0045	66.2 ± 10.7	74.2 ± 10.9
11	0.0924 ± 0.0045	64.9 ± 10.6	68.9 ± 10.7
12	0.0924 ± 0.0045	54.9 ± 10.2	72.8 ± 10.8
	cpm$_{avg}$ + r.e + s.e	62.0 ± 10.5	69.5 ± 10.7
13	0.1232 ± 0.0060	99.1 ± 11.5	97.1 ± 11.5
14	0.1232 ± 0.0060	103.1 ± 11.6	99.4 ± 11.5
15	0.1232 ± 0.0060	97.1 ± 11.5	99.8 ± 11.5
16	0.1232 ± 0.0060	99.4 ± 11.5	103.0 ± 11.6
	cpm$_{avg}$ + r.e + s.e	99.7 ± 11.5	99.8 ± 11.5
17	0.1848 ± 0.0090	132.5 ± 12.4	152.6 ± 12.8
18	0.1848 ± 0.0090	133.6 ± 12.4	144.3 ± 12.6
19	0.1848 ± 0.0090	136.1 ± 12.4	135.1 ± 12.4
20	0.1848 ± 0.0090	130.3 ± 12.3	153.0 ± 12.8
	cpm$_{avg}$ + r.e + s.e	133.1 ± 12.4	146.3 ± 16.6
21	0.2464 ± 0.0012	183.8 ± 13.5	197.4 ± 13.8
22	0.2464 ± 0.0012	181.8 ± 13.5	201.6 ± 14.0
23	0.2464 ± 0.0012	198.9 ± 13.8	195.1 ± 13.8
24	0.2464 ± 0.0012	187.8 ± 13.6	194.9 ± 13.8
	cpm$_{avg}$ + r.e + s.e	187.8 ± 17.2	197.4 ± 13.8
25	0.3080 ± 0.0150	238.3 ± 14.3	255.6 ± 14.8
26	0.3080 ± 0.0150	233.2 ± 14.4	243.3 ± 14.6
27	0.3080 ± 0.0150	237.0 ± 14.4	242.2 ± 14.6
28	0.3080 ± 0.0150	242.7 ± 14.6	241.2 ± 14.6
	cpm$_{avg}$ + r.e + s.e	238.1 ± 14.6	245.6 ± 14.7

Note: r.e stands for random error in the counts and s.e is the systematic error encountered while performing the experiments. The data is from LSC notebook #1, p 29 - 31.



$y = -3.79 + 777.63x \quad R^2 = 0.996$ .....(1) on AgO/Ag/Glass

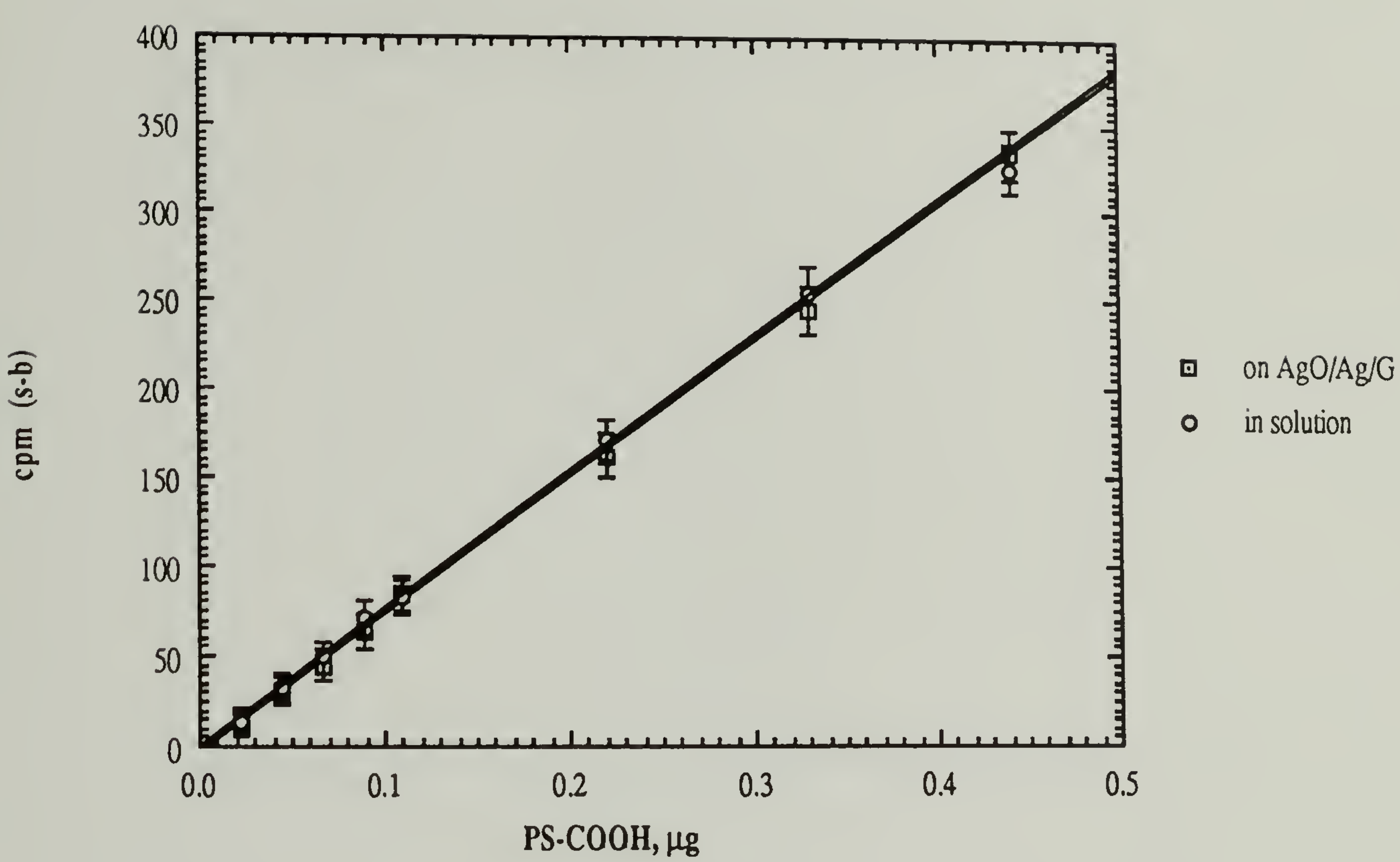
$y = 1.46 + 791.10x \quad R^2 = 0.999$ .....(2) in solution

Figure B.4 cpm vs Amount of Carboxylic Acid-Terminated Polystyrene. Number average molecular weight - 5000

Table B.6 Counts Per Minute Obtained from Different Amounts of Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on AgO/Ag/Glass; M_n = 10000

No	PS-COOH, μg	cpm(s-b)$_{\text{Ago/Ag/G}}$ + r.e	cpm(s-b)$_{\text{solution}}$ + r.e
1	0.0220 ± 0.0012	13.1 ± 7.3	12.8 ± 7.3
2	0.0220 ± 0.0012	11.9 ± 7.2	13.9 ± 7.3
3	0.0220 ± 0.0012	15.4 ± 7.4	14.6 ± 7.4
4	0.0220 ± 0.0012	10.0 ± 7.1	15.1 ± 7.4
	cpm$_{avg}$ + r.e + s.e	12.6 ± 7.3	14.1 ± 7.3
5	0.0440 ± 0.0024	34.0 ± 8.2	29.7 ± 8.1
6	0.0440 ± 0.0024	29.1 ± 8.1	30.8 ± 8.1
7	0.0440 ± 0.0024	27.5 ± 8.0	36.3 ± 8.2
8	0.0440 ± 0.0024	32.6 ± 8.1	32.4 ± 8.1
	cpm$_{avg}$ + r.e + s.e	30.8 ± 8.1	32.3 ± 8.1
9	0.0660 ± 0.0036	41.9 ± 8.4	49.2 ± 8.8
10	0.0660 ± 0.0036	45.1 ± 8.6	43.1 ± 8.5
11	0.0660 ± 0.0036	48.7 ± 8.7	46.8 ± 8.7
12	0.0660 ± 0.0036	43.5 ± 8.5	45.3 ± 8.6
	cpm$_{avg}$ + r.e + s.e	44.8 ± 8.6	46.1 ± 8.6
13	0.0880 ± 0.0048	64.8 ± 9.2	56.0 ± 9.1
14	0.0880 ± 0.0048	58.1 ± 9.1	59.2 ± 9.2
15	0.0880 ± 0.0048	66.4 ± 9.2	63.4 ± 9.3
16	0.0880 ± 0.0048	63.1 ± 9.2	65.4 ± 9.3
	cpm$_{avg}$ + r.e + s.e	63.1 ± 9.2	61.0 ± 9.2
17	0.1100 ± 0.0060	85.1 ± 9.9	78.4 ± 9.7
18	0.1100 ± 0.0060	81.9 ± 9.8	83.5 ± 9.9
19	0.1100 ± 0.0060	83.6 ± 9.9	84.1 ± 9.9
20	0.1100 ± 0.0060	86.2 ± 9.9	85.2 ± 9.9
	cpm$_{avg}$ + r.e + s.e	84.2 ± 9.9	82.8 ± 9.8
21	0.2200 ± 0.0120	156.3 ± 11.8	177.8 ± 12.3
22	0.2200 ± 0.0120	159.8 ± 11.9	171.4 ± 12.1
23	0.2200 ± 0.0120	166.2 ± 12.0	166.6 ± 12.0
24	0.2200 ± 0.0120	167.7 ± 12.0	170.2 ± 12.1
	cpm$_{avg}$ + r.e + s.e	162.5 ± 11.9	171.5 ± 12.1
25	0.4400 ± 0.0240	338.5 ± 15.2	334.1 ± 15.1
26	0.4400 ± 0.0240	328.9 ± 15.0	317.7 ± 14.8
	cpm$_{avg}$ + r.e + s.e	333.7 ± 15.1	325.9 ± 15.0
27	2.2000 ± 0.1200	1684.9 ± 29.0	1691.8 ± 29.0
28	2.2000 ± 0.1200	1670.5 ± 28.8	1695.0 ± 29.0
	cpm$_{avg}$ + r.e + s.e	1677.7 ± 28.9	1693.4 ± 29.0
29	4.4000 ± 0.2400	3341.2 ± 39.3	3329.8 ± 39.2
30	4.4000 ± 0.2400	3378.0 ± 39.5	3368.4 ± 39.4
	cpm$_{avg}$ + r.e + s.e	3359.6 ± 39.4	3349.1 ± 39.3

Note: The data is from LSC notebook #1, p 32 - 33.



y = - 4.2 + 764.5x R^2 = 1.000 ......(1) on AgO/Ag/Glass

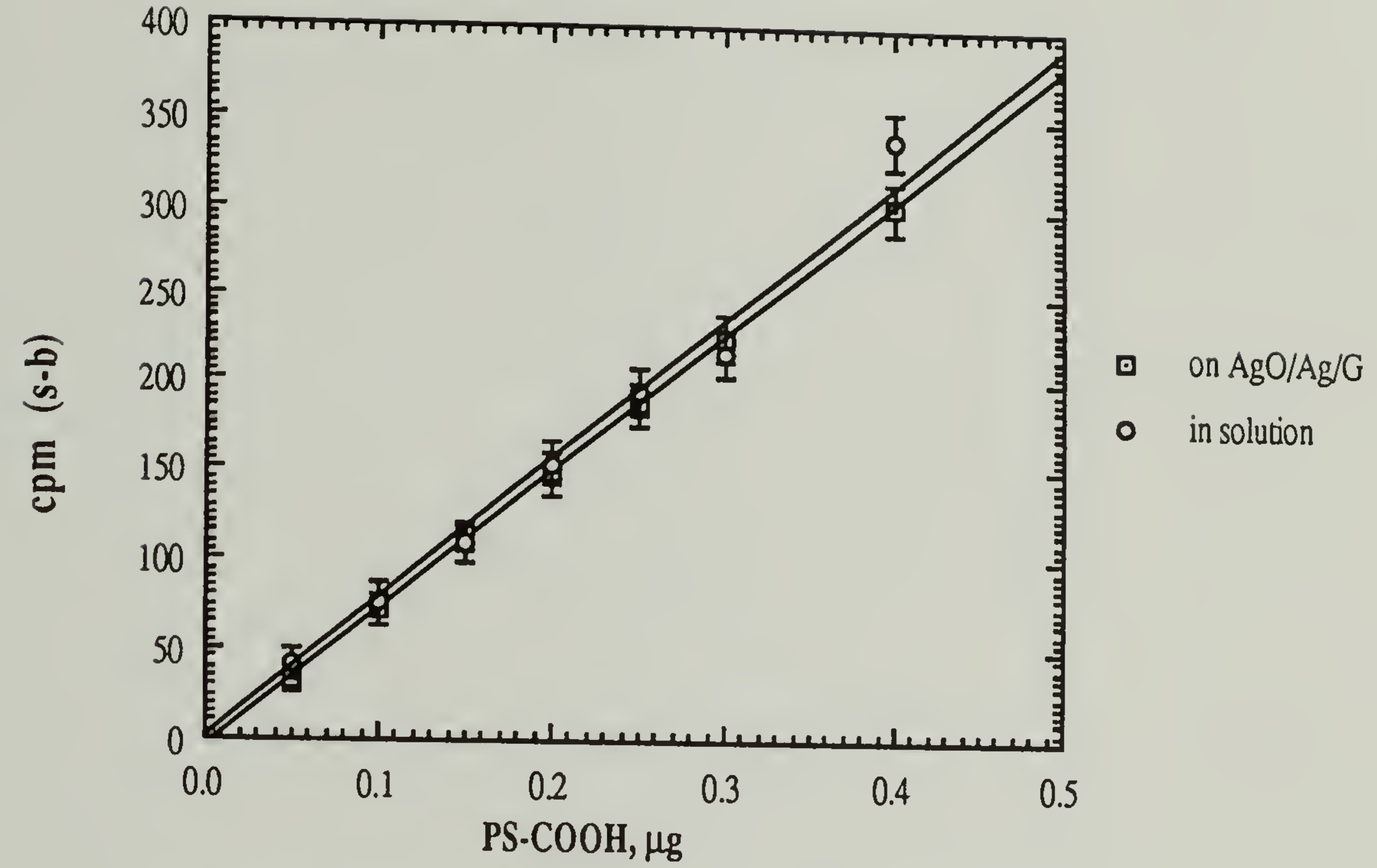
y = - 1.3 + 768.6x R^2 = 1.000 .....(2) in solution

Figure B.5 cpm vs Amount of Carboxylic Acid-Terminated Polystyrene. Number average molecular weight - 10000

Table B.7 Counts Per Minute Obtained from Different Amounts of Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on AgO/Ag/Glass; M_n = 30000

No	PS-COOH, µg	$cpm_{(s-b)Ago/Ag/G}$ + r.e	$cpm_{(s-b)solution}$ + r.e
1	0.050 ± 0.004	34.6 ± 8.2	42.9 ± 8.5
2	0.050 ± 0.004	36.9.± 8.3	41.4 ± 8.4
3	0.050 ± 0.004	29.3 ± 8.1	41.3 ± 8.4
	cpm_{avg} + r.e + s.e	33.6 ± 8.2	41.9 ± 8.4
4	0.100 ± 0.008	72.0 ± 9.5	74.2 ± 9.5
5	0.100 ± 0.008	73.4 ± 9.5	79.6 ± 9.6
6	0.100 ± 0.008	70.1 ± 9.5	77.4 ± 9.6
	cpm_{avg} + r.e + s.e	71.8 ± 9.5	77.1 ± 9.6
7	0.150 ± 0.012	101.6 ± 10.4	110.1 ± 10.6
8	0.150 ± 0.012	107.9 ± 10.5	106.8 ± 10.5
9	0.150 ± 0.012	120.2 ± 10.8	108.6 ± 10.5
	cpm_{avg} + r.e + s.e	109.9 ± 18.5	108.5 ± 10.5
10	0.200 ± 0.016	149.1 ± 11.6	150.4 ± 11.6
11	0.200 ± 0.016	147.7 ± 11.6	163.0 ± 11.9
12	0.200 ± 0.016	147.5 ± 11.6	148.3 ± 11.6
	cpm_{avg} + r.e + s.e	148.1 ± 11.6	153.9 ± 15.6
13	0.250 ± 0.020	178.1 ± 12.2	199.7 ± 12.6
14	0.250 ± 0.020	191.3 ± 12.5	191.3 ± 12.6
15	0.250 ± 0.020	189.2 ± 12.5	194.6 ± 12.6
	cpm_{avg} + r.e + s.e	186.2 ± 13.9	195.2 ± 12.6
16	0.300 ± 0.024	221.8 ± 13.1	216.6 ± 13.0
17	0.300 ± 0.024	228.6 ± 13.2	210.8 ± 12.9
18	0.300 ± 0.024	222.8 ± 13.1	219.4 ± 13.1
	cpm_{avg} + r.e + s.e	224.4 ± 13.2	215.6 ± 13.0
19	0.400 ± 0.032	294.9.± 14.5	344.2 ± 15.3
20	0.400 ± 0.032	309.1 ± 14.7	332.9 ± 15.1
21	0.400 ± 0.032	298.1 ± 14.5	337.8 ± 15.2
	cpm_{avg} + r.e + s.e	300.7 ± 14.6	338.3 ± 15.2
22	0.800 ± 0.064	616.2 ± 19.0	629.5 ± 19.1
23	0.800 ± 0.064	595.4 ± 18.8	602.9 ± 18.8
	cpm_{avg} + r.e + s.e	605.8 ± 28.8	616.2 ± 36.9
24	1.200 ± 0.096	899.3 ± 22.1	949.7 ± 22.7
25	1.200 ± 0.096	922.7 ± 22.4	919.5 ± 22.4
	cpm_{avg} + r.e + s.e	911.0 ± 32.4	934.6± 41.9

Note: The data is from LSC notebook #1, p 37 - 38.



$y = -4.50 + 762.92x$ $R^2 = 1.000$ .....(1) on AgO/Ag/Glass

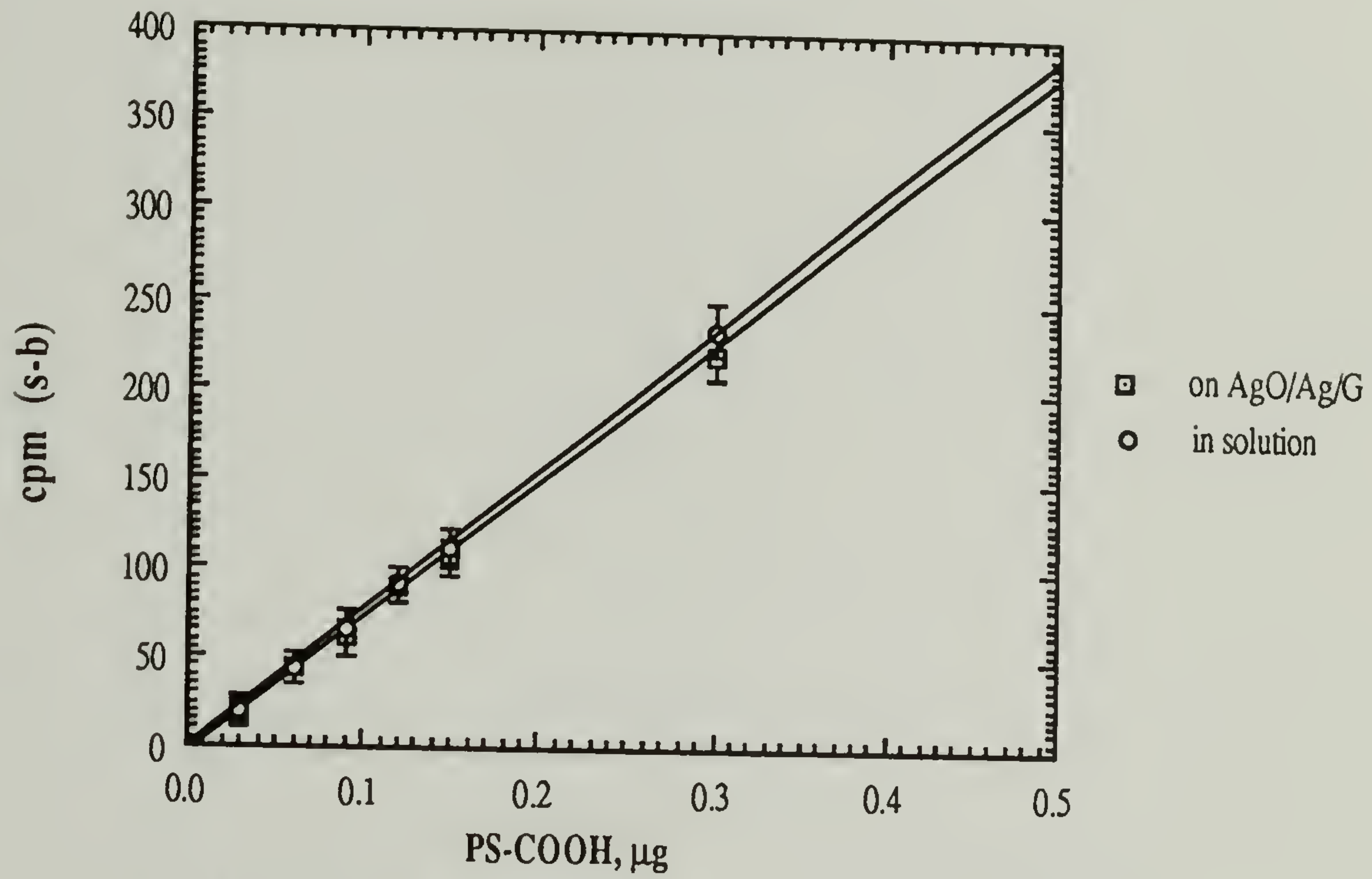
$y = -0.81 + 779.31x$ $R^2 = 0.998$ .....(2) in solution

Figure B.6 cpm vs Amount of Carboxylic Acid-Terminated Polystyrene. Number average molecular weight - 30000

Table B.8 Counts Per Minute Obtained from Different Amounts of Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on AgO/Ag/Glass; M_n = 140000

No	PS-COOH, μg	cpm(s-b)$_{\text{Ago/Ag/G}}$ + r.e	cpm(s-b)$_{\text{solution}}$ + r.e
1	0.030 ± 0.0015	18.7 ± 7.5	19.1 ± 7.5
2	0.030 ± 0.0015	21.2.± 7.7	23.0 ± 7.7
3	0.030 ± 0.0015	21.3 ± 7.7	16.7 ± 7.5
	cpm$_{avg}$ + r.e + s.e	20.4 ± 7.6	19.6 ± 7.6
4	0.060 ± 0.003	39.8 ± 8.5	45.6 ± 8.6
5	0.060 ± 0.003	47.1 ± 8.7	43.1 ± 8.5
6	0.060 ± 0.003	46.6 ± 8.7	43.0 ± 8.5
	cpm$_{avg}$ + r.e + s.e	44.5 ± 8.6	43.9 ± 8.6
7	0.090 ± 0.0045	66.1 ± 9.2	72.0 ± 9.4
8	0.090 ± 0.0045	58.7 ± 9.1	61.9 ± 9.2
9	0.090 ± 0.0045	55.8 ± 9.0	65.3 ± 9.3
	cpm$_{avg}$ + r.e + s.e	60.2 ± 9.1	66.4 ± 9.3
10	0.120± 0.0060	85.6 ± 10.0	84.9 ± 10.0
11	0.120 ± 0.060	92.3 ± 10.1	91.6 ± 10.1
12	0.120 ± 0.0060	93.3 ± 10.1	98.0 ± 10.3
	cpm$_{avg}$ + r.e + s.e	90.4 ± 10.1	91.5 ± 10.1
13	0.150 ± 0.0075	103.9 ± 10.4	118.7 ± 10.7
14	0.150 ± 0.0075	108.2 ± 10.5	109.2 ± 10.5
15	0.150 ± 0.0075	106.2 ± 10.5	108.4 ± 10.5
	cpm$_{avg}$ + r.e + s.e	106.1 ± 10.5	112.1 ± 10.6
16	0.300 ± 0.015	218.5 ± 13.0	241.4 ± 13.5
17	0.300 ± 0.015	227.1 ± 13.2	230.8 ± 13.4
18	0.300 ± 0.015	216.5 ± 13.0	232.2 ± 13.4
	cpm$_{avg}$ + r.e + s.e	220.7 ± 13.1	234.8 ± 13.4
19	0.600 ± 0.030	463.2.± 17.0	469.4 ± 17.1
20	0.600 ± 0.030	438.1 ± 16.6	473.1 ± 17.2
21	0.600 ± 0.030	445.7 ± 16.8	459.1 ± 17.0
	cpm$_{avg}$ + r.e + s.e	449.0 ± 25.2	467.2 ± 17.1

Note: The data is from LSC notebook #1, p 39 - 41.



y = - 4.5 + 760.0x R^2 = 1.000 .....(1) on AgO/Ag/Glass

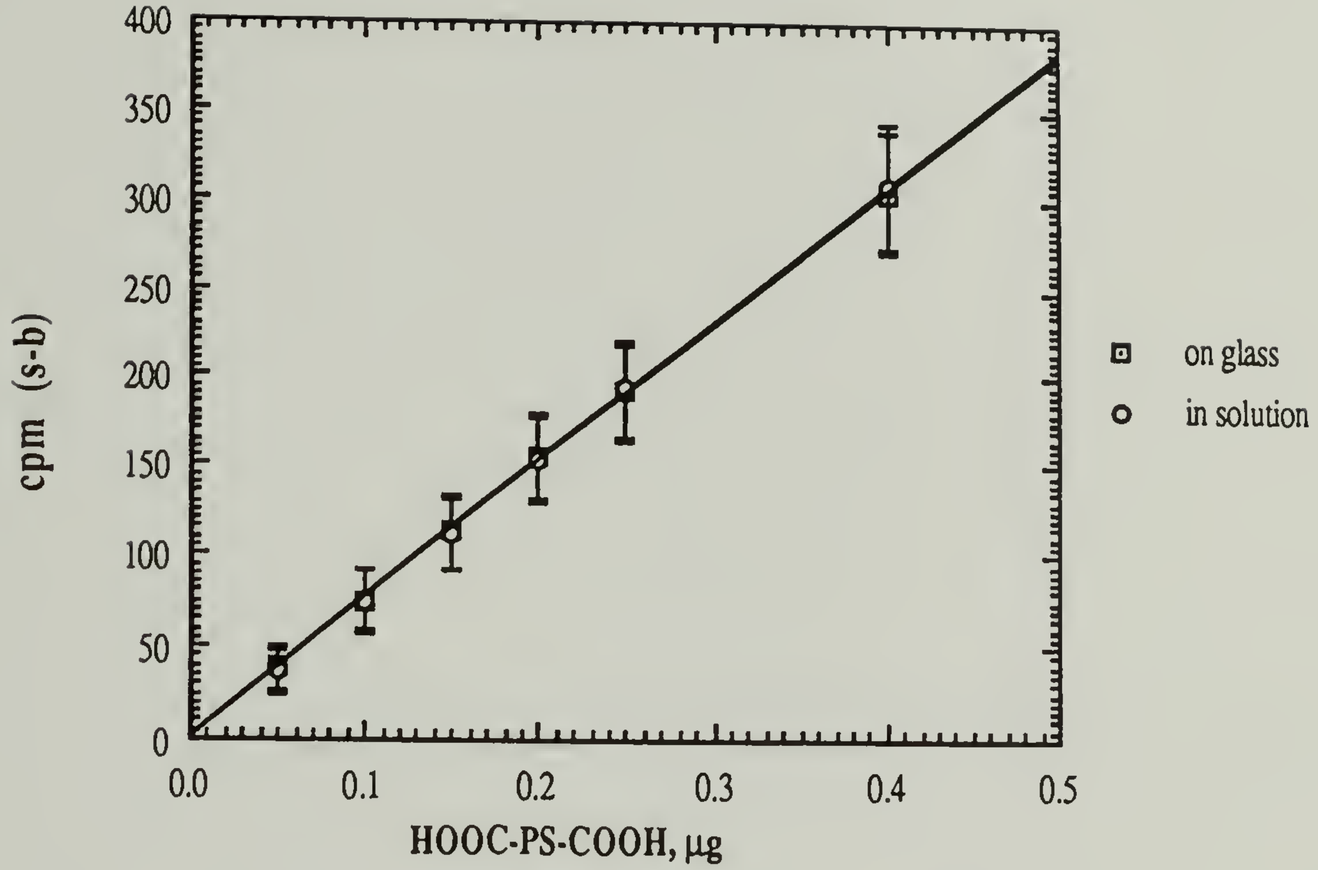
y = - 2.1 + 774.93x R^2 = 1.000 .....(2) in solution

Figure B.7 cpm vs Amount of Carboxylic Acid-Terminated Polystyrene. Number average molecular weight - 140000

Table B.9 Counts Per Minute Obtained from Different Amounts of Di-Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on Glass; M_n = 10000

No	PS-COOH, µg	$cpm(s\text{-}b)_G$ + r.e	$cpm(s\text{-}b)_{solution}$ + r.e
1	0.050 ± 0.005	30.6 ± 7.0	37.3 ± 7.3
2	0.050 ± 0.005	47.0 ± 7.7	40.1 ± 7.4
3	0.050 ± 0.005		33.1 ± 7.2
	cpm_{avg} + r.e + s.e	38.8 ± 22.7	36.8 ± 7.3
4	0.100 ± 0.010	72.7 ± 8.6	79.7 ± 8.8
5	0.100 ± 0.010	75.1 ± 8.7	75.9 ± 8.7
6	0.100 ± 0.010		69.3 ± 8.5
	cpm_{avg} + r.e + s.e	73.9 ± 8.6	75.0 ± 10.3
7	0.150 ± 0.015	112.1 ± 9.8	111.5 ± 9.8
8	0.150 ± 0.015	113.3 ± 9.8	118.1 ± 9.9
9	0.150 ± 0.015		104.5 ± 9.6
	cpm_{avg} + r.e + s.e		111.4 ± 13.3
10	0.200 ± 0.020	151.5 ± 10.8	151.3 ± 10.8
11	0.200 ± 0.020	158.2 ± 10.9	157.8 ± 10.9
12	0.200 ± 0.020		149.9 ± 10.8
	cpm_{avg} + r.e + s.e	154.9 ± 10.8	153.0 ± 10.8
13	0.250 ± 0.025	201.5 ± 11.9	205.2 ± 12.0
14	0.250 ± 0.025	181.4 ± 11.5	185.4 ± 11.6
15	0.250 ± 0.025		188.1 ± 11.6
	cpm_{avg} + r.e + s.e	191.5 ± 27.9	192.9 ± 21.0
16	0.400 ± 0.040	291.8 ± 13.6	311.1 ± 14.0
17	0.400 ± 0.040	318.0 ± 14.1	304.5 ± 13.8
	cpm_{avg} + r.e + s.e	304.9 ± 36.3	307.8 ± 13.9
18	4.000 ± 0.400		3002.7 ± 36.8
19	4.000 ± 0.400		3046.8 ± 37.0
20	4.000 ± 0.400		3082.4 ± 37.2
	cpm_{avg} + r.e + s.e		3044.0 ± 78.3

Note: The data is from synthesis alone notebook #4, p 110 - 111.



y = - 0.30 + 764.6x R^2 = 1.000 .....(1) on glass

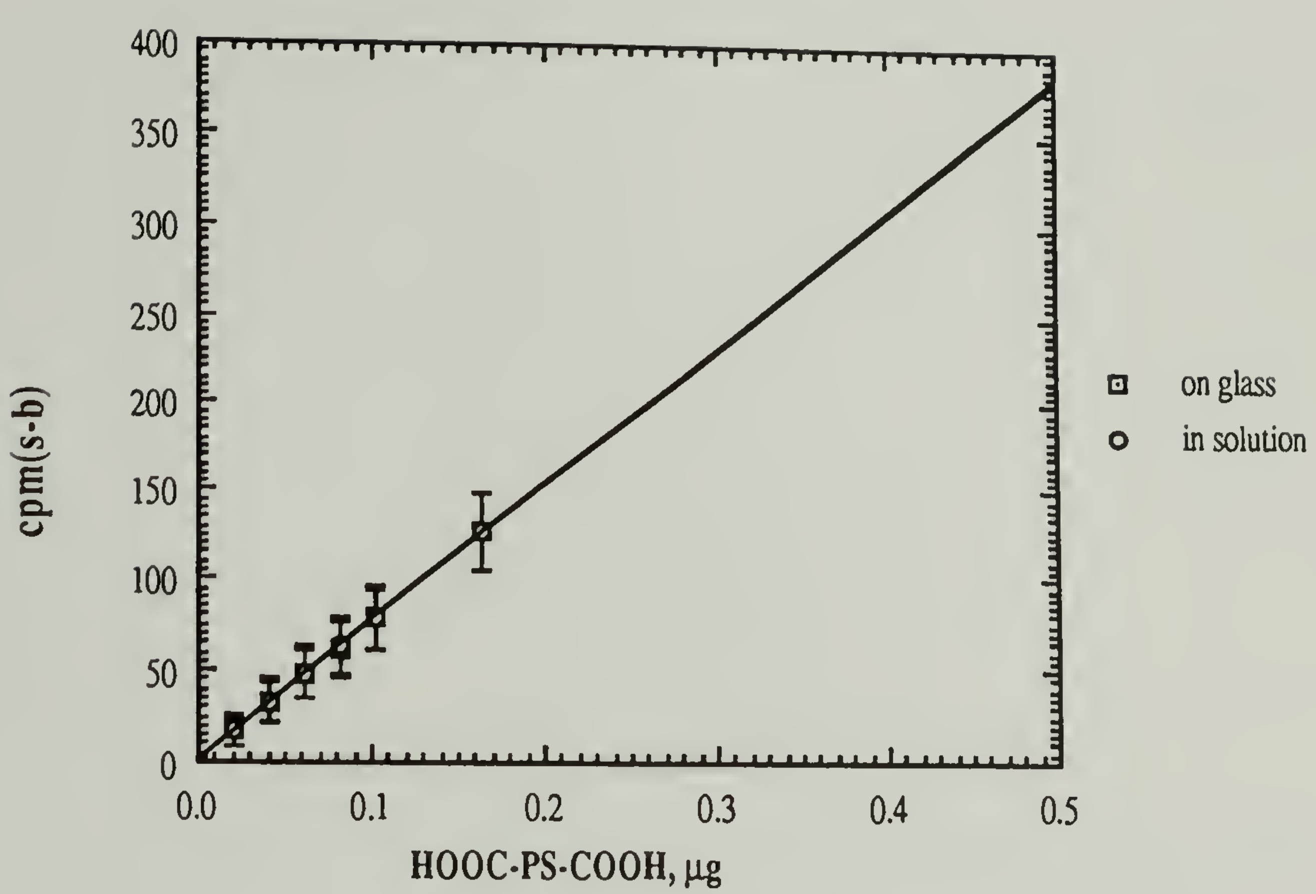
y = 0.41 + 760.98x R^2 = 1.000 .....(2) in solution

Figure B.8 cpm vs Amount of Di-Carboxylic Acid-Terminated Polystyrene. Number average molecular weight - 10000

Table B.10 Counts Per Minute Obtained from Different Amounts of Di-Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on Glass; M_n = 30000

No	PS-COOH, µg	$cpm(s\text{-}b)_G$ + r.e	$cpm(s\text{-}b)_{solution}$ + r.e
1	0.021 ± 0.002	18.1 ± 6.4	19.9 ± 6.5
2	0.021 ± 0.002	16.5 ± 6.3	15.4 ± 6.3
3	0.021 ± 0.002		17.8 ± 6.4
	cpm_{avg} + r.e + s.e	17.3 ± 6.3	17.7 ± 6.4
4	0.041 ± 0.004	32.1 ± 7.2	32.3 ± 7.2
5	0.041 ± 0.004	33.7 ± 7.2	33.8 ± 7.2
6	0.041 ± 0.004		33.7 ± 7.2
	cpm_{avg} + r.e + s.e	32.9 ± 7.2	33.3 ± 7.2
7	0.062 ± 0.006	46.4 ± 7.6	54.7 ± 8.0
8	0.062 ± 0.006	48.8 ± 7.7	46.5 ± 7.6
9	0.062 ± 0.006		44.4 ± 7.6
	cpm_{avg} + r.e + s.e		48.5 ± 10.7
10	0.082 ± 0.008	54.9 ± 8.0	66.2 ± 8.4
11	0.082 ± 0.008	68.7 ± 8.5	60.6 ± 8.3
12	0.082 ± 0.008		61.8 ± 8.3
	cpm_{avg} + r.e + s.e	61.8 ± 19.1	62.9 ± 8.3
13	0.103 ± 0.012	74.3 ± 8.6	73.3 ± 8.6
14	0.103 ± 0.012	80.9 ± 8.9	84.5 ± 9.0
15	0.103 ± 0.012		78.8 ± 8.8
	cpm_{avg} + r.e + s.e	77.6 ± 8.8	78.9 ± 11.0
16	0.164 ± 0.016	132.6 ± 10.3	128.1 ± 10.2
17	0.164 ± 0.016	119.2 ± 10.0	124.3 ± 10.1
	cpm_{avg} + r.e + s.e	125.9 ± 18.6	126.2 ± 10.2
18	1.640 ± 0.160		1226.0 ± 24.6
19	1.640 ± 0.160		1248.3 ± 24.8
20	1.640 ± 0.160		1284.2 ± 25.1
	cpm_{avg} + r.e + s.e		1252.8 ± 57.6

Note: The data is from sythesis alon notebook #4, p 112 - 113.



y = 0.78 + 758.5x R^2 = 0.999 .....(1) on glass

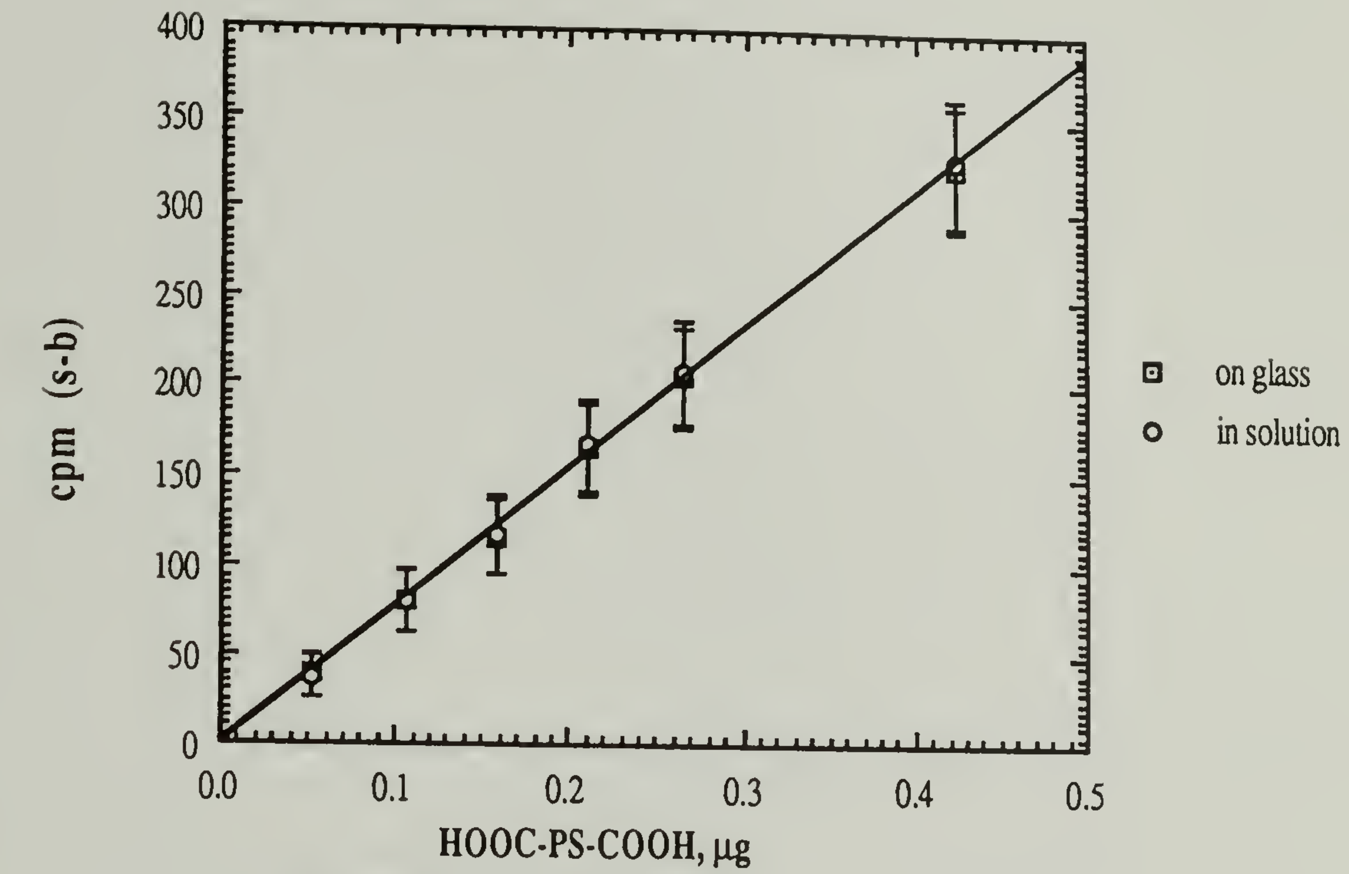
y = 1.06 + 763.26x R^2 = 1.000 .....(2) in solution

Figure B.9 cpm vs Amount of Di-Carboxylic Acid-Terminated Polystyrene. Number average molecular weight - 30000

Table B.11 Counts Per Minute Obtained from Different Amounts of Di-Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on Glass; M_n = 60000

No	PS-COOH, µg	$cpm(s-b)_G$ + r.e	$cpm(s-b)_{solution}$ + r.e
1	0.053 ± 0.005	39.1 ± 7.4	38.5 ± 7.4
2	0.053 ± 0.005	37.5 ± 7.4	41.7 ± 7.4
3	0.053 ± 0.005		33.0 ± 7.2
	cpm_{avg} + r.e + s.e	38.3 ± 7.4	37.7 ± 8.6
4	0.106 ± 0.010	81.2 ± 8.9	86.4 ± 9.0
5	0.106 ± 0.010	78.5 ± 8.8	77.9 ± 8.8
6	0.106 ± 0.010		78.2 ± 8.8
	cpm_{avg} + r.e + s.e	79.9 ± 8.8	80.2 ± 8.9
7	0.158 ± 0.015	111.5 ± 9.8	124.0 ± 10.1
8	0.158 ± 0.015	121.5 ± 10.0	110.9± 9.8
9	0.158 ± 0.015		118.5 ± 10.0
	cpm_{avg} + r.e + s.e	116.5 ± 9.9	117.8 ± 12.9
10	0.212 ± 0.020	158.9 ± 11.0	173.7 ± 11.3
11	0.212 ± 0.020	171.7 ± 11.3	165.9 ± 11.2
12	0.212 ± 0.020		162.8 ± 11.1
	cpm_{avg} + r.e + s.e	165.3 ± 17.7	167.5 ± 11.2
13	0.263 ± 0.025	201.3 ± 11.9	196.4 ± 11.8
14	0.263 ± 0.025	208.1 ± 12.0	216.1 ± 12.2
15	0.263 ± 0.025		207.7 ± 12.0
	cpm_{avg} + r.e + s.e	204.7 ± 11.9	206.7 ± 19.4
16	0.422 ± 0.040	329.8 ± 14.3	314.1 ± 14.0
17	0.422 ± 0.040	318.4 ± 14.1	339.7 ± 14.4
	cpm_{avg} + r.e + s.e	324.1 ± 14.2	326.9 ± 35.5
18	4.220 ± 0.400		3274.9 ± 38.3
19	4.220 ± 0.400		3222.5 ± 38.0
20	4.220 ± 0.400		3319.7 ± 25.1
	cpm_{avg} + r.e + s.e		3272.4 ± 95.4

Note: The data is from synthesis alone notebook #4, p 114 - 116.



y = - 1.50 + 774.10x R^2 = 0.999 .....(1) on glass

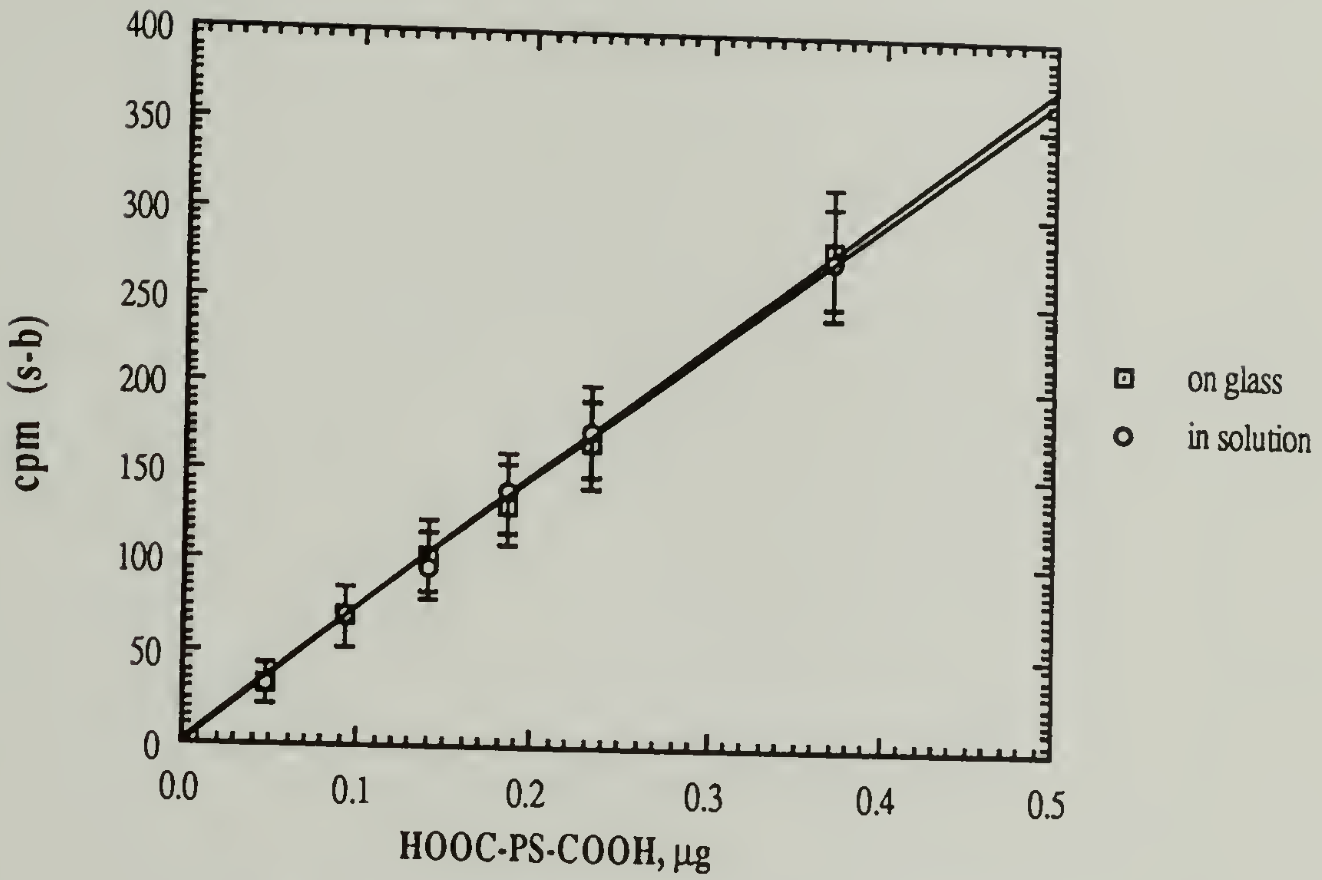
y = - 0.34 + 774.85x R^2 = 1.000 .....(2) in solution

Figure B.10 cpm vs Amount of Di-Carboxylic Acid-Terminated Polystyrene. Number Average molecular weight - 60000

Table B.12 Counts Per Minute Obtained from Different Amounts of Di-Carboxylic Acid-Terminated Polystyrene from Solution and as Cast Film on Glass; M_n = 140000

No	PS-COOH, μg	cpm(s-b)$_G$ + r.e	cpm(s-b)$_{solution}$ + r.e
1	0.0465 ± 0.0045	33.4 ± 7.2	36.0 ± 7.3
2	0.0465 ± 0.0045	33.3 ± 7.2	32.3 ± 7.2
3	0.0465 ± 0.0045		30.9 ± 7.1
	cpm$_{avg}$ + r.e + s.e	33.4 ± 7.2	33.1 ± 7.2
4	0.093 ± 0.009	79.7 ± 8.8	68.6 ± 8.5
5	0.093 ± 0.009	59.9 ± 8.2	71.3 ± 8.6
6	0.093 ± 0.009		69.0 ± 8.5
	cpm$_{avg}$ + r.e + s.e	69.8 ± 27.4	69.6 ± 8.5
7	0.1395 ± 0.0135	102.2 ± 19.8	98.5 ± 9.4
8	0.1395 ± 0.0135	102.4 ± 19.8	92.7 ± 9.2
9	0.1395 ± 0.0135		100.9 ± 9.5
	cpm$_{avg}$ + r.e + s.e	102.3 ± 19.8	97.4 ± 9.4
10	0.1860 ± 0.0180	139.7 ± 10.5	139.6 ± 10.5
11	0.1860 ± 0.0180	124.7 ± 10.1	144.2 ± 10.6
12	0.1860 ± 0.0180		134.6 ± 10.4
	cpm$_{avg}$ + r.e + s.e	132.2 ± 22.5	139.5 ± 10.5
13	0.2325 ± 0.0225	167.4 ± 11.1	177.6 ± 11.4
14	0.2325 ± 0.0225	167.6 ± 11.1	173.1 ± 11.3
15	0.2325 ± 0.0225		175.4 ± 11.3
	cpm$_{avg}$ + r.e + s.e	167.5 ± 11.1	175.4 ± 11.3
16	0.3720 ± 0.0360	274.6 ± 13.3	281.3 ± 13.4
17	0.3720 ± 0.0360	285.8 ± 13.5	263.5 ± 13.1
	cpm$_{avg}$ + r.e + s.e	280.2 ± 13.4	272.4 ± 24.7
18	3.730 ± 0.360		2666.4 ± 34.8
19	3.730 ± 0.360		2780.1 ± 35.5
20	3.730 ± 0.360		2721.4 ± 35.1
	cpm$_{avg}$ + r.e + s.e		2722.6 ± 111.4

Note: The data is from synthesis alone notebook #4, p 117 - 118.



$y = -1.83 + 746.35x$ $R^2 = 0.999$ .....(1) on glass

$y = 0.98 + 729.72x$ $R^2 = 1.000$ .....(2) in solution

Figure B.11 cpm vs Amount of Di-Carboxylic Acid-Terminated Polystyrene. Number average molecular weight - 140000

Table B.13 Equations Representing the CPM versus the Amount of Polymer

sample	M_n	substrate/solution	equation
PS-COOH	5000	AgO/Ag/glass	cpm = -3.79 + 777.63x
		solution	cpm = 1.46 + 791.10x
PS-COOH	10000	AgO/Ag/glass	cpm = -4.20 + 764.50x
		solution	cpm = -1.30 + 768.60x
PS-COOH	30000	AgO/Ag/glass	cpm = -4.50 + 762.92x
		solution	cpm = -0.81 + 779.31x
PS-COOH	140000	AgO/Ag/glass	cpm = -4.50 + 760.00x
		solution	cpm = 1.46 + 791.10x
HOOC-PS-COOH	10000	glass	cpm = -0.30 + 764.60x
		solution	cpm = 0.41 + 760.98x
HOOC-PS-COOH	30000	glass	cpm = 0.78 + 758.50x
		solution	cpm = 1.06 + 763.26x
HOOC-PS-COOH	60000	glass	cpm = -1.50 + 774.10x
		solution	cpm = -0.34 + 774.85x
HOOC-PS-COOH	140000	glass	cpm = -1.83 + 746.35x
		solution	cpm = 0.98 + 729.72x

where x is the amount of polymer in µg, cast as a film on the surface / added directly to the cocktail from a dilute solution using a finnpipette.

Table B.14 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; $M_n = 5000$

time (h)	PS-COOH	PS-OH	PS-H
	concentration = 1.0 mg/ml		
0.25	240.1 ± 5.1	41.3 ± 2.4	33.4 ± 2.3
0.5	241.5 ± 5.1	43.2 ± 2.5	34.1 ± 2.3
1.0	242.2 ± 5.1	45.6 ± 2.5	35.3 ± 2.3
2.0	246.7 ± 5.1	48.9 ± 2.6	39.4 ± 2.4
3.0	274.1 ± 5.4	52.4 ± 2.7	49.8 ± 2.6
6.0	268.9 ± 5.3	56.8 ± 2.8	52.4 ± 2.7
16.0	293.6 ± 5.5	61.5 ± 2.8	44.7 ± 2.6
24.0	281.8 ± 5.4	60.4 ± 2.8	50.4 ± 2.6
	concentration = 0.1 mg/ml		
0.25	177.8 ± 4.5	20.6 ± 2.0	24.7 ± 2.1
0.5	184.2 ± 4.6	21.6 ± 2.1	23.0 ± 2.1
1.0	186.2 ± 4.6	25.1 ± 2.1	24.2 ± 2.1
3.0	190.2 ± 4.6	25.9 ± 2.2	26.5 ± 2.2
6.0	195.4 ± 4.7	34.8 ± 2.4	28.2 ± 2.2
12.0	197.3 ± 4.7	37.7 ± 2.5	30.9 ± 2.3
24.0	199.6 ± 4.7	36.6 ± 2.4	30.6 ± 2.3
	concentration = 0.01 mg/ml		
0.25	83.6 ± 3.3	28.3 ± 2.2	19.3 ± 2.0
0.5	81.1 ± 3.3	30.2 ± 2.3	21.1 ± 2.0
1.0	84.6 ± 3.3	30.8 ± 2.3	24.5 ± 2.1
2.0	85.8 ± 3.3	29.5 ± 2.3	25.5 ± 2.2
3.0	83.7 ± 3.3	31.5 ± 2.3	27.1 ± 2.2
4.0	87.9 ± 3.4	31.0 ± 2.3	23.8 ± 2.1
8.0	84.8 ± 3.3	33.4 ± 2.4	23.6 ± 2.1
24.0	84.7 ± 3.3	30.9 ± 2.3	24.6 ± 2.1
	concentration = 0.001 mg/ml		
0.25	44.1 ± 2.6	14.1 ± 1.8	13.3 ± 1.8
0.5	46.7 ± 2.7	15.6 ± 1.9	14.0 ± 1.8
1.0	49.2 ± 2.7	17.7 ± 1.9	15.3 ± 1.8
2.0	52.4 ± 2.8	19.4 ± 2.0	16.8 ± 1.9
3.0	51.9 ± 2.8	22.9 ± 2.1	18.5 ± 2.0
4.0	49.9 ± 2.7	24.2 ± 2.1	19.1 ± 2.0
8.0	51.4 ± 2.7	24.7 ± 2.1	19.8 ± 2.0
24.0	51.2 ± 2.7	24.1 ± 2.1	20.1 ± 2.0

Note : The data is from LSC notebook #1, p 116 - 121 and LSC notebook #2, p 35 - 42.

Table B.15 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; M_n = 10000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
concentration =					1.51 mg/ml	1.45 mg/ml
0.25					203.6 ± 5.3	53.3 ± 3.3
0.50					212.7 ± 5.5	50.1 ± 3.3
1.0					228.8 ± 5.8	44.2 ± 3.2
2.0					230.2 ± 5.8	47.7 ± 3.2
3.0					231.5 ± 5.8	50.3 ± 3.3
6.0					234.5 ± 5.9	56.0 ± 3.4
12.0					243.0 ± 6.0	50.7 ± 3.3
24.0					242.2 ± 5.9	51.7 ± 3.3
concentration = 1.0 mg/ml					0.94 mg/ml	0.94 mg/ml
0.25	261.8 ± 5.3	41.5 ± 2.5	29.4 ± 2.3	0.25	59.9 ± 3.2	26.0 ± 2.8
0.50	376.5 ± 6.2	49.0 ± 2.7	36.1 ± 2.4	0.50	72.8 ± 3.7	31.1 ± 2.9
1.0	324.1 ± 5.8	54.8 ± 2.8	49.7 ± 2.7	1.0	63.0 ± 3.2	28.5 ± 2.8
3.0	313.1 ± 5.7	69.3 ± 3.1	64.1 ± 3.0	2.0	71.0 ± 3.7	27.9 ± 2.8
6.0	317.9 ± 5.8	79.1 ± 3.2	77.1 ± 3.2	3.0	72.8 ± 3.7	26.9 ± 2.8
16.0	332.6 ± 5.9	81.2 ± 3.3	74.9 ± 3.2	6.0	73.2 ± 3.7	25.2 ± 2.7
24.0	329.5 ± 5.9	80.0 ± 3.2	76.0 ± 3.2	12.0	73.6 ± 3.7	26.6 ± 2.8
				24.0	72.0 ± 3.7	27.3 ± 2.8
concentration = 0.1 mg/ml					0.15 mg/ml	0.19 mg/ml
0.25	160.7 ± 4.4	22.0 ± 2.1	30.9 ± 2.3	0.25	36.5 ± 3.0	16.5 ± 2.5
0.5	167.4 ± 4.5	28.8 ± 2.3	36.1 ± 2.5	0.50	34.5 ± 3.0	19.4 ± 2.7
1.0	178.3 ± 4.6	41.3 ± 2.6	41.3 ± 2.6	1.0	32.6 ± 2.9	16.9 ± 2.6
3.0	181.1 ± 4.6	45.4 ± 2.7	51.4 ± 2.8	3.0	35.7 ± 3.0	19.3 ± 2.6
6.0	177.4 ± 4.6	43.8 ± 2.7	48.5 ± 2.6	6.0	41.2 ± 3.1	17.9 ± 2.6
12.0	182.4 ± 4.7	45.5 ± 2.8	51.8 ± 2.8	12.0	34.1 ± 3.0	15.9 ± 2.5
24.0	184.6 ± 4.7	46.0 ± 2.8	50.9 ± 2.8	24.0	35.4 ± 3.0	14.1 ± 2.5
48.0	189.8 ± 4.7					

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Table B.15 Continued

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; $M_n = 10000$

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
concentration = 0.01 mg/ml					0.015 mg/ml	0.019 mg/ml
0.5	54.6 ± 2.8	31.5 ± 2.3	28.1 ± 2.2	0.25	26.5 ± 2.8	11.2 ± 2.5
1.0	44.6 ± 2.6	32.8 ± 2.3	29.3 ± 2.2	0.50	23.0 ± 2.8	14.6 ± 2.5
2.0	61.0 ± 2.9	36.5 ± 2.4	33.7 ± 2.4	1.0	20.1 ± 2.7	13.3 ± 2.5
4.0	64.0 ± 3.0	38.4 ± 2.5	34.4 ± 2.4	3.0	20.9 ± 2.7	13.2 ± 2.5
6.0	60.3 ± 2.9	38.9 ± 2.5	35.1 ± 2.4	6.0	23.9 ± 2.8	10.4 ± 2.4
15.0	67.6 ± 3.0	42.5 ± 2.5	2.6 ± 2.3	12.0	22.9 ± 2.8	13.4 ± 2.5
24.0	61.1 ± 2.9	39.3 ± 2.5	31.8 ± 2.3	24.0	26.9 ± 2.8	11.1 ± 2.5
48.0	64.2 ± 3.0	39.8 ± 2.5	34.1 ± 2.4			
concentration = 0.001 mg/ml						
0.25	30.0 ± 2.3	17.0 ± 1.8	10.2 ± 1.7			
0.5	33.2 ± 2.3	19.0 ± 1.9	13.1 ± 1.8			
1.0	35.8 ± 2.4	23.6 ± 2.1	16.6 ± 1.9			
2.0	38.7 ± 2.4	26.7 ± 2.2	19.6 ± 1.9			
3.0	39.5 ± 2.5	31.5 ± 2.2	25.7 ± 2.2			
4.0	49.9 ± 2.7	33.1 ± 2.3	29.3 ± 2.3			
8.0	41.2 ± 2.5	34.3 ± 2.3	30.7 ± 2.3			
24.0	39.4 ± 2.4	33.0 ± 2.3	30.5 ± 2.3			

Note: The data is from LSC notebook #1, p 145 - 147; LSC notebook #2, p 3 - 7; synthesis alone notebook #4, p 121 - 135; and LSC notebook #3, p 30 - 32.

Table B.16 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; M_n = 30000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	PS(COOH)$_2$	PS(OH)$_2$
concentration =					2.43 mg/ml	2.71 mg/ml
				0.50	406.7 ± 9.4	235.3 ± 5.7
				1.0	353.4 ± 8.3	197.4 ± 5.2
				3.0	447.7 ± 10.0	208.1 ± 5.4
				6.0	513.5 ± 11.5	198.2 ± 5.2
				12.0	443.8 ± 10.1	199.2 ± 5.2
				24.0	497.4 ± 11.1	203.2 ± 5.3
concentration = 1.0 mg/ml					1.1 mg/ml	1.12 mg/ml
0.25	396.9 ± 6.5	99.6 ± 3.6	86.8 ± 3.4	0.25	217.2 ± 5.5	83.9 ± 3.9
0.5	430.1 ± 6.7	109.3 ± 3.7	113.2 ± 3.8	0.50	201.6 ± 5.3	65.3 ± 3.6
1.0	429.5 ± 6.7	122.9 ± 3.9	118.3 ± 3.8	1.0	208.2 ± 5.4	63.0 ± 3.2
2.0	444.0 ± 6.8	129.3 ± 4.0	130.3 ± 4.0	2.0	211.5 ± 5.5	70.4 ± 3.7
3.0	439.2 ± 6.8	134.1 ± 4.0	128.3 ± 4.0	3.0	194.0 ± 5.3	79.7 ± 3.8
7.0	428.6 ± 6.7	124.6 ± 3.9	126.4 ± 3.9	6.0	206.9 ± 5.4	68.1 ± 3.6
15.0	420.7 ± 6.6	122.6 ± 3.9	126.8 ± 3.9	12.0	223.0 ± 5.7	72.0 ± 3.7
24.0	426.7 ± 6.7	134.1 ± 4.0	120.7 ± 3.9	24.0	212.5 ± 5.5	70.6 ± 3.7
concentration =					0.54 mg/ml	0.56 mg/ml
				1.0	158.9 ± 4.8	37.4 ± 3.0
				2.0	154.9 ± 4.8	40.0 ± 3.1
				3.0	158.3 ± 4.8	41.9 ± 3.1
				4.0	150.3 ± 4.7	39.2 ± 3.1
				5.0	158.4 ± 4.8	39.4 ± 3.1
				24.0	159.5 ± 4.9	38.9 ± 3.1
concentration = 0.1 mg/ml					0.15 mg/ml	0.20 mg/ml
0.083	132.3 ± 4.1	38.7 ± 2.6	29.4 ± 2.3			
0.25	232.6 ± 5.2	71.4 ± 3.2	66.3 ± 3.1	0.25	41.8 ± 3.1	18.7 ± 2.6
0.5	272.1 ± 5.5	85.7 ± 3.7	79.4 ± 3.3	0.50	39.0 ± 3.1	18.3 ± 2.6
1.0	308.9 ± 5.9	78.7 ± 3.3	71.7 ± 3.2	1.0	41.9 ± 3.1	16.7 ± 2.6
2.0	285.1 ± 5.7	81.8 ± 3.4	76.9 ± 3.3	2.0	44.3 ± 3.2	17.4 ± 2.6
3.0	280.8 ± 5.6	83.9 ± 3.4	76.8 ± 3.3	3.0	38.6 ± 3.1	16.6 ± 2.6
6.0	271.3 ± 5.5	77.4 ± 3.3	77.3 ± 3.3	6.0	37.6 ± 3.1	18.0 ± 2.6
12.0	277.4 ± 5.6	82.3 ± 3.4	74.1 ± 3.3	12.0	40.3 ± 3.1	16.3 ± 2.5
24.0	281.9 ± 5.6	81.9 ± 3.4	73.8 ± 3.2	24.0	39.8 ± 3.1	16.5 ± 2.5

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Table B.16 Continued

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; M_n = 30000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 0.01 mg/ml				0.016 mg/ml	0.013 mg/ml
0.25	95.4 ± 3.5	60.9 ± 2.9	54.4 ± 2.8	0.25	28.4 ± 2.9	11.5 ± 2.4
0.5	100.2 ± 3.6	64.6 ± 3.0	57.8 ± 2.9	0.50	25.7 ± 2.8	8.4 ± 2.3
1.0	105.8 ± 3.6	63.2 ± 3.0	59.5 ± 2.9	1.0	22.7 ± 2.7	8.3 ± 2.3
2.0	107.9 ± 3.7	67.5 ± 3.1	60.4 ± 2.9	2.0	24.3 ± 2.8	8.0 ± 2.3
3.0	114.1 ± 3.8	65.7 ± 3.0	59.1 ± 2.9	3.0	21.8 ± 2.7	8.7 ± 2.3
4.0		70.0 ± 3.1	59.6 ± 2.9			
6.0	115.8 ± 3.8		65.5 ± 3.0	6.0	28.2 ± 2.9	9.8 ± 2.4
8.0		64.8 ± 3.0	62.3 ± 3.0			
12.0	112.3 ± 3.7	66.2 ± 3.0	60.1 ± 2.9	12.0	25.5 ± 2.8	10.6 ± 2.4
24.0	114.3 ± 3.8	64.2 ± 3.0	64.9 ± 3.0	24.0	27.5 ± 2.8	10.7 ± 2.4
	concentration = 0.001 mg/ml					
0.25	68.5 ± 3.0	35.0 ± 2.4	28.2 ± 2.2			
0.5	71.0 ± 3.1	39.0 ± 2.5	34.1 ± 2.4			
1.0	72.9 ± 3.1	41.9 ± 2.5	39.6 ± 2.5			
2.0		43.8 ± 2.6	43.2 ± 2.6			
3.0	74.0 ± 3.1					
4.0		49.2 ± 2.7	47.3 ± 2.6			
6.0	76.5 ± 3.2	49.4 ± 2.7	50.6 ± 2.7			
8.0		52.9 ± 2.8	54.5 ± 2.8			
12.0	81.9 ± 3.3					
24.0	76.8 ± 3.2	49.1 ± 2.7	50.2 ± 2.7			

Note: The data is from LSC notebook #1, p 14 - 26; LSC notebook #2, p 23 -30; and LSC notebook #3, p 38 - 63.

Table B.17 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; M_n = 60000

time (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 1.92 and 2.23 mg/ml	
1.0	532.9 ± 10.7	329.2 ± 6.6
2.0	464.8 ± 9.3	291.4 ± 5.8
3.0	471.2 ± 9.4	320.2 ± 6.4
6.0	486.2 ± 9.7	269.6 ± 5.4
12.0	505.4 ± 10.1	294.3 ± 5.9
24.0	572.1 ± 11.4	308.5 ± 6.2
48.0	470.1 ± 9.4	268.4 ± 5.4
48.0	343.8 ± 8.1	232.3 ± 5.9
	concentration = 1.00 and 1.11 mg/ml	
0.5	336.2 ± 8.0	231.4 ± 5.8
1.0	354.7 ± 8.2	222.2 ± 5.7
2.0	343.0 ± 8.0	235.9 ± 5.9
3.0	333.0 ± 7.8	247.3 ± 6.2
6.0	325.8 ± 7.8	267.8 ± 6.6
12.0	346.4 ± 8.2	227.5 ± 5.8
24.0	346.7 ± 8.2	235.5 ± 5.9
48.0	343.8 ± 8.1	232.3 ± 5.9
	concentration = 0.57 and 0.71 mg/ml	
0.5	278.8 ± 6.8	174.3 ± 5.1
1.0	265.3 ± 5.6	196.3 ± 5.3
2.0	295.5 ± 7.1	192.8 ± 5.3
3.0	286.5 ± 7.0	192.7 ± 5.2
6.0	304.1 ± 7.3	183.9 ± 5.1
12.0	286.0 ± 7.0	179.1 ± 5.1
24.0	281.0 ± 6.9	191.4 ± 5.2
48.0	281.6 ± 6.9	189.8 ± 5.2

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Table B.17 Continued

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; $M_n = 60000$

time (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 0.10 and 0.12 mg/ml	
0.5	107.8 ± 4.2	74.5 ± 3.7
1.0	110.3 ± 4.3	78.4 ± 3.8
2.0	120.2 ± 4.4	72.0 ± 3.7
3.0	117.7 ± 4.3	75.4 ± 3.8
6.0	115.2 ± 4.3	72.8 ± 3.7
12.0	116.7 ± 4.3	77.0 ± 3.8
24.0	114.1 ± 4.3	72.5 ± 3.7
48.0	114.8 ± 4.3	73.0 ± 3.7
	concentration = 0.013 and 0.017 mg/ml	
0.5	80.9 ± 3.8	52.0 ± 3.4
1.0	89.6 ± 3.9	57.6 ± 3.5
2.0	99.6 ± 4.1	47.9 ± 3.3
3.0	89.9 ± 3.9	55.7 ± 3.4
6.0	88.0 ± 3.9	55.2 ± 3.4
12.0	98.0 ± 4.1	45.8 ± 3.2
24.0	85.4 ± 3.9	49.3 ± 3.3
48.0	90.2 ± 3.9	50.6 ± 3.3

Note : Random error from the counting process alone is shown. The data is from LSC notebook #3, p 64 - 77.

Table B.18 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; M_n = 140000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration =				2.41 mg/ml	2.55 mg/ml
				0.50	410.9 ± 9.2	201.3 ± 5.3
				1.0	498.9 ± 11.2	268.4 ± 6.5
				2.0	451.9 ± 10.2	259.2 ± 6.5
				3.0	444.5 ± 10.1	265.5 ± 6.5
				6.0	395.6 ± 9.1	229.9 ± 6.0
				12.0	446.3 ± 10.1	244.6 ± 6.1
				24.0	474.4 ± 10.7	243.6 ± 6.1
	concentration =	1mg/ml			1.15 mg/ml	1.29 mg/ml
0.25	313.9 ± 5.8		163.6 ± 4.4			
0.5	322.2 ± 5.9		191.1 ± 4.7	0.50	425.4 ± 9.7	189.0 ± 5.1
1.0	333.3 ± 5.9		206.9 ± 4.8	1.0	476.8 ± 10.7	200.4 ± 5.2
2.0	326.7 ± 5.7		205.5 ± 4.7	2.0	432.5 ± 9.8	188.0 ± 5.1
3.0	322.9 ± 5.8		187.7 ± 4.6	3.0	481.4 ± 10.8	200.8 ± 5.2
4.0	315.9 ± 5.6		204.3 ± 4.6	5.0	482.8 ± 10.8	210.7 ± 5.4
12.0	325.9 ± 5.9		201.4 ± 4.8	12.0	462.7 ± 10.8	198.6 ± 5.2
15.0	325.1 ± 5.9		205.2 ± 4.8			
24.0	325.6 ± 5.9		205.7 ± 4.8	24.0	477.0 ± 10.7	195.8 ± 5.2
	concentration =				0.57 mg/ml	0.62 mg/ml
				0.50	372.4 ± 8.7	157.9 ± 4.9
				1.0	339.5 ± 7.9	157.1 ± 4.9
				2.0	362.1 ± 8.5	158.9 ± 4.9
				3.0	368.8 ± 8.6	163.0 ± 5.0
				5.0	360.2 ± 8.4	158.3 ± 4.9
				12.0	344.8 ± 8.0	160.1 ± 4.9
				24.0	375.5 ± 8.8	165.0 ± 5.0

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Table B.18 Continued

substrate - glass; solvent - cyclohexane; temperature - 36.7± 0.1°C; M_n = 140000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 0.1 mg/ml				0.11 mg/ml	0.13 mg/ml
0.25	174.4 ± 4.5		108.7 ± 3.7			
0.5	175.9 ± 4.5		118.3 ± 3.8	0.50	262.0 ± 6.1	134.3 ± 4.5
1.0	227.2 ± 5.0		120.6 ± 3.8	1.0	283.7 ± 6.9	129.6 ± 4.5
2.0	194.0 ± 4.7		131.3 ± 4.0	2.0	280.7 ± 6.8	125.6 ± 4.5
4.0	190.7 ± 4.7		146.2 ± 4.2	3.0	307.4 ± 7.3	136.0 ± 4.6
6.0	192.3 ± 4.7		153.1 ± 4.3	5.0	273.5 ± 6.5	127.3 ± 4.5
15.0	188.0 ± 4.7		177.8 ± 4.6	12.0	281.3 ± 6.8	136.4 ± 4.6
24.0	190.7 ± 4.7		151.5 ± 4.3	24.0	273.0 ± 6.5	131.1 ± 4.5
	concentration = 0.01 mg/ml				0.013 mg/ml	0.015 mg/ml
0.50	129.4 ± 3.9		124.8 ± 3.9	0.25	230.8 ± 5.8	98.2 ± 3.9
1.0	131.3 ± 4.0		126.1 ± 3.9	0.50	231.3 ± 5.8	111.5 ± 4.2
2.0	134.9 ± 4.0		127.5 ± 3.9	1.0	217.5 ± 5.5	115.1 ± 4.2
3.0	135.7 ± 4.0		129.4 ± 3.9	2.0	241.4 ± 6.0	113.5 ± 4.2
6.0	142.2 ± 4.0		133.1 ± 4.0	3.0	237.4 ± 5.9	117.4 ± 4.3
12.0	142.8 ± 4.0		134.1 ± 4.0	5.0	242.9 ± 6.0	108.0 ± 4.1
24.0	142.4 ± 4.0		133.3 ± 4.0	12.0	229.5 ± 5.8	109.8 ± 4.1
48.0	140.5 ± 4.0		133.4 ± 4.0	24.0	227.1 ± 5.7	112.7 ± 4.2
	concentration = 0.001 mg/ml					
0.50	93.9 ± 3.5		63.0 ± 3.0			
1.0	101.6 ± 3.6		67.8 ± 3.0			
2.0	106.9 ± 3.6		76.5 ± 3.2			
3.0	111.6 ± 3.7		85.1 ± 3.3			
6.0	113.1 ± 3.7		93.8 ± 3.5			
12.0	115.7 ± 3.8		106.6 ± 3.6			
24.0	115.1 ± 3.8		110.9 ± 3.7			
48.0	115.4 ± 3.8		110.7 ± 3.7			

Note: The data is from LSC notebook #1, p 126 - 130; LSC notebook #2, p 19, 20, 45 - 50; and LSC notebook #3, p 79 -89.

Table B.19 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 5000

time (h)	PS-COOH	PS-OH	PS-H
	concentration = 1.0 mg/ml		
0.083	206.1 ± 4.9	14.2 ± 1.9	Below detection limit
0.167	168.2 ± 4.5	17.7 ± 2.0	
0.5	131.0 ± 4.0	15.9 ± 1.9	
1.0	116.3 ± 3.9	15.8 ± 1.9	
2.0	124.9 ± 4.0	17.5 ± 2.0	
4.0	127.5 ± 4.0	21.5 ± 2.1	
12.0	120.0 ± 3.9	19.7 ± 2.1	
24.0	114.6 ± 3.8	27.5 ± 2.3	
72.0	111.8 ± 3.8	25.0 ± 2.2	
120.0	116.1 ± 3.8	22.8 ± 2.1	
360.0	116.4 ± 3.9	22.9 ± 2.1	
	concentration = 0.1 mg/ml		
0.25	170.4 ± 4.1	1.8 ± 1.1	Below detection limit
0.5	159.2 ± 4.0	1.3 ± 1.1	
1.0	128.1 ± 3.6	1.5 ± 1.1	
2.0	147.1 ± 3.8		
3.0		2.4 ± 1.2	
5.0	146.6 ± 4.1		
6.0		2.7 ± 1.3	
12.0		4.5 ± 1.4	
15.0	116.8 ± 3.8		
24.0	133.0 ± 4.0	3.1 ± 1.4	
48.0	118.5 ± 3.8	4.1 ± 1.4	
96.0		3.1 ± 1.4	
124.0	105.4 ± 3.6		
168.0	100.9 ± 3.6		
360.0	98.5 ± 3.5	3.4 ± 1.4	

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Table B.19 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; $M_n = 5000$

time (h)	PS-COOH	PS-OH	PS-H
	concentration = 0.01 mg/ml		
0.25	18.3 ± 1.5	Below detection limit	Below detection limit
0.5	16.2 ± 1.5		
1.0	10.9 ± 1.3		
2.0	11.6 ± 1.3		
4.0	6.3 ± 1.2		
8.0	6.4 ± 1.2		
24.0	6.2 ± 1.1		
48.0	6.4 ± 1.2		
72.0	5.9 ± 1.1		
360.0	6.1 ± 1.1		
	concentration = 0.001 mg/ml		
0.25	4.0 ± 1.1	Below detection limit	Below detection limit
0.50	3.4 ± 1.0		
1.0	2.4 ± 1.0		
2.0	1.6 ± 0.9		
4.0	2.9 ± 1.0		
8.0	1.4 ± 0.9		
24.0	1.4 ± 0.9		
48.0	0.7 ± 0.9		
72.0	1.1 ± 0.9		

Note: The data is from LSC notebook #1, p 45 - 54, p 70 - 109 and LSC notebook #2, p 49 - 52.

Table B.20 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 10000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration =				1.5 mg/ml	
0.083					161.8 ± 4.8	
0.25					169.2 ± 4.9	
0.50					144.6 ± 4.6	
1.0					196.3 ± 5.2	
2.0					185.3 ± 5.1	
3.0					164.3 ± 4.8	
6.0					168.1 ± 4.9	
12.0					198.9 ± 5.2	
24.0					160.5 ± 4.8	
	concentration = 1.0 mg/ml				1.05 mg/ml	1.06 mg/ml
0.25	428.6 ± 6.6	18.0 ± 2.0	4.4 ± 1.4	0.083	163.3 ± 4.8	83.6 ± 3.8
0.50	189.8 ± 4.6	19.8 ± 2.0	7.6 ± 1.6	0.25	147.4 ± 4.6	113.3 ± 4.2
1.0	180.4 ± 4.5	21.7 ± 2.1	8.8 ± 1.6	0.50	151.1 ± 4.7	105.6 ± 4.1
3.0	203.6 ± 4.8	22.1 ± 2.1	11.2 ± 1.7	1.0	135.9 ± 4.5	103.7 ± 4.1
6.0	177.5 ± 4.5	22.8 ± 2.1	11.6 ± 1.7	2.0	141.5 ± 4.6	100.8 ± 4.1
12.0	159.1 ± 4.3	25.1 ± 2.2	14.9 ± 1.9	3.0	133.1 ± 4.4	88.7 ± 3.9
12.0	175.6 ± 4.5	21.8 ± 2.1	12.1 ± 1.8	6.0	166.9 ± 4.9	89.1 ± 3.9
24.0	145.5 ± 4.1	23.1 ± 2.1	12.3 ± 1.8	12.0	157.6 ± 4.8	101.4 ± 4.1
48.0	137.9 ± 4.1	22.8 ± 2.1	12.9 ± 1.8	24.0	162.3 ± 4.8	99.2 ± 4.0
120.0	134.4 ± 4.0	21.5 ± 2.1	12.2 ± 1.8			
360.0	138.7 ± 4.1					
	concentration =				0.56 mg/ml	0.5 mg/ml
				0.083	172.5 ± 4.9	61.6 ± 3.5
				0.25	160.4 ± 4.8	69.3 ± 3.6
				0.50	137.1 ± 4.6	64.4 ± 3.5
				1.0	148.2 ± 4.7	72.8 ± 3.7
				2.0	143.7 ± 4.6	70.4 ± 3.6
				3.0	149.0 ± 4.7	65.8 ± 3.5
				6.0	157.1 ± 4.8	62.2 ± 3.5
				12.0	140.2 ± 4.6	66.6 ± 3.5
				24.0	153.6 ± 4.7	69.5 ± 3.6

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Table B.20 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 10000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
concentration = 0.1 mg/ml					0.12 mg/ml	0.12 mg/ml
0.083	95.7 ± 3.4	6.3 ± 1.5	1.6 ± 1.3	0.083	149.2 ± 4.7	46.5 ± 3.2
0.25	76.6 ± 3.2	8.0 ± 1.6	2.0 ± 1.3	0.25	120.9 ± 4.3	49.4 ± 3.4
0.5	72.9 ± 3.1	5.7 ± 1.5	2.0 ± 1.3	0.50	114.7 ± 4.3	53.6 ± 3.3
1.0	68.4 ± 3.0	5.1 ± 1.4	4.8 ± 1.4	1.0	127.6 ± 4.4	50.7 ± 3.3
2.0	75.1 ± 3.1	5.2 ± 1.4	3.4 ± 1.4	2.0	130.3 ± 4.5	50.2 ± 3.2
3.0	72.5 ± 3.1	7.8 ± 1.6	3.7 ± 1.4	3.0	125.2 ± 4.4	52.9 ± 3.3
4.0	73.1 ± 3.1	6.5 ± 1.5	3.5 ± 1.4	6.0	124.5 ± 4.4	49.8 ± 3.3
15.0	71.7 ± 3.1	7.2 ± 1.5	4.7 ± 1.4	12.0	130.8 ± 4.5	54.4 ± 3.4
24.0	76.9 ± 3.2	8.0 ± 1.6	5.6 ± 1.5	24.0	123.8 ± 4.4	47.9 ± 3.2
48.0	80.5 ± 3.2	7.0 ± 1.5	5.5 ± 1.5			
336.0	75.6 ± 3.1					
concentration =					0.067 mg/ml	0.056 mg/ml
				0.083	151.5 ± 4.6	30.7 ± 2.8
				0.25	142.6 ± 4.6	31.0 ± 2.8
				0.50	128.5 ± 4.4	34.7 ± 3.2
				1.0	116.5 ± 4.2	31.7 ± 2.9
				2.0	120.3 ± 4.3	29.0 ± 2.7
				3.0	110.5 ± 4.1	26.0 ± 2.7
				6.0	103.9 ± 4.1	33.4 ± 2.9
				14.0	113.0 ± 4.2	28.8 ± 2.7
				24.0	108.6 ± 4.1	31.1 ± 2.8
concentration = 0.01 mg/ml					0.015 mg/ml	0.019 mg/ml
0.25	19.8 ± 2.0	Below detection limit	Below detection limit	0.083	89.0 ± 3.8	19.7 ± 2.5
0.5	18.6 ± 2.0			0.25	63.7 ± 3.4	24.7 ± 2.7
1.0	16.8 ± 1.9			0.50	51.5 ± 3.2	19.8 ± 2.5
2.0	17.1 ± 1.9			1.0	78.8 ± 3.7	19.4 ± 2.5
4.0	15.2 ± 1.8			2.0	59.7 ± 3.3	16.6 ± 2.4
				3.0	68.2 ± 3.5	14.1 ± 2.3
				6.0	74.6 ± 3.6	16.5 ± 2.4
15.0	13.8 ± 1.8			14.0	60.2 ± 3.4	16.1 ± 2.4
24.0	13.0 ± 1.8			24.0	47.6 ± 3.2	15.5 ± 2.4
48.0	14.5 ± 1.8			48.0	45.4 ± 3.2	14.4 ± 2.3
96.0	12.9 ± 1.8			96.0	50.2 ± 3.2	13.5 ± 2.3
120.0	13.5 ± 1.8			120.0	47.7 ± 3.2	13.4 ± 2.3

Continued, next page

Table B.20 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 10000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
concentration = 0.001 mg/ml						
0.25	7.3 ± 1.6	Below detection limit	Below detection limit			
0.5	7.0 ± 1.5					
1.0	6.4 ± 1.5					
2.0	6.2 ± 1.5					
4.0	5.7 ± 1.5					
8.0	4.1 ± 1.4					
24.0	4.2 ± 1.4					
48.0	3.4 ± 1.4					
72.0	3.6 ± 1.4					

Note: The data is from LSC notebook #1, p 141 - 143; LSC notebook #2, p 2 -5, p 8 - 9; and LSC notebook #3, p 8 - 31.

Table B.21 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 30000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	PS(COOH)$_2$	PS(OH)$_2$
concentration =					2.6 mg/ml	2.21 mg/ml
				0.083	201.8 ± 5.2	50.3 ± 3.3
				0.25	181.3 ± 5.1	40.2 ± 3.1
				0.50	201.1 ± 5.2	40.3 ± 3.1
				1.0	207.8 ± 5.4	38.6 ± 3.0
				2.0	204.0 ± 5.3	39.6 ± 3.1
				3.0	208.7 ± 5.4	41.0 ± 3.1
				6.0	211.8 ± 5.4	40.1 ± 3.1
				12.0	206.4 ± 5.3	39.9 ± 3.1
				24.0	205.0 ± 5.3	37.5 ± 3.0
				48.0	205.4 ± 5.3	37.4 ± 3.0
concentration = 1.0 mg/ml					0.71 mg/ml	1.03 mg/ml
0.083	243.4 ± 5.1	14.9 ± 1.8	7.6 ± 1.6	0.083	208.3 ± 5.4	38.4 ± 3.0
0.25	200.6 ± 4.7	16.5 ± 1.9	10.1 ± 1.7	0.25	212.9 ± 5.4	39.0 ± 3.1
0.50	188.1 ± 4.6	19.1 ± 2.0	15.0 ± 1.8	0.50	203.7 ± 5.3	38.0 ± 3.0
1.0	203.6 ± 4.8	20.6 ± 2.0	16.6 ± 1.9	1.0	201.2 ± 5.2	42.7 ± 3.2
2.0	170.2 ± 4.4	22.6 ± 2.1	18.3 ± 1.9	2.0	180.9 ± 5.0	39.2 ± 3.1
3.0	176.1 ± 4.4	22.8 ± 2.1	21.9 ± 2.0	3.0	183.8 ± 5.1	46.3 ± 3.2
6.0	164.0 ± 4.3	23.5 ± 2.1	25.3 ± 2.1	6.0	201.9 ± 5.2	45.3 ± 3.1
12.0	143.9 ± 4.1	25.0 ± 2.1	23.7 ± 2.1	12.0	200.6 ± 5.2	39.1 ± 3.1
24.0	136.4 ± 4.0	27.7 ± 2.2	25.1 ± 2.1	24.0	198.5 ± 5.2	38.4 ± 3.0
48.0	147.3 ± 4.1	29.4 ± 2.2	21.8 ± 2.0	48.0	204.1 ± 5.3	37.0 ± 3.0
72.0	138.7 ± 4.1	28.5 ± 2.2				
concentration =					0.48 mg/ml	0.52 mg/ml
				0.083	145.5 ± 4.6	37.5 ± 3.0
				0.25	146.1 ± 4.6	30.8 ± 2.8
				0.50	130.9 ± 4.4	23.0 ± 2.6
				1.0	151.8 ± 4.7	22.4 ± 2.6
				2.0	131.0 ± 4.4	26.9 ± 2.7
				3.0	133.7 ± 4.4	24.4 ± 2.6
				6.0	146.2 ± 4.6	24.4 ± 2.6
				12.0	144.1 ± 4.6	22.6 ± 2.6
				24.0	142.9 ± 4.5	22.4 ± 2.6
				48.0	142.2 ± 4.5	23.4 ± 2.6

Continued, next page

Table B.21 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 30000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 0.1 mg/ml				0.12 mg/ml	0.15 mg/ml
0.083	70.7 ± 3.1	6.3 ± 1.5	5.9 ± 1.5	0.083	82.6 ± 3.8	18.1 ± 2.5
0.25	49.4 ± 2.7	8.0 ± 1.6	7.2 ± 1.5	0.25	86.7 ± 3.8	17.1 ± 2.5
0.5	47.6 ± 2.7	5.7 ± 1.5	6.8 ± 1.5	0.50	90.1 ± 3.9	16.4 ± 2.4
1.0	31.4 ± 2.3	5.1 ± 1.4	8.1 ± 1.6	1.0	97.5 ± 4.0	17.7 ± 2.5
2.0		5.2 ± 1.4	8.9 ± 1.6	2.0	99.0 ± 4.0	16.2 ± 2.4
3.0	34.2 ± 2.4	7.8 ± 1.6	9.4 ± 1.6	3.0	84.1 ± 3.8	15.6 ± 2.4
6.0		6.5 ± 1.5		6.0	91.6 ± 3.9	16.8 ± 2.5
12.0	27.6 ± 2.2	7.2 ± 1.5	11.7 ± 1.7	12.0	95.3 ± 4.0	15.3 ± 2.4
24.0	25.1 ± 2.1	15.1 ± 1.8	12.4 ± 1.7	24.0	94.0 ± 3.9	15.1 ± 2.4
48.0	29.0 ± 2.2	16.3 ± 1.9	18.2 ± 1.9	48.0	96.6 ± 4.0	15.1 ± 2.4
96.0	27.1 ± 2.2	14.9 ± 1.8	12.3 ± 1.7			
120.0	28.1 ± 2.2	15.2 ± 1.8				
	concentration = 0.01 mg/ml				0.021 mg/ml	0.014 mg/ml
0.5	19.8 ± 2.0	Below detection	Below detection	0.083	35.9 ± 3.0	6.5 ± 2.2
1.0	18.6 ± 2.0			0.25	40.4 ± 3.0	7.6 ± 2.2
2.0	16.8 ± 1.9	0.6 ± 0.9	0.3 ± 0.8	0.50	50.1 ± 3.2	7.8 ± 2.2
4.0	17.1 ± 1.9	0.8 ± 0.9	1.4 ± 0.9	1.0	57.2 ± 3.3	8.3 ± 2.2
6.0	15.2 ± 1.8	1.7 ± 0.9	0.9 ± 0.9	2.0	68.9 ± 3.5	8.4 ± 2.2
12.0		3.0 ± 1.0	1.5 ± 0.9	3.0	71.0 ± 3.6	8.7 ± 2.2
24.0		3.6 ± 1.0	3.2 ± 1.0	6.0	61.3 ± 3.4	9.1 ± 2.2
48.0	13.8 ± 1.8	3.3 ± 1.0	2.5 ± 1.0	14.0	71.2 ± 3.6	9.3 ± 2.2
120.0	13.0 ± 1.8	3.0 ± 1.0	2.1 ± 1.0	24.0	69.3 ± 3.5	9.6 ± 2.2
336.0	14.5 ± 1.8			48.0	67.1 ± 3.5	9.4 ± 2.2
360.0	12.9 ± 1.8	3.1 ± 1.0	2.4 ± 1.0			
120.0	13.5 ± 1.8					

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Table B.21 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 30000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
concentration = 0.0011 mg/ml						
0.5	7.3 ± 1.6	0.4 ± 0.9	Below detection limit			
1.0	7.0 ± 1.5	0.3 ± 0.8				
2.0	6.4 ± 1.5	0.2 ± 0.8				
4.0	6.2 ± 1.5	0.2 ± 0.8				
6.0	5.7 ± 1.5	0.2 ± 0.8				
12.0	4.1 ± 1.4	0.2 ± 0.8				
24.0	4.2 ± 1.4	0.2 ± 0.8				
48.0	3.4 ± 1.4	0.2 ± 0.8				
120.0	3.6 ± 1.4	0.2 ± 0.8				
360.0		0.2 ± 0.8				

Note: The data is from LSC notebook #1, p 45 -54, p 70 - 109; LSC notebook #2, p 37-39; and LSC notebook #3, p 39 - 75.

Table B.22 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 60000

time (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 1.9 mg/ml	
0.083	104.4 ± 4.1	91.8 ± 3.4
0.25	108.4 ± 4.2	101.1 ± 3.6
0.50	107.2 ± 4.2	93.1 ± 3.4
1.0	109.6 ± 4.2	97.6 ± 3.5
2.0	107.5 ± 4.2	95.8 ± 3.4
3.0	107.8 ± 4.2	90.9 ± 3.4
6.0	107.5 ± 4.2	89.7 ± 3.4
12.0	110.0 ± 4.2	89.2 ± 3.4
24.0	114.4 ± 4.2	88.8 ± 3.3
48.0	109.4 ± 4.2	89.6 ± 3.4
	concentration = 1.0 mg/ml	
0.083	98.2 ± 3.5	70.9 ± 3.1
0.25	103.4 ± 3.6	83.4 ± 3.3
0.50	102.4 ± 3.6	84.9 ± 3.3
1.0	100.9 ± 3.5	85.9 ± 3.3
2.0	98.6 ± 3.5	88.7 ± 3.4
3.0	98.0 ± 3.5	89.2 ± 3.4
6.0	101.2 ± 3.5	89.6 ± 3.4
12.0	102.7 ± 3.6	88.9 ± 3.4
24.0	100.9 ± 3.5	88.6 ± 3.4
48.0	100.4 ± 3.5	88.2 ± 3.3
	concentration = 0.6 and 0.65 mg/ml	
0.083	87.0 ± 3.8	46.7 ± 3.1
0.25	87.6 ± 3.8	49.6 ± 3.2
0.50	79.5 ± 3.7	47.6 ± 3.1
1.0	85.1 ± 3.8	51.7 ± 3.2
2.0	84.2 ± 3.8	47.5 ± 3.1
3.0	81.2 ± 3.7	51.9 ± 3.2
6.0	80.5 ± 3.7	50.0 ± 3.2
12.0	78.1 ± 3.7	49.2 ± 3.2
24.0	80.3 ± 3.7	45.9 ± 3.1
48.0	76.7 ± 3.6	46.3 ± 3.1

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Table B.22 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 60000

time (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 0.12 and 0.13 mg/ml	
0.083	58.6 ± 3.3	10.2 ± 2.3
0.25	59.8 ± 3.3	9.2 ± 2.3
0.50	65.4 ± 3.5	11.4 ± 2.3
1.0	61.9 ± 3.4	11.4 ± 2.3
2.0	60.2 ± 3.3	11.5 ± 2.3
3.0	65.1 ± 3.5	8.6 ± 2.2
6.0	61.9 ± 3.4	10.3 ± 2.3
12.0	61.7 ± 3.4	10.2 ± 2.3
24.0	60.7 ± 3.3	10.2 ± 2.3
48.0	60.0 ± 3.3	10.1 ± 2.2

Note: The data is from LSC notebook #3, p 65 - 97.

Table B.23 Counts Per Minute Per Square Centimeter Obtained after Adsorption with Time

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 140000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	PS(COOH)$_2$	PS(OH)$_2$
concentration =					2.34 mg/ml	2.55 mg/ml
				0.25	161.0 ± 4.8	51.1 ± 3.2
				0.50	167.8 ± 4.9	56.2 ± 3.4
				1.0	167.1 ± 4.9	59.4 ± 3.4
				2.0	170.7 ± 4.9	58.3 ± 3.4
				3.0	165.1 ± 4.8	61.7 ± 3.4
				6.0	164.4 ± 4.8	61.1 ± 3.4
				12.0	165.9 ± 4.8	60.3 ± 3.4
				24.0	166.4 ± 4.9	60.5 ± 3.4
concentration = 1.2 mg/ml					1.27 mg/ml	1.29 mg/ml
0.167	69.5 ± 3.0		29.2 ± 2.2	0.25	157.8 ± 4.8	42.1 ± 3.1
0.25	59.2 ± 2.9		17.2 ± 1.9	0.50	162.4 ± 4.8	53.3 ± 3.3
0.50	50.2 ± 2.7		16.4 ± 1.9	1.0	164.2 ± 4.9	56.6 ± 3.4
1.0	56.2 ± 2.8		25.0 ± 2.1	2.0	157.7 ± 4.8	52.9 ± 3.3
4.0	45.7 ± 2.6		30.1 ± 2.3	3.0	163.8 ± 4.9	53.7 ± 3.3
12.0	64.5 ± 3.1		35.8 ± 2.5	6.0	165.8 ± 4.9	52.1 ± 3.3
24.0	54.7 ± 2.8		39.0 ± 2.5	12.0	163.5 ± 4.9	50.7 ± 3.3
72.0	62.2 ± 3.0		39.4 ± 2.6	24.0	163.7 ± 4.9	52.0 ± 3.3
96.0	66.6 ± 3.1		41.3 ± 2.6			
336.0	58.3 ± 2.9		40.1 ± 2.6			
360.0	64.4 ± 3.1		39.6 ± 2.6			
concentration =					0.586mg/ml	0.62 mg/ml
				0.25	93.9 ± 3.9	20.4 ± 2.5
				0.50	96.5 ± 3.9	22.2 ± 2.6
				1.0	98.0 ± 3.9	22.3 ± 2.6
				2.0	9.7 ± 4.0	22.5 ± 2.6
				3.0	99.8 ± 4.0	23.0 ± 2.5
				6.0	98.5 ± 3.9	23.5 ± 2.6
				12.0	100.3 ± 4.0	24.4 ± 2.6
				24.0	100.5 ± 4.0	25.0 ± 2.7

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Table B.23 Continued

substrate - glass; solvent - toluene; temperature - 23.0 ± 1.0°C; M_n = 140000

t (h)	PS-COOH	PS-OH	PS-H	t (h)	$PS(COOH)_2$	$PS(OH)_2$
	concentration = 0.12 mg/ml				0.164 mg/ml	0.126 mg/ml
0.5	11.2 ± 1.7		11.4 ± 1.7	0.25	59.4 ± 3.4	6.6 ± 2.1
1.0	13.9 ± 1.8		12.7 ± 1.8	0.50	68.5 ± 3.5	7.1 ± 2.1
2.0	47.6 ± 2.7		13.8 ± 1.8	1.0	78.1 ± 3.7	7.3 ± 2.2
4.0	15.4 ± 1.9		15.8 ± 1.9	2.0	54.9 ± 3.3	5.9 ± 2.1
12.0			18.4 ± 2.0	3.0	60.1 ± 3.4	7.0 ± 2.1
24.0	19.5 ± 2.0		17.4 ± 2.0	6.0	75.0 ± 3.6	6.8 ± 2.1
48.0	18.0 ± 2.0		17.9 ± 2.0	12.0	71.4 ± 3.6	7.2 ± 2.1
72.0	20.1 ± 2.0			24.0	77.0 ± 3.7	7.1 ± 2.1
96.0	20.6 ± 2.1		19.0 ± 2.0			
336.0	20.8 ± 2.1					
360.0	20.5 ± 2.0		18.5 ± 2.0			
	concentration = 0.012 mg/ml				0.021 mg/ml	0.015 mg/ml
0.5	6.1 ± 1.5		5.7 ± 1.5	0.25	16.3 ± 2.4	1.9 ± 2.0
1.0	6.8 ± 1.5		6.0 ± 1.5	0.50	23.5 ± 2.6	2.3 ± 2.0
2.0	6.3 ± 1.5		6.2 ± 1.5	1.0	26.0 ± 2.6	3.7 ± 2.0
4.0	6.7 ± 1.5		6.1 ± 1.5	2.0	27.5 ± 2.6	5.3 ± 2.1
12.0	7.2 ± 1.5		6.3 ± 1.5	3.0	28.4 ± 2.7	4.8 ± 2.0
24.0	9.0 ± 1.6		7.0 ± 1.5	6.0	29.6 ± 2.8	4.9 ± 2.0
48.0	7.4 ± 1.6		6.3 ± 1.5	14.0	28.6 ± 2.7	5.2 ± 2.1
96.0	8.4 ± 1.6		6.2 ± 1.5	24.0	29.2 ± 2.8	5.3 ± 2.1
360.0	7.5 ± 1.6		6.2 ± 1.5			
	concentration = 0.0014 mg/ml					
24.0	0.9 ± 1.2		0.5 ± 1.2			
48.0	1.1 ± 1.2		0.6 ± 1.2			
96.0	1.0 ± 1.2		0.4 ± 1.2			
360.0	1.2 ± 1.2		0.4 ± 1.2			

Note: The data is from LSC notebook #1, p 127 - 139; LSC notebook #2, p 11 - 18; and LSC notebook #3, p 79 - 100.

Table B.24 Surface density, Distance between Graft Sites, Graft Density and Solution Characteristics in Cyclohexane

Number averaged Molecular weight - 5000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	$S \times 10^{-13}$ (cm^{-2})	D (Å)	σ
PS-COOH							
20.0	0.80	0.0015	14.4	0.3	0.86	34.2	0.049
		0.0120	115.0	2.4	1.37	27.0	0.080
		0.1100	1060.0	22.0	3.12	17.9	0.180
		0.5600	5380.0	112.0	3.85	16.1	0.220
		1.0300	9900.0	206.0	4.41	15.1	0.250
PS-OH							
20.0	0.80	0.0011	10.6	0.22	0.43	48.0	0.025
		0.0110	105.6	2.2	0.53	43.4	0.030
		0.1100	1056.2	22.0	0.64	39.6	0.036
		0.5300	5088.8	106.0	0.88	33.7	0.050
		1.0500	10081.6	210.0	0.98	32.0	0.054
PS-H							
20.0	0.80	0.0012	11.5		0.37	51.8	0.021
		0.0160	153.6		0.43	48.0	0.025
		0.1200	1152.2		0.53	43.4	0.030
		0.5100	4896.8		0.72	37.2	0.041
		1.0800	10369.7		0.82	34.9	0.047

Note: R_g is the radius of gyration of the above polystyrenes at 34.5 °C in cyclohexane from reference 24 (Chapter 4). S_0 is the number of coils per square centimeter of the surface if there were no interaction with the surface and the coils just pack the surface. S is the number of coils per square centimeter after adsorption at equilibrium and is called the surface density [6, Chapter 4]. If $S > S_0$ then the polystyrene buoys will overlap. Conc stands for the concentration of the solution in mg/ml. S.C. stands for the concentration of the polystyrene segments in moles/liter while E.C. stands for the concentration of the end group (-COOH or -OH) in moles/liter. D is the distance in angstrom between grafted chains and σ is the normalized grafting density (unit less) as defined by de Gennes [22, Chapter 4].

Table B.25 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Cyclohexane

Number averaged Molecular weight - 10000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	$S \times 10^{-13}$ (cm^{-2})	D (Å)	σ
PS-COOH							
28.5	0.39	0.0011	10.6	0.11	0.34	54.0	0.020
		0.010	96.0	1.0	0.55	42.5	0.032
		0.095	912.1	9.5	1.53	25.6	0.087
		0.480	4608.7	48.0	2.37	20.6	0.135
		1.150	11041.8	115.0	2.60	19.6	0.148
PS-OH							
28.5	0.39	0.0014	13.4	0.14	0.30	58.2	0.017
		0.013	124.8	1.3	0.36	53.0	0.020
		0.105	1008.2	10.5	0.40	50.2	0.023
		0.550	5280.8	55.0	0.54	43.2	0.031
		1.085	10417.7	108.5	0.66	38.9	0.038
PS-H							
28.5	0.39	0.0010	9.6		0.28	60.1	0.016
		0.011	105.6		0.30	57.6	0.017
		0.118	1133.0		0.44	47.7	0.025
		0.520	4992.8		0.49	45.3	0.028
		1.155	11089.8		0.63	39.8	0.036
HOOC-PS-COOH							
28.5	0.39	0.015	144.0	3.0	0.19	73.2	0.011
		0.150	1440.2	30.0	0.28	60.1	0.016
		0.938	9006.2	187.6	0.57	41.8	0.033
		1.510	14498.3	302.0	1.91	22.9	0.109
HO-PS-OH							
28.5	0.39	0.019	182.4	3.8	0.09	105.2	0.005
		0.190	1824.3	38.0	0.14	85.0	0.008
		0.935	8977.4	187.0	0.22	67.9	0.012
		1.450	13922.2	290.0	0.41	49.4	0.023

Note: The terminology is the same as in Table B.24.

Table B.26 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Cyclohexane

Number averaged Molecular weight - 30000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	S x 10^{-13} (cm^{-2})	D (Å)	σ
PS-COOH							
49.3	0.13	0.0011	10.6	0.037	0.22	67.9	0.012
		0.012	115.2	0.4	0.32	56.5	0.018
		0.112	1075.4	3.73	0.75	36.6	0.043
		0.505	4848.8	16.8	0.99	31.9	0.056
		1.018	9774.4	33.9	1.13	29.7	0.064
PS-OH							
49.3	0.13	0.0012	11.5	0.04	0.14	84.4	0.008
		0.011	105.6	0.37	0.18	74.0	0.011
		0.108	1037.0	3.6	0.23	66.1	0.012
		0.535	5136.8	17.8	0.33	54.9	0.018
		1.094	10504.1	36.5	0.37	52.3	0.020
PS-H							
49.3	0.13	0.0010	9.6		0.14	83.2	0.008
		0.011	105.6		0.18	73.6	0.011
		0.112	1075.4		0.21	69.5	0.012
		0.540	5184.8		0.31	57.1	0.018
		1.060	10177.6		0.35	53.8	0.020
HOOC-PS-COOH							
49.3	0.13	0.016	153.6	1.07	0.07	119.3	0.004
		0.150	1440.2	10.0	0.10	98.8	0.006
		0.540	5184.8	36.0	0.42	48.8	0.024
		1.100	10561.7	73.3	0.56	42.3	0.032
		2.430	23331.7	162.0	1.22	28.6	0.070
HO-PS-OH							
49.3	0.13	0.027	259.2	1.80	0.026	195.7	0.0015
		0.203	1949.1	13.53	0.04	154.0	0.002
		0.560	5376.9	37.33	0.10	99.8	0.006
		1.120	10753.7	74.67	0.18	73.6	0.011
		2.710	26020.2	180.67	0.53	43.4	0.030

Note: The terminology is the same as in Table B.24.

Table B.27 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Cyclohexane

Number average molecular weight - 60000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	S x 10^{-13} (cm^{-2})	D (Å)	σ
HOOC-PS-COOH							
69.8	0.065	0.013	124.8	0.43	0.12	91.9	0.007
		0.101	969.8	3.37	0.15	81.5	0.009
		0.567	5444.1	18.9	0.37	52.2	0.021
		1.004	9639.9	33.5	0.45	47.3	0.026
		1.922	18454.2	64.1	0.64	39.5	0.037
HO-PS-OH							
69.8	0.065	0.017	163.2	0.57	0.07	121.9	0.004
		0.120	1152.2	4.0	0.10	101.9	0.006
		0.711	6826.7	23.7	0.25	63.5	0.014
		1.110	10657.7	37.0	0.30	57.4	0.017
		2.234	21449.8	74.5	0.38	51.2	0.022

Note: R_g is the radius of gyration of the above polystyrenes at 34.5 °C in cyclohexane from reference 24 (Chapter 4). S_0 is the number of coils per square centimeter of the surface if there were no interaction with the surface and the coils just pack the surface. S is the number of coils per square centimeter after adsorption at equilibrium and is called the surface density [6, Chapter 4]. If $S > S_0$ then the polystyrene buoys will overlap. Conc stands for the concentration of the solution in mg/ml. S.C. stands for the concentration of the polystyrene segments in moles/liter while E.C. stands for the concentration of the end group (-COOH or -OH) in moles/liter. D is the distance in angstrom between grafted chains and σ is the normalized grafting density (unit less) as defined by de Gennes [22, Chapter 4].

Table B.28 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Cyclohexane

Number average molecular weight - 140000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. $\times 10^6$ (moles/l)	E.C. $\times 10^6$ (moles/l)	$S \times 10^{-13}$ (cm^{-2})	D (Å)	σ
PS-COOH							
108.1	0.027	0.0012	11.5	0.009	0.07	121.3	0.004
		0.011	105.6	0.079	0.08	109.7	0.005
		0.108	1037.0	0.77	0.11	95.1	0.006
		0.535	5136.8	3.82	0.16	78.3	0.009
		1.094	10504.1	7.81	0.19	73.2	0.011
PS-OH							
108.1	0.027						
PS-H							
108.1	0.027	0.0014	13.4		0.07	123.7	0.004
		0.016	153.6		0.08	113.3	0.004
		0.115	1104.2		0.09	105.7	0.005
		0.517	4964.0		0.11	96.0	0.006
		1.045	10033.6		0.12	91.6	0.007
HOOC-PS-COOH							
108.1	0.027	0.013	124.8	0.19	0.07	121.3	0.004
		0.109	1046.6	1.56	0.08	109.7	0.005
		0.570	5472.9	8.14	0.11	95.1	0.006
		1.147	11013.0	16.39	0.16	78.3	0.009
		2.410	23139.7	34.43	0.19	73.2	0.011
HO-PS-OH							
108.1	0.027	0.015	144.0	0.21	0.064	125.3	0.0036
		0.126	1209.8	1.80	0.077	114.3	0.0044
		0.620	5953.0	8.86	0.093	104.0	0.0053
		1.294	12424.4	18.49	0.12	92.8	0.0066
		2.553	24512.7	36.47	0.14	85.2	0.0079

Note: The terminology is the same as in Table B.24.

Table B.29 Surface density, Distance between Graft Sites, Graft Density and Solution Characteristics in Toluene

Number average molecular weight - 5000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	S x 10^{-13} (cm^{-2})	D (Å)	σ
PS-COOH							
22.0	0.66	0.0015	14.4	0.3	0.07	117.6	0.004
		0.010	96.0	2.0	0.16	79.9	0.009
		0.054	518.5	10.8	0.95	32.4	0.054
		0.102	979.4	20.4	1.59	25.1	0.091
		0.150	1440.2	30.0	1.67	24.4	0.095
		1.100	10561.7	220.0	1.71	24.2	0.098
PS-OH							
22.0	0.66	0.0011	10.6	0.22			
		0.010	96.0	2.0			
		0.052	499.3	10.4	0.05	144.1	0.003
		0.105	1008.2	21.0	0.11	96.0	0.006
		0.153	1469.0	30.6	0.16	79.9	0.009
		1.030	9889.6	206.0	0.39	50.9	0.022
PS-H							
22.0	0.66	0.0018	17.3				
		0.015	144.0				
		0.055	528.1				
		0.112	1075.4				
		0.540	5184.8				
		1.120	10753.7				

Note: R_g is the radius of gyration of the above polystyrenes at 23.0 °C in toluene from reference 24 [Chapter 4]. S_0 is the number of coils per square centimeter of the surface if there were no interaction with the surface and the coils just pack the surface. S is the number of coils per square centimeter after adsorption at equilibrium and is called the surface density [6, Chapter 4]. If $S > S_0$ then the polystyrene buoys will overlap. Conc stands for the concentration of the solution in mg/ml. S.C. stands for the concentration of the polystyrene segments in moles/liter while E.C. stands for the concentration of the end group (-COOH or -OH) in moles/liter. D is the distance in angstrom between grafted chains and σ is the normalized grafting density (unit less) as defined by de Gennes [24, Chapter 4].

Table B.30 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Toluene

Number average molecular weight - 10000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	S x 10^{-13} (cm^{-2})	D (Å)	σ
PS-COOH							
33.0	0.29	0.0012	11.5	0.12	0.06	128.9	0.003
		0.012	115.0	1.2	0.14	85.0	0.008
		0.058	556.9	5.8	0.35	53.5	0.020
		0.115	1104.2	11.5	0.65	39.2	0.037
		0.575	5520.9	57.5	0.93	32.7	0.053
		1.142	10965.0	114.2	1.11	30.0	0.064
PS-OH							
33.0	0.29	0.0011	10.6	0.11			
		0.010	96.0	1.0			
		0.051	489.7	5.1	0.04	166.3	0.002
		0.104	998.6	10.4	0.08	108.9	0.005
		0.500	480.1	50.0	0.18	75.7	0.010
		1.002	9620.7	100.2	0.22	67.9	0.012
PS-H							
33.0	0.29	0.0014	13.4				
		0.017	163.2				
		0.058	556.9		0.03	182.2	0.002
		0.118	1133.0		0.07	117.6	0.004
		0.520	4992.8		0.10	98.8	0.006
		1.155	11089.8		0.13	86.9	0.008
HOOC-PS-COOH							
33.0	0.29	0.015	144.0	3.0	0.39	50.5	0.022
		0.067	643.3	13.4	0.87	34.0	0.049
		0.120	1152.2	24.0	1.01	31.4	0.058
		0.560	5376.9	112.0	1.21	28.7	0.069
		1.050	10081.6	210.0	1.26	28.1	0.072
		1.500	14402.3	300.0	1.29	27.8	0.074
HO-PS-OH							
33.0	0.29	0.019	182.4	3.8	0.11	93.5	0.007
		0.056	537.7	11.2	0.25	63.6	0.014
		0.120	1152.2	24.0	0.39	50.5	0.022
		0.497	4772.0	99.4	0.55	42.7	0.031
		1.060	10177.6	212.0	0.78	35.7	0.045

Note: The terminology is the same as in Table B.29.

Table B.31 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Toluene

Number average molecular weight - 30000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	$S \times 10^{-13}$ (cm^{-2})	D (Å)	σ
PS-COOH							
62.9	0.08	0.0011	10.6	0.037	0.01	288.1	0.001
		0.012	115.0	0.4	0.02	223.2	0.001
		0.051	489.7	1.7	0.05	147.2	0.003
		0.112	1075.4	3.73	0.08	108.9	0.005
		0.505	4848.8	16.8	0.22	67.3	0.013
		1.018	9774.4	33.9	0.27	60.5	0.016
PS-OH							
62.9	0.08	0.0015	14.4	0.05			
		0.015	144.0	0.5	0.02	223.2	0.001
		0.050	480.0	1.67	0.04	161.9	0.002
		0.153	1469.0	5.1	0.05	138.4	0.003
		1.145	10993.8	38.2	0.09	107.6	0.005
PS-H							
62.9	0.08	0.0015	14.4				
		0.014	134.4		0.02	235.3	0.001
		0.067	643.3		0.04	171.2	0.002
		0.136	1305.8		0.05	150.5	0.003
		1.261	12107.5		0.09	117.6	0.004
HOOC-PS-COOH							
62.9	0.08	0.021	201.6	1.40	0.17	75.7	0.010
		0.119	1142.6	7.93	0.25	62.9	0.014
		0.479	4599.1	31.93	0.38	51.6	0.021
		0.709	6807.5	47.27	0.54	43.1	0.031
		2.600	24964.0	173.33	0.54	43.0	0.031
HO-PS-OH							
62.9	0.08	0.014	134.4	0.93	0.002	212.8	0.0013
		0.150	1440.2	10.0	0.004	161.9	0.0022
		0.520	4992.8	34.67	0.006	128.9	0.0034
		1.030	9889.6	68.67	0.010	101.9	0.0055
		2.210	21219.4	147.33	0.010	101.9	0.0055

Note: The terminology is the same as in Table B.29.

Table B.32 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Toluene

Number average molecular weight - 60000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. x 10^6 (moles/l)	E.C. x 10^6 (moles/l)	S x 10^{-13} (cm^{-2})	D (Å)	σ
HOOC-PS-COOH							
94.2	0.036	0.012	115.2	0.40	0.066	122.9	0.0038
		0.119	1142.6	3.97	0.080	111.6	0.0046
		0.603	5789.7	20.10	0.110	96.9	0.0061
		1.020	9793.6	34.00	0.130	86.9	0.0076
		1.890	18146.9	63.00	0.140	83.5	0.008
HO-PS-OH							
94.2	0.036	0.014	134.4	0.47	0.013	276.8	0.0007
		0.129	1238.6	4.30	0.015	257.7	0.0009
		0.649	6231.4	21.63	0.066	122.9	0.0038
		0.965	9265.5	32.17	0.116	92.7	0.0066
		1.900	18242.9	63.33	0.118	91.9	0.0068

Note: R_g is the radius of gyration of the above polystyrenes at 23 °C in toluene from reference 24 [Chapter 4]. S_0 is the number of coils per square centimeter of the surface if there were no interaction with the surface and the coils just pack the surface. S is the number of coils per square centimeter after adsorption at equilibrium and is called the surface density [6, Chapter 4]. If $S > S_0$ then the polystyrene buoys will overlap. Conc stands for the concentration of the solution in mg/ml. S.C. stands for the concentration of the polystyrene segments in moles/liter while E.C. stands for the concentration of the end group (-COOH or -OH) in moles/liter. D is the distance in angstrom between grafted chains and σ is the normalized grafting density (unit less) as defined by de Gennes [24, Chapter 4].

Table B.33 Surface Density, Distance between Graft Sites, Graft Density and Solution Characteristics in Toluene

Number average molecular weight - 140000

R_g (Å)	$S_0 \times 10^{-13}$ (cm^{-2})	Conc (mg/ml)	S.C. $\times 10^6$ (moles/l)	E.C. $\times 10^6$ (moles/l)	S $\times 10^{-13}$ (cm^{-2})	D (Å)	σ
PS-COOH							
157.0	0.013	0.0014	13.4	0.010	0.003	576.2	0.0002
		0.012	115.2	0.086	0.007	381.2	0.0004
		0.054	518.5	0.386	0.009	332.7	0.0005
		0.120	1152.2	0.857	0.014	269.5	0.0008
		0.582	5588.1	4.157	0.030	177.2	0.0020
		1.204	11560.2	8.6	0.039	160.7	0.0022
PS-OH							
157.0	0.013						
PS-H							
157.0	0.013	0.0014	13.4		0.0003	622.4	0.0002
		0.013	124.8		0.001	407.5	0.0003
		0.057	547.3		0.008	349.8	0.0005
		0.118	1133.0		0.013	278.4	0.0007
		0.590	5664.9		0.028	189.1	0.0016
		1.171	11243.4		0.030	200.2	0.0014
HOOC-PS-COOH							
157.0	0.013	0.021	201.6	0.30	0.018	235.3	0.0010
		0.164	1574.7	2.34	0.044	151.0	0.0025
		0.586	5626.5	8.37	0.059	130.3	0.0034
		1.269	12184.3	18.13	0.096	102.3	0.0054
		2.342	22486.8	33.46	0.097	101.6	0.0055
HO-PS-OH							
157.0	0.013	0.015	144.0	0.21	0.004	482.1	0.0002
		0.126	1209.8	1.8	0.005	440.1	0.0003
		0.620	5953.0	8.86	0.016	254.1	0.0009
		1.294	12424.4	18.49	0.031	179.7	0.0018
		2.553	24512.7	36.47	0.036	166.3	0.0021

Note: The terminology is the same as in Table B.29.

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