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
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GRAFT COPOLYMER STABILIZERS
FOR NON-AQUEOUS POLYMER DISPERSIONS

by

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A Doctoral Thesis
submitted in partial fulfilment of the requirements
for the award of Doctor of Philosophy
of the Loughborough University of Technology

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Department of Chemistry

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ORIGINALITY

The work presented in this thesis has been carried out by the author, except where otherwise acknowledged, and has not been previously submitted to this University or any other Institution.

To my wife Bethan
for her patience and understanding

ABSTRACT

Free-radical solution polymerization techniques have been used to prepare carboxyl-terminated poly(methyl methacrylate) and poly(2-ethyl hexyl acrylate) homopolymers. The molar masses of these prepolymers were readily controlled and they were found to be approximately monofunctional with respect to carboxyl groups. These carboxyl-terminated prepolymers were converted to methacrylate-terminated macromonomers via acyl chloride-terminated intermediates. The macromonomer functionalities obtained by this procedure were high, typically 0.90-1.05 methacrylate groups per molecule on average. The prepolymers and macromonomers were characterized using End-group analysis (EGA), Infra-red spectroscopy (IR), ^1H Nuclear Magnetic Resonance spectroscopy (^1H NMR) and Gel-permeation Chromatography (GPC).

Polystyrene-graft-poly(methyl methacrylate) and polystyrene-graft-poly(2-ethyl hexyl acrylate) copolymers were prepared by the free-radical solution copolymerization of macromonomers (M_2) with styrene (M_1). A dual detector GPC method was used to estimate macromonomer conversions. Unreacted macromonomer and styrene were removed and the purified graft copolymers were characterized by Thin-layer Chromatography (TLC), GPC, IR and ^1H NMR. It was shown that efficient grafting had occurred by copolymerization of the macromonomer end-group and that ungrafted polystyrene backbone was not produced. The graft copolymer chemical compositions and physical architectures were controlled by changing the comonomer feed composition or the macromonomer molar mass. Reactivity ratios (r_1) were determined by the Jaacks, Finemann-Ross and Kelen-Tüdös methods. It was shown that the reactivities of the methacrylate-terminated macromonomers were approximately similar to conventional methacrylates and independent of the macromonomer molar mass or composition within the limits investigated.

The polystyrene-graft-poly(2-ethyl hexyl acrylate) copolymers have been used as stabilizers in the free-radical non-aqueous dispersion polymerization of methyl methacrylate in aliphatic hydrocarbons. The poly(methyl methacrylate) particles were characterized by Transmission Electron Microscopy (TEM) in order to determine their size, shape and state of aggregation. Ultra-violet spectroscopy (UV) was used to determine the graft copolymer content of the particles, from which an estimate of surface coverage was made. The effects of varying the polymerization method, and both the composition and concentration of stabilizers used, were studied. The average particle size, particle size distribution and the state of aggregation were found to be dependent upon these parameters.

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CHAPTER ONE

INTRODUCTION

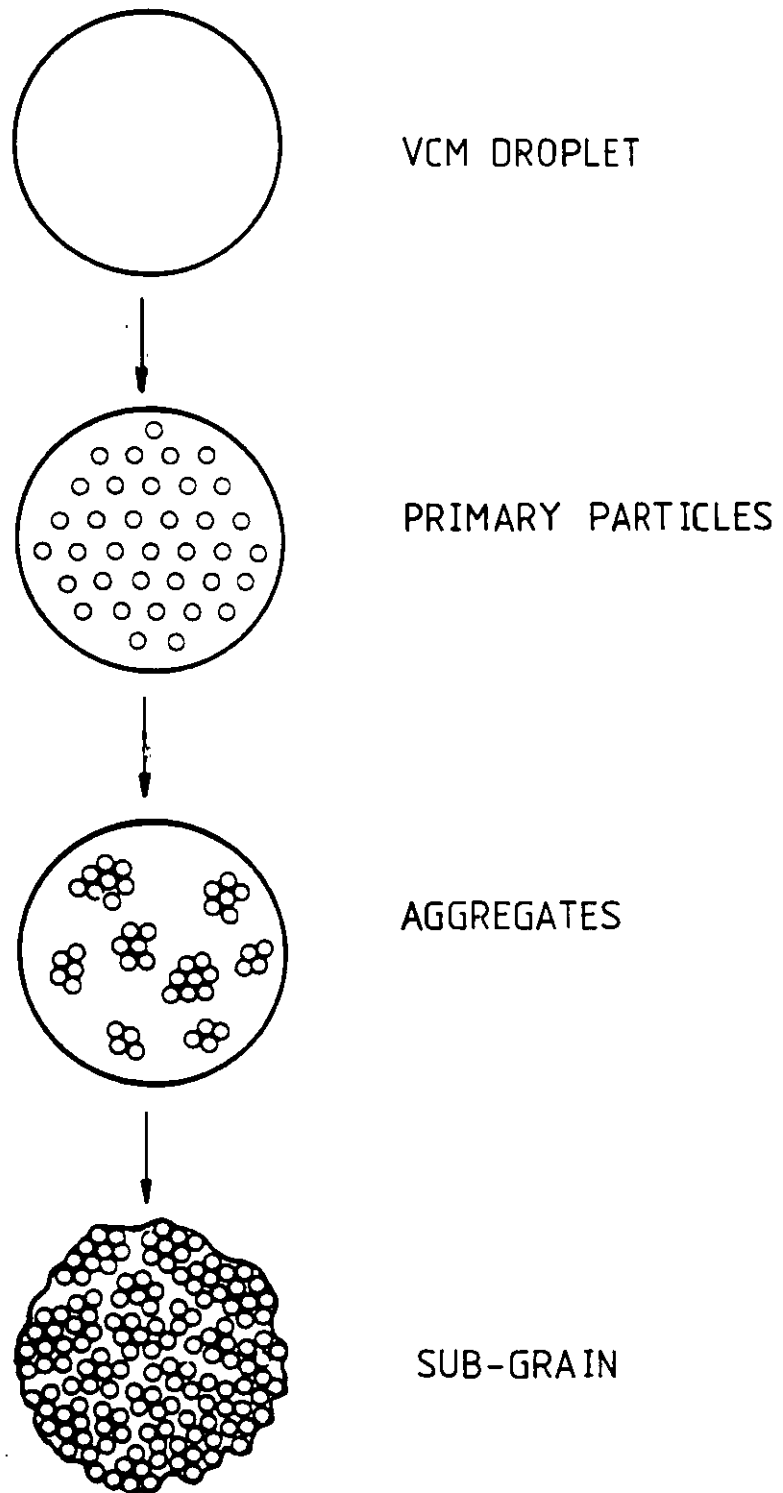
INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the world's major thermoplastics. Approximately 80% of PVC is produced by suspension polymerization [1]. In the suspension polymerization of vinyl chloride monomer (VCM), VCM is initially emulsified in water as droplets by agitation in the presence of a non-ionic protective colloid. This is generally termed the primary stabilizer which is water-soluble and typically a poly[(vinyl acetate)-co-(vinyl alcohol)] copolymer with a high vinyl alcohol content [1]. Polymerization of VCM is initiated by the thermal decomposition of a monomer-soluble free-radical initiator and the monomer droplets are converted to PVC grains.

Each monomer droplet can be considered as a miniature bulk polymerization. The formation of PVC within each monomer droplet is depicted in figure 1.1. The nomenclature used is that given by Allsopp [2]. VCM polymerizes and at a certain chain length the growing PVC radicals become insoluble and precipitate, although they are swollen by monomer which allows polymerization to continue. Polymer molecules which are produced in close proximity agglomerate to form basic particles or microdomains (10-20nm). These basic particles are unstable and agglomerate repeatedly until primary particle nuclei are formed at <5% conversion. These primary particle nuclei or domains are colloidally stable initially with a size of 0.1-0.2 μ m. However, as polymerization proceeds, primary particles grow and coalesce to form aggregates with an initial size of 1-2 μ m at <10% conversion. The aggregates and their constituent primary particles grow throughout the polymerization resulting in final primary particle sizes of 0.6-0.8 μ m and final aggregate sizes of 2-10 μ m. Very porous structures are formed, the PVC grains. Figure 1.1 is simplified since there is a marked density change as VCM is converted to PVC. This results in contraction of the original monomer droplets and modification of the steric barrier

FIGURE 1.1

PVC PARTICLE FORMATION IN THE SUSPENSION
POLYMERIZATION OF VCM



provided by the primary stabilizer [1,2]. These changes reduce the stability of the partially polymerized droplets and some coalescence occurs. Therefore, the final PVC grains (~150 μ m) often contain several original monomer droplets (~40 μ m). The polymerized droplets are often termed sub-grains.

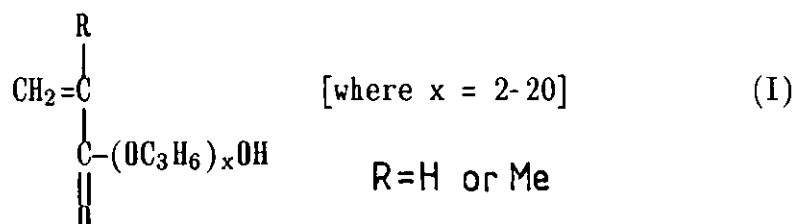
PVC must be capable of absorbing various process stabilizers, lubricants and plasticizers for processing. The gelling characteristics of the grains must allow processing to occur as rapidly as possible. Also, any residual VCM must be removed efficiently since it is carcinogenic. All of these properties require PVC grains with some degree of porosity. The actual internal porosity of the grains normally amounts to 20-30%, depending upon the application [3]. The precipitation and agglomeration processes inside the monomer phase are important to resin porosity. It is the structure and morphology of the PVC grains, particularly the aggregation of primary particles, which largely controls the processing characteristics of PVC [4]. The morphology of the grains depends on many factors including the agitation speed, the primary stabilizer used and the polymerization temperature [5]. Often, so-called secondary stabilizers are added in order to increase porosity. Poly[(vinyl acetate)-co-(vinyl alcohol)] copolymers with a low vinyl alcohol content are typically used [6]. Such secondary stabilizers have a higher solubility in the VCM phase than primary stabilizers, which are water-soluble. The role of the secondary stabilizers is almost certainly to influence the agglomeration processes [1] illustrated in figure 1.1.

The stabilization of PVC particles swollen by VCM represents a problem in the stabilization of polymer particles in non-aqueous media. The prevention of flocculation of polymer particles in such media can be achieved by surrounding the particles with surface layers of polymeric stabilizer [7]. Such a mechanism, often known as steric stabilization, has been used in the surface coatings industry for dispersion polymerization in non-aqueous

media, particularly by Barrett et al [8]. The most successful type of steric stabilizer devised for use in dispersion polymerization has been based on a block or graft copolymer which consists of two essential components, one soluble and one insoluble in the continuous phase [9]. The insoluble component physically adsorbs on to the particle surface and the soluble component protrudes into the continuous phase. In this way, the soluble components are firmly attached at the surface and provide a swollen layer covering the particle surface.

It must be emphasized that from this point, unless otherwise stated, the terms stabilizer and stabilization used in this thesis imply the use of a method for producing polymer dispersions which are stable towards aggregation processes. This is, of course, quite different from the definition in which these terms are used in other branches of polymer science where they refer to processes and additives which confer on treated polymers an enhanced stability towards thermal, oxidative or photolytic degradation processes.

In reference to PVC suspension polymerization, there are few examples in the literature of the use of secondary stabilizers to control particle morphology. Murray [4] has patented his invention of polymerizing VCM in the presence of a comonomer of the general formula:

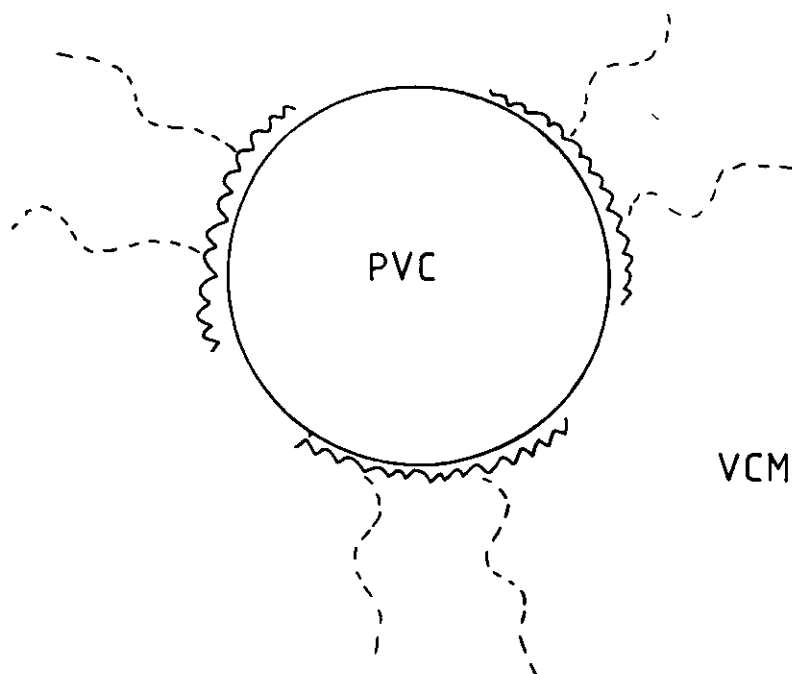




It is thought that such comonomers are covalently bound to the PVC particle surfaces and that the poly(oxypropylene) tails

protrude into the VCM phase, thereby providing steric stabilization of primary particles. Törnelli and Uustalu [10] have found that the addition of poly[ethylene-co-(vinyl acetate)] or poly(methyl methacrylate) (PMMA) gave increased stability to PVC primary particles, with the largest effect obtained using PMMA. In this case, it is thought that stabilization is achieved by the action of a graft copolymer formed in situ by the grafting of PVC from PMMA. The PVC component then anchors the PMMA component to the particle surface and the PMMA component provides stabilization by being soluble in the VCM. However, there are no examples in the open literature of the use of preformed block or graft copolymers as secondary stabilizers for PVC particles formed during the suspension polymerization of VCM. It has been shown that the use of such polymers in dispersion polymerization can produce controlled dispersed-phase properties which depend on both the composition and concentration of stabilizers used [8,11]. The ultimate objective of this research programme was to produce well-characterized secondary stabilizers capable of stabilizing and controlling the PVC primary particle size during suspension polymerization (also see recommendations section 5.2).

Preformed block and graft copolymers can be prepared by a variety of methods [12]. There has been much interest in recent years in the synthesis of graft copolymers from the copolymerization of macromonomers with conventional monomers [13,14]. Macromonomer molecules which copolymerize result in grafts whereas the comonomer(s) which copolymerize essentially constitute the backbone of the resulting graft copolymers. This method is favourable since it is possible to produce graft copolymers with well-defined and controlled compositions. From the use of block and graft copolymers in dispersion polymerization, a suitable graft copolymer secondary stabilizer for PVC particles surrounded by VCM can be envisaged as containing a backbone insoluble in VCM with the grafts soluble in VCM. This is illustrated in figure 1.2. However, it is often preferable in dispersion polymerization for the insoluble component in the stabilizer to

FIGURE 1.2 THE STERIC STABILIZATION OF PVC PARTICLES IN VCM
USING PREFORMED COMB-GRAFT COPOLYMERS



-  Copolymer backbone insoluble in VCM
-  Copolymer side chains soluble in VCM

be identical in composition to the dispersed-phase polymer [9]. This means that it would be preferable to produce graft copolymers with PVC backbones for the stabilization of PVC particles. Graft copolymers prepared via macromonomers are normally prepared by free-radical solution copolymerization [13,14]. The first problem is that the true solution (co)polymerization of VCM is extremely difficult to achieve [15] due to the poor solubility of PVC in many solvents and the tendency of PVC radicals to chain transfer to solvents. However, it has been shown in several studies in dispersion polymerization that it is not necessary for the insoluble anchoring component of the stabilizers to be identical in composition to the dispersed-phase polymer. This has been illustrated more conclusively in the open literature for block copolymer rather than graft copolymer stabilizers. For example, Shakir [16] and Taylor [17] have extensively studied the dispersion polymerization of methyl methacrylate using block copolymer stabilizers containing polystyrene (PS) anchor components. Waldbridge [9] also claims that the anchor components of graft copolymer stabilizers can be different in chemical composition to the dispersed phase, but in many of his examples these compositions were quite similar. Nevertheless, it may be possible to simply rely upon the insolubility of the graft copolymer backbone in VCM to provide the anchoring. The second problem is that of macromonomer reactivity in their copolymerizations with conventional monomers. The copolymerization behaviour of macromonomers is disputed in the literature with conflicting reports of the ability of the macromonomer chain to affect the reactivity of its terminal polymerizable end-group [13,18]. This has implications on the ability to control the chemical composition and physical chain architecture of the graft copolymers produced by this method.

The objectives of the present work were determined with these problems in mind. Firstly, a model system was chosen to study the copolymerization behaviour of macromonomers. This model system was chosen as the free-radical copolymerization of PMMA

macromonomers with styrene to produce polystyrene-graft-poly(methyl methacrylate) copolymers (PS-graft-PMMA). This system was chosen as a result of its potential ease of characterization. A very thorough characterization of the graft copolymers produced was performed in order to determine both macromonomer reactivities and how readily graft copolymer compositions could be controlled. Macromonomers can be synthesized by a variety of methods [14] but free-radical polymerization was used, since it is easier to perform than ionic polymerizations and it is more versatile, being more applicable to a wider range of monomers [12]. The principles of PMMA macromonomer synthesis and copolymerization with styrene were then applied to prepare poly(2-ethyl hexyl acrylate) (PEHA) macromonomers and polystyrene-graft-poly(2-ethyl hexyl acrylate) copolymers (PS-graft-PEHA). The same detailed characterization of the PS-graft-PEHA copolymers were performed as for PS-graft-PMMA copolymers in order to determine how these graft copolymer compositions could be controlled and whether the PEHA macromonomer reactivities differed to the PMMA macromonomers. PEHA macromonomers were studied since PEHA is soluble in VCM [19], and the incorporation of PEHA macromonomers represents grafts capable of behaving as the soluble component for graft copolymer secondary stabilizers used to stabilize PVC particles swollen by VCM in suspension polymerization. The synthesis of PS-graft-PEHA copolymers prepared from the copolymerization of PEHA macromonomers with styrene represents novel polymers and such a detailed characterization of all graft copolymers has not been achieved previously. The use of graft or block copolymers as stabilizers in dispersion polymerization requires the anchor component to have sufficient molar mass for it to be insoluble in the continuous phase [9]. It has been shown for the stabilization of polymer particles in n-alkanes that PS anchor blocks in stabilizing block copolymer molecules should have a number average molar mass (\bar{M}_n) of at least 10^4 g.mol⁻¹ [17]. The soluble component must also be large enough to provide a sufficient barrier to prevent flocculation [7,9]. It has been

shown that for graft copolymer stabilizers, grafts with molar masses of $\bar{M}_n \approx 1500 \text{ g.mol}^{-1}$ are sufficiently long to provide stability [9]. The conditions for the synthesis of all PS-graft-PMMA and PS-graft-PEHA copolymers were made with this in mind. Therefore, macromonomers with molar masses of at least $\bar{M}_n = 1500 \text{ g.mol}^{-1}$ were synthesized and copolymerized with styrene to produce backbone molar masses of approximately $\bar{M}_n = 10^4 \text{ g.mol}^{-1}$. The PS-graft-PEHA copolymers were then tested for their capabilities as stabilizers. The difference in the solubilities of PS and PEHA in hydrocarbons suggests that PS-graft-PEHA copolymers may be useful for stabilizing polymer particles in aliphatic hydrocarbon media. The soluble PEHA grafts could provide the stabilizing layer and could be anchored to the dispersed particles by the insoluble PS backbone. The use of PS-graft-PEHA copolymers as stabilizers in the free-radical dispersion polymerization of methyl methacrylate in aliphatic hydrocarbon was studied and, in particular, the effect of graft copolymer composition and concentration on the morphology of the PMMA dispersed phase. The dispersion polymerization of methyl methacrylate was chosen since many of the kinetic and mechanistic studies of dispersion polymerization reported have involved (meth)acrylate monomers [8]. The preparation of PMMA dispersions stabilized by PS-graft-PEHA copolymers represents novel systems. The PS anchor component is completely different in chemical composition to the PMMA dispersed phase.

CHAPTER TWO

THEORY

2.1 THE THEORY OF STERIC STABILIZATION

2.1.1 FORCES OF ATTRACTION

An important physical property of colloidal dispersions is the tendency of particles to aggregate. Encounters between particles dispersed in liquid media occur frequently and the stability of a dispersion depends upon the interactions between particles during these encounters. In the absence of a stabilization mechanism, the number of free particles is rapidly reduced to zero as a result of the mutual attraction between particles. Interactions between the atoms or molecules of two adjacent particles gives rise to an attractive force, usually called the van der Waals force. Three types of such intermolecular attraction are recognized [20], which were originally postulated to explain non-ideal gas behaviour.

- (i) Two molecules with permanent dipoles mutually orientate each other in such a way that, on average, attraction results.
- (ii) Dipolar molecules induce dipoles in other molecules so that attraction results.
- (iii) Attractive forces are also recognized between non-polar molecules. London [21] showed that the attraction between two inert gas molecules was a quantum-mechanical effect. Applying the Heisenberg Uncertainty Principle, he showed that random fluctuations in the charge distribution of one molecule could result in a transient dipole capable of inducing dipoles in other molecules. The London attractive force (also known as a dispersion force) between two adjacent molecules is therefore due to the attraction between transient dipoles.

Except for highly polar materials, London dispersion forces account for nearly all of the van der Waals attraction which is

operative. Since random fluctuations in the electric fields are involved, one molecule can readily participate in London interactions with several other molecules at the same time. This behaviour forms the basis of the concept of 'pair-wise' additivity for London dispersion forces. The London attractive potential energy (V_A) between two molecules is short range and decreases with the distance of separation (r) as follows

$$V_A = \frac{-L}{r^6} \quad (2.1)$$

where L is the London interaction constant.

For an assembly of molecules, the attractive force between two particles can be calculated by summing the attractions between all interparticle molecule pairs. Hamaker [22] calculated the magnitude of the attractive potential energy (V_A) generated by the London interaction between condensed bodies in a vacuum. He assumed that the pair-wise additivity concept used for calculating the London attraction between gas molecules could be applied to the corresponding interactions between molecules in different condensed bodies. However, Overbeek [23] recognized that values of V_A would be overestimated at large distances owing to a neglect of the finite time required for propagation of electromagnetic radiation between any fluctuating dipoles (the retardation effect). It must also be realized that the Hamaker method, the so-called microscopic approach, considers the sum of the attraction between pairs of elements, one on each particle, as if each were in complete isolation. In reality, each element is also affected by strong interactions from other elements within the same particle. Therefore, the interaction between elements in real particles would be expected to be significantly different to the same interaction between isolated elements. Hamaker [22] originally assumed that the two condensed bodies were separated by a vacuum. Therefore, for colloidal particles suspended in a liquid medium, it is necessary to consider the influence of the medium on the attractive forces. The presence of

a medium reduces the attractive forces in two ways. The primary effect describes the effect of the liquid medium on the transmission of the London field and it depends upon the dielectric constant of the medium. The secondary medium effect involves the finite attraction of the particles for the medium. This depends upon the difference between the energy required to separate two particle-medium pairs and the energy released by the formation of particle-particle and medium-medium pairs.

Another method for calculating the attractive energy between two bodies is the macroscopic approach of Lifschitz [24], in which both the interacting particles and the intervening medium are treated as continuous phases. This has the advantage that it automatically incorporates the medium and retardation effects which are introduced as separate corrections in the Hamaker microscopic model. However, the mathematical calculations required are complex and the Hamaker approach still finds widespread use, despite its fundamental defects.

2.1.2 THE STABILIZATION OF COLLOIDAL PARTICLES AGAINST FLOCCULATION

As a result of the forces of attraction described in the previous section, colloidal particles would flocculate in the absence of a stabilization mechanism. Colloidal stability is therefore achieved by the generation of repulsive forces of sufficient magnitude to overcome these inherent attractive forces. The predominant mechanism in an ionic, aqueous medium is recognized as being electrostatic charge stabilization. Deryagin and Landau [25] and Verwey and Overbeek [23] independently developed a quantitative theory for this, estimating the repulsive energy due to the overlap of electrical double layers and the attractive energy due to the London dispersion forces. However, non-aqueous media of low polarity are generally non-ionic (with low dielectric constants) and repulsive forces must be generated by

mechanisms other than electrostatic charge stabilization. This is achieved by surrounding the particle surfaces with a layer of soluble polymer; this mechanism is generally known as steric stabilization [7].

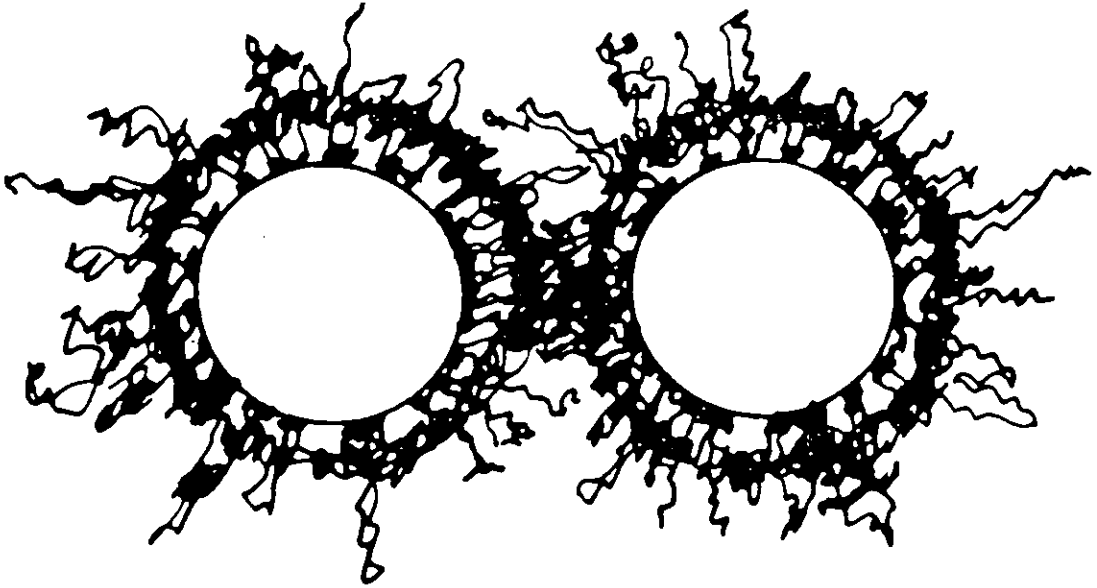
The interaction between particles with adsorbed polymers will be discussed by considering two particles surrounded by surface layers of soluble polymer chains, as depicted in figure 2.1(a). An adsorbed polymeric stabilizing chain may be attached to the particle surface at one or more points in various configurations, as shown in figure 2.1(b). The segments of the polymer chain which are in direct contact with the surface are termed 'trains', those in between which extend into solutions are called 'loops' and the free ends of the chain extending into solution are termed 'tails'. It is assumed that the stabilizing chains are firmly anchored to the particle surfaces. This leads to the concept of constant adsorption, where the fraction of segments adsorbed at the surface remains constant. In terms of figure 2.1(b), the loops and tails which protrude into the medium may redistribute themselves during contact but there is no desorption of trains. When two particles which have polymer molecules attached to their surfaces approach one another in a medium in which the polymer molecules are soluble, the polymer molecules interact. This 'steric' interaction between adsorbed polymer layers produces a change in the Gibbs free energy (ΔG) given by the equation

$$\Delta G = \Delta H - T\Delta S \quad (2.2)$$

where ΔH is the change in enthalpy and ΔS is the change in entropy.

If ΔG is negative, flocculation will result but if ΔG is positive, stabilization will result. The steric interactions between adsorbed polymer chains are generally divided into two categories; entropic and mixing interactions [7]. The adsorbed polymer chains may be compressed without penetrating into one another, as illustrated in figure 2.2(a). This 'denting'

FIGURE 2.1(a) A SCHEMATIC REPRESENTATION OF STERIC STABILIZATION



(b) POSSIBLE CONFIGURATIONS OF ADSORBED POLYMERS

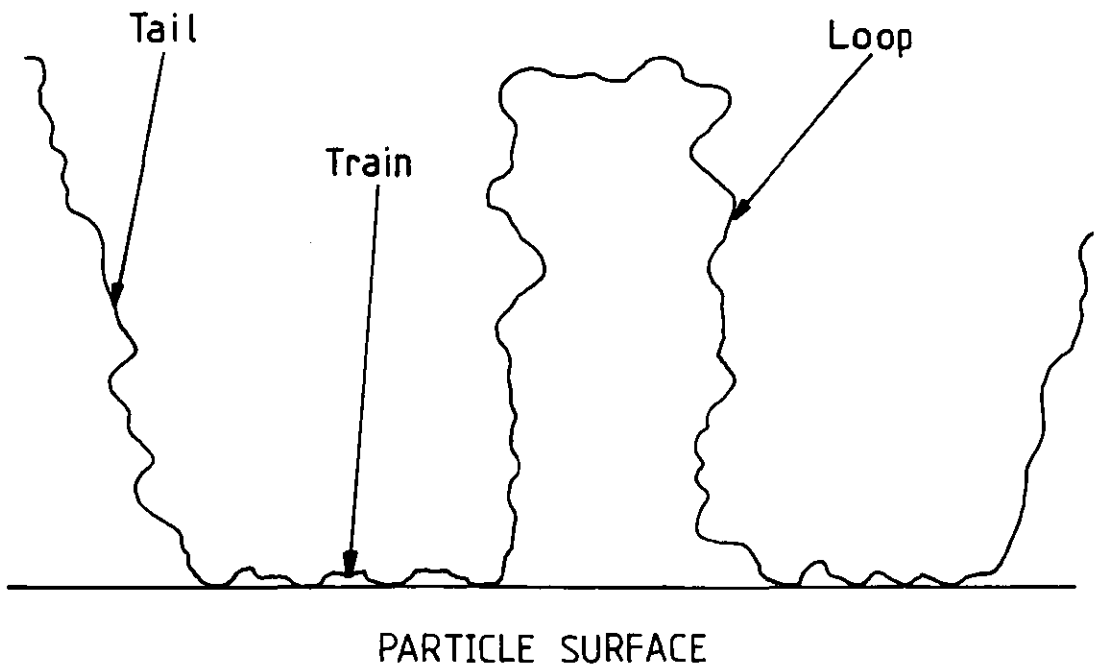
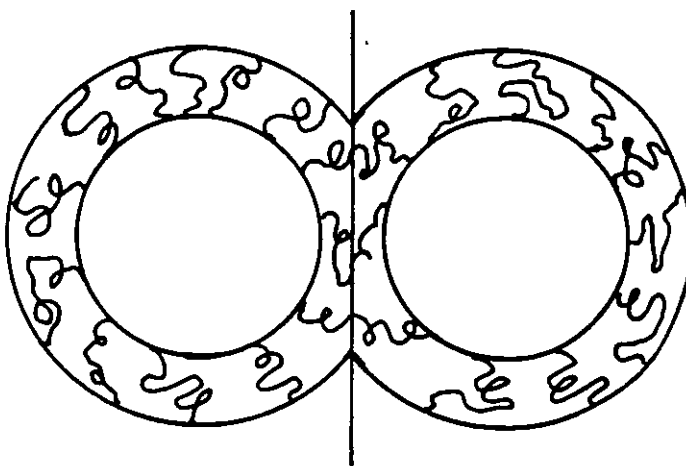
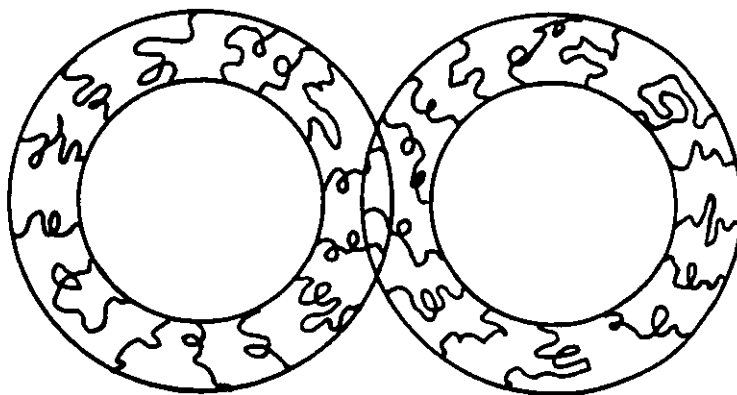


FIGURE 2.2 THE INTERACTION BETWEEN ADSORBED POLYMERS ON
STERICALLY STABILIZED PARTICLES

(a) ENTROPIC INTERACTIONS



(b) MIXING INTERACTIONS



mechanism will reduce the number of conformations available to the adsorbed polymer molecules, resulting in a decrease in entropy and an increase in free energy. This is called the entropic, volume restriction or elastic effect [7]; the change in free energy due to the entropic effect is represented by ΔG_{VR} . It is also possible for the adsorbed polymer chains to interpenetrate (see figure 2.2(b)) and produce a local increase in the concentration of polymer segments. This produces an osmotic pressure and an increase in free energy. Solvent for the stabilizing chains then diffuses into regions of higher polymer concentration and forces the particles apart until the adsorbed polymer chains are no longer in contact. This is termed the mixing, osmotic or enthalpic effect [7]; the change in free energy due to this is represented by ΔG_M . The total interaction free energy ΔG_T between two polymer-covered particles is given by

$$\Delta G_T = V_A + V_R + \Delta G_S \quad (2.3)$$

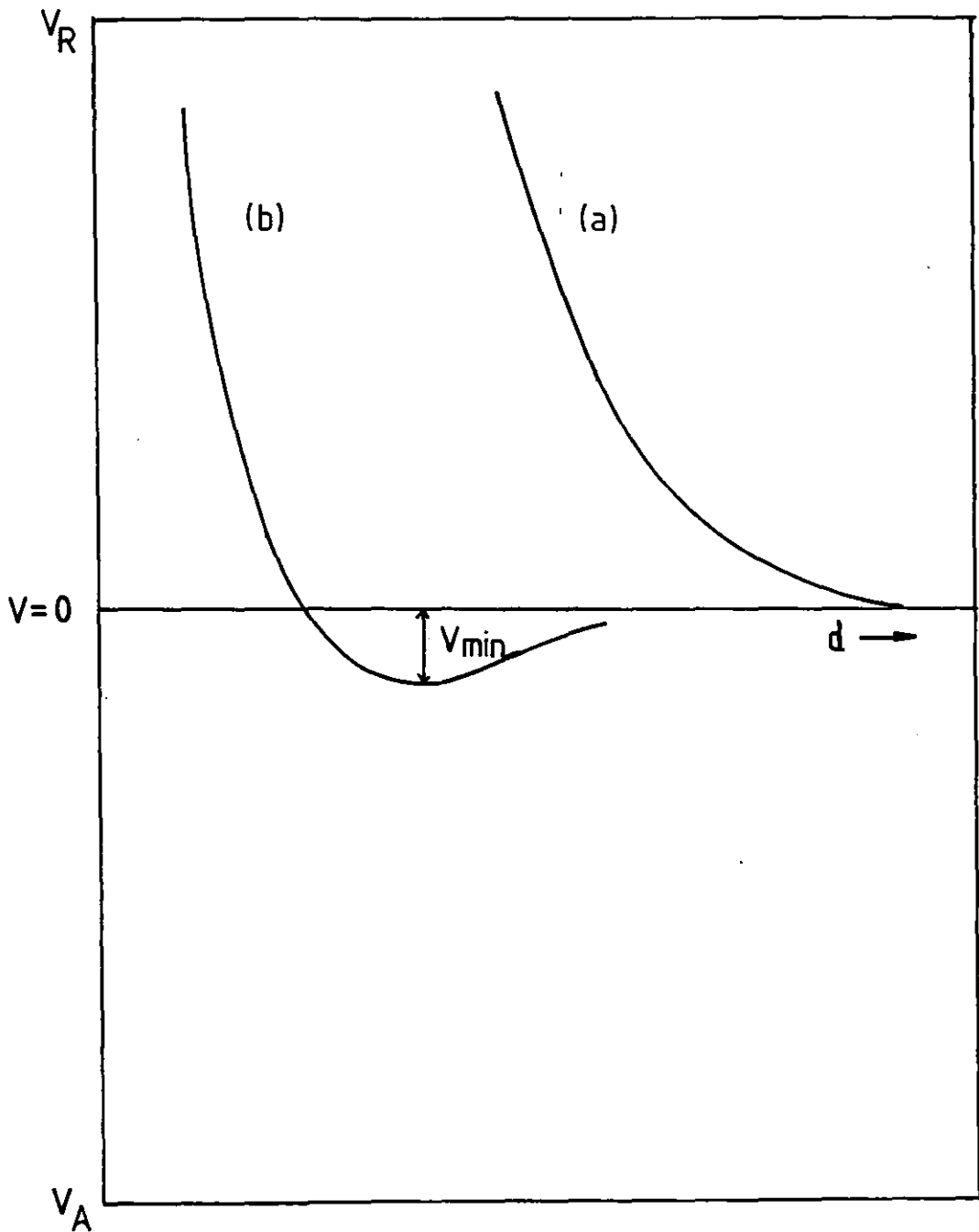
where V_A is the attractive potential energy, V_R is the repulsive potential energy (small for uncharged particles) and ΔG_S is the total steric interaction. It is often assumed that the entropic and mixing contributions to ΔG_S are additive, i.e.

$$\Delta G_S = \Delta G_{VR} + \Delta G_M \quad (2.4)$$

The variation of net potential energy with interparticle distance, for a dispersion of particles stabilized by layers of soluble polymer in a good solvent for the stabilizing chains, is shown in figure 2.3(a). The idea that repulsive forces are generated only when the soluble stabilizing polymer chains interact is fundamental to the concept of steric stabilization. As this overlap occurs and particles approach one another, the repulsive potential energy exceeds the attractive potential energy by an ever increasing amount. The net repulsive energy is always positive and increases rapidly at decreasing particle separation. It is possible that for certain combinations of layer thickness and particle size, a significant attractive force may

FIGURE 2.3 THE FORM OF NET POTENTIAL ENERGY CURVES AS A
FUNCTION OF PARTICLE SURFACE SEPARATION(d) FOR STERIC
STABILIZATION

- (a) LARGE ADSORBED LAYER THICKNESS
- (b) SMALL ADSORBED LAYER THICKNESS



exist, giving rise to a secondary minimum (V_{\min}) corresponding to weak flocculation. This is illustrated in figure 2.3(b). If the steric barrier is relatively small, an appreciable V_{\min} results. As the steric barrier increases, the minimum is considerably reduced in size until eventually it does not occur [7]. V_{\min} plays an important role in controlling the stability and flocculation behaviour of sterically stabilized dispersions. This is discussed further in section 2.1.3.

There is the important question of whether entropic interactions (compression) predominate over mixing interactions (interpenetration) or vice versa. Interpenetration of the adsorbed layers without compression only applies for separations greater than one adsorbed layer thickness. At small separations, compression should predominate. Whether interpenetration or compression or both occur also depends upon the segment density. If the segment concentration is high, compression will be favoured. However, if the segment concentration is low, interpenetration is likely to be dominant. It is probable that both processes occur simultaneously, the one which predominates depending on both the particle separation and the segment concentration in the adsorbed layer.

2.1.2.1 Models for steric stabilization

Mackor [26] was the first to model entropic interactions between sterically stabilized particles. He proposed a model in which the polymer chains were represented by rigid rods, attached flexibly at one end to a flat surface. Mackor showed that the repulsion was a result of the decrease in the number of possible conformations of the stabilizing chains when the two particles approached one another. However, the stabilizing chains in the model were assumed to be volumeless (i.e. length only). Therefore, mutual interactions were ignored and so the theory only applied to small surface coverages. Mackor and van der

Waals [27] subsequently allowed for these interactions by introducing a lattice model for the adsorbed polymer and the medium. Although this model was valid for higher surface coverages, it was restricted to dilute solutions. A quantitative treatment of the entropic repulsion mechanism has been performed by Clayfield and Lumb [28] using Monte Carlo computer simulation methods. Originally, the polymer stabilizing chains were modelled as terminally adsorbed homopolymers on a cubic lattice. In contrast to the Mackor model, the flexibility of the polymer chains were considered by simulating random flight chains and the excluded volume effect was taken into account. Subsequently, Clayfield and Lumb also allowed for solvent interactions [29] and extended their model to random copolymers with a loop-type adsorption [30]. However, in all these cases, the adsorbed layers were assumed not to interpenetrate, although it was claimed that the error arising from this in calculations on the prevention of flocculation was small [31].

Fischer [32] proposed the first theory to recognize and quantify mixing interactions in steric stabilization. In calculating ΔG_M , Fischer considered the overlap of polymer layers attached to two spherical particles and he made several assumptions. The segment concentration was assumed to be uniform in each adsorbed layer, and in the overlap region it was assumed to be the sum of the individual segment concentrations of the adsorbed layers. Also, the free energy of mixing of the adsorbed layers was assumed to be the same as that obtained for a dilute polymer solution (Flory-Krigbaum theory [33]). Fischer derived an expression of the form

$$\Delta G = A.B \quad (2.5)$$

where A is the geometric term and B is the thermodynamic term, i.e. the second virial coefficient of polymer in solution. B itself is proportional to $(0.5 - \chi)$, where χ is the polymer-solvent interaction parameter. This means that the thermodynamic state of the solvent for the stabilizing chains is an important

factor in controlling ΔG_M . Similar expressions have also been derived by Ottewill and Walker [34] and Napper [35]. The main disadvantages of the Fischer model are that the concentration of the polymer segments is assumed uniform and that the redistribution of polymer segments in the overlap zone is neglected. Both lead to an overestimation of the repulsive forces generated, particularly in the early stages of interaction.

The problem with all of the previous models is that either entropic or mixing interactions were considered in isolation. However, both effects are likely to occur as outlined earlier. Meier [36] was the first to publish a theory of steric stabilization which incorporated both entropic and mixing interactions and was based on random flight statistics applied to a model of stabilizing molecules adsorbed terminally to planar surfaces. Hesselink [37] subsequently modified Meier's theory and Hesselink et al [38] extended it to loops for homopolymers, where all segments had an equal opportunity to become adsorbed at the interface. Subsequently, copolymer stabilizers with anchor segments statistically distributed along the chains were also treated.

Meier and Hesselink et al both calculated the entropic and mixing interactions separately and they assumed that the total steric interaction was the sum of these two contributions. Dolan and Edwards [39] pointed out that these terms were interdependent. They avoided the separate treatment of entropy and mixing effects by treating the interactions between segments as an excluded volume effect, thereby including the whole of the free energy as a configurational entropy term. This self-consistent mean field theory was also developed by Gerber and Moore [40] and Levine et al [41]. The most detailed mean field theory for polymers at interfaces has been proposed by Scheutjens and Fleer who have published numerous papers on a self-consistent lattice model. Originally, the model was used to describe the

adsorption of homopolymers from solution at one interface [42,43]. The interface was represented by a flat surface and the polymer solution was represented by a lattice of various geometries with lattice sites occupied by either polymer segments or solvent molecules. This model is illustrated in figure 2.4. The probability of a given conformation was determined by the product of so-called 'segmental weighting factors'. These factors described the energy and entropy changes which occurred when a polymer segment was brought from bulk solution to its position on the lattice. A matrix procedure was used to generate all conformations and from the conformation probabilities, a segment concentration profile was computed by summing over all possible conformations. All sites within one layer were assumed to be equivalent, i.e. the segment density within one layer was homogenous and the mean-field approximation applied parallel to the surface. Subsequently, the Scheutjens-Fleer theory was extended to homopolymers between two surfaces [44,45], a case relevant for colloid stability. The Scheutjens-Fleer theory has also been applied to the structure of grafted polymer molecules at interfaces and also to the behaviour of copolymers [46]. The advantage of the model is that any type of copolymer can be treated, because the ranking number of each segment is taken into account. Scheutjens and Fleer have also compared their theory to others [46]. They argue that theories which treat entropic and mixing interactions separately are incorrect because, in effect, the segmental weighting factors are all assumed to be equal.

In addition to the various mean-field theories for the behaviour of polymers at interfaces, scaling theories have also been developed. The starting point of the scaling analysis is the representation of dilute polymer solutions with overlapping coils [47]. This is illustrated in figure 2.5(a). The most characteristic feature is the mesh size, which decreases as the volume fraction of polymer increases. De Gennes [48] reasons that for a polymer adsorbed on to a wall, the local mesh size at any distance Z from the wall is equal to Z itself, i.e. the layer

FIGURE 2.4

A LATTICE MODEL FOR ADSORBED POLYMER CHAINS WITH
TWO POSSIBLE CONFORMATIONS FOR A CHAIN WITH 14
SEGMENTS AND 13 BONDS

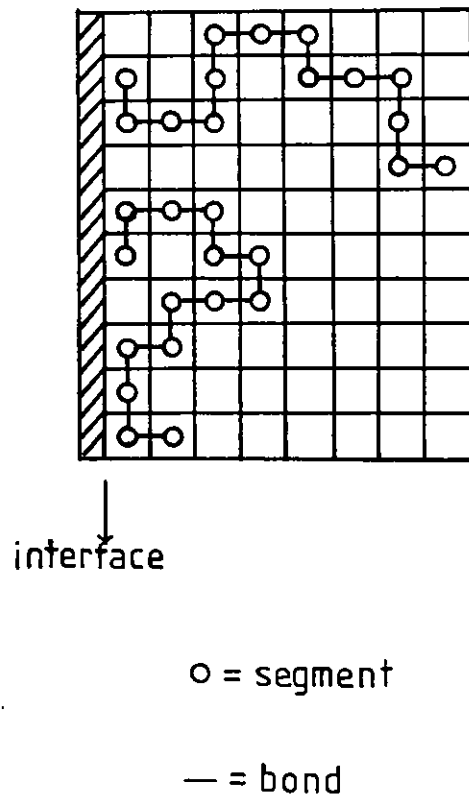
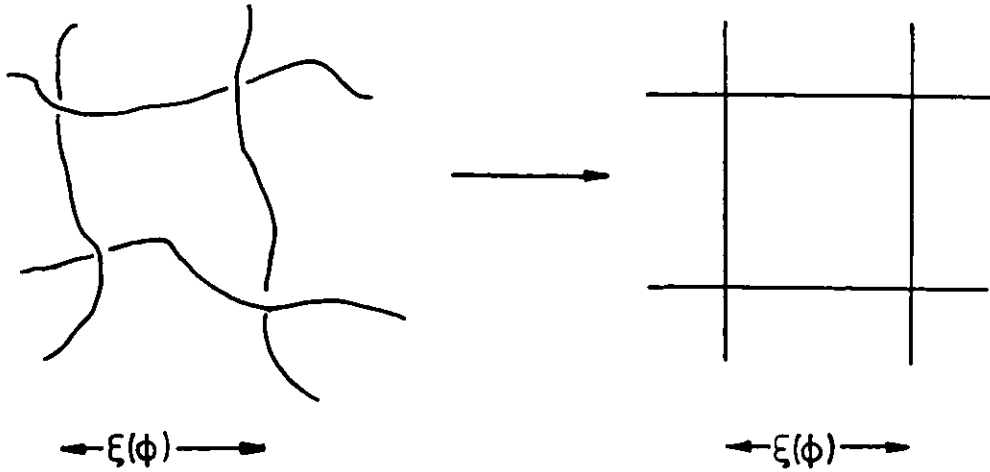
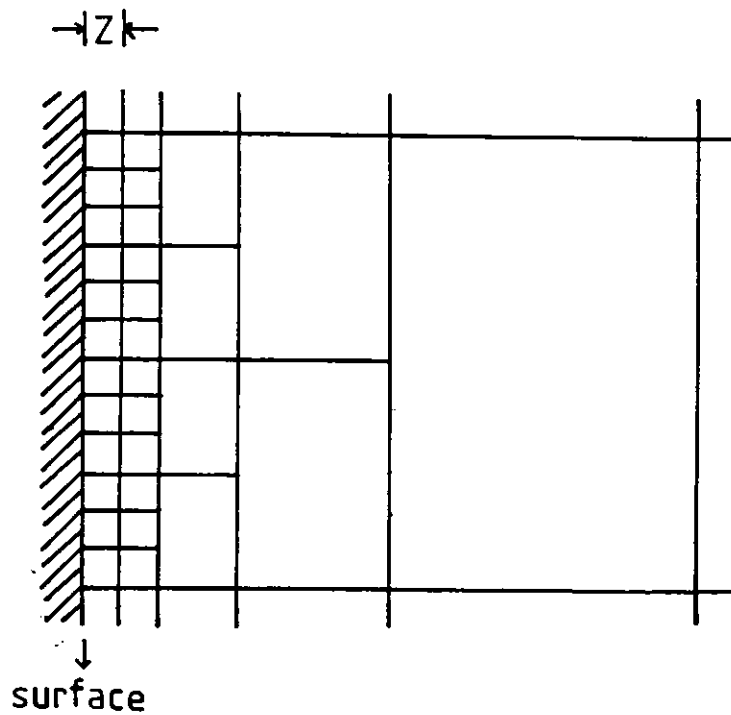


FIGURE 2.5(a) A POLYMER SOLUTION (VOLUME FRACTION ϕ) IDEALIZED AS A "GRID" WITH THE SAME MESH SIZE, $\xi(\phi)$



(b) 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



has a 'self-similar grid structure' as depicted in figure 2.5(b). Such scaling theories have been developed to describe grafted chains on one surface and they have been extended to cover interactions between two surfaces containing either adsorbed polymer or grafted chains [48].

Recently, there has been some discussion as to whether the mean-field theory or the scaling theory is more accurate for describing the behaviour of polymers at interfaces. The central idea in the Scheutjens-Fleer mean-field theory is that the segment density is essentially homogenous parallel to the particle surfaces. De Gennes [48] argues that adsorbed layers are strongly fluctuating systems and that this approximation is generally invalid. Fleer [46] agrees with this only for conditions of low overlap and suggests that the scaling theory is more appropriate in this situation. However, Fleer et al [49], point out that the scaling theory is based on dilute solutions and that in general, apart from situations with low overlap, the densities encountered when adsorbed layers interact are too high for scaling laws to apply. The two theories appear to complement each other and in combination describe many of the characteristics of macromolecules adsorbed at interfaces and interactions between them.

2.1.3 THE STABILITY AND FLOCCULATION OF COLLOIDAL DISPERSIONS

It is essential that the repulsive forces involved in sterically stabilized dispersions are not relieved during a particle collision. The criteria that need to be fulfilled for a dispersion stabilized by adsorbed polymer to remain stable [7,9] are summarized as follows.

- (i) The stabilizing chains need to be firmly anchored to the particle surface in order to prevent both desorption during a particle collision and lateral

movement on the particle surface.

- (ii) The particle surface should be saturated, i.e. there should be complete coverage of the particle surface by the stabilizing chains.
- (iii) The adsorbed polymer layer needs to be thick enough so that V_{min} is negligibly small (see figure 2.3(b)). If points (ii) and (iii) are not fulfilled, then direct contact between unprotected areas on the particle surface may occur, leading to flocculation.
- (iv) The dispersion medium should be a thermodynamically good solvent for the stabilizing polymer chains.

Instability can readily be induced in a sterically stabilized dispersion by reducing the solvency of the dispersion medium for the stabilizing polymer chains. This can be achieved through temperature changes or by the addition of non-solvent [8]. Under such conditions, the dispersions often exhibit a sharp transition from long-term stability to fast flocculation. It has been demonstrated that a strong correlation exists between the critical flocculation point and the θ -point of the stabilizing chains in free solution [16,17,50].

2.2 DISPERSION POLYMERIZATION IN NON-AQUEOUS MEDIA

The following description of dispersion polymerization will be confined to free-radical systems, since the mechanism of dispersion polymerization has largely been derived from these.

2.2.1 GENERAL FEATURES OF FREE-RADICAL POLYMERIZATION [51,52]

This is a type of addition polymerization which is known to take place via a chain reaction. It has clearly defined reaction stages [51,52] which are illustrated in scheme 2.1.

(i) Initiation.

The chain reaction is generally started by adding an initiator. This generates free-radicals which can be produced by a variety of thermal, photochemical and redox methods. Thermal decomposition is the most widely used method. The radicals produced from the initiator are termed primary radicals. Each primary radical adds to the first monomer molecule to produce the chain initiating species R_1^* .

(ii) Propagation.

This consists of the growth of R_1^* by the successive additions of large numbers (10^2 - 10^6) of monomer molecules. Each addition creates a new radical which has the same identity as the one previously, except that it is larger by one monomer unit.

(iii) Termination.

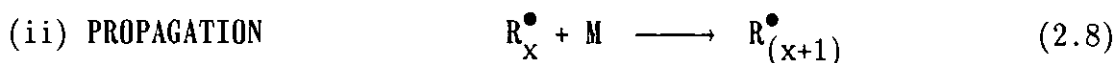
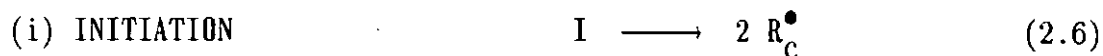
At some point, the propagating polymer chain stops growing and terminates. A bimolecular termination reaction between two active chains can occur in two different ways, combination and disproportionation. Combination involves the formation of a single 'dead' polymer chain when two growing free-radical chains react. Disproportionation involves hydrogen abstraction from one growing chain end by the radical end of another to produce two 'dead' polymer molecules, one with a saturated terminal unit and the other with an unsaturated terminal unit. It is possible for both combination and disproportionation to occur simultaneously.

(iv) Chain Transfer.

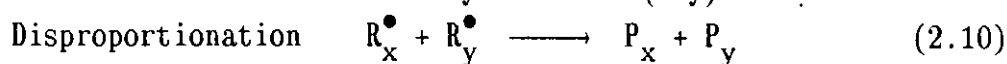
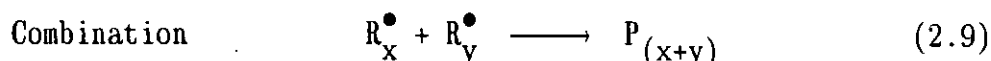
This occurs when a radical is terminated by interaction with another species which is not a free-radical. The other species may be solvent molecules, monomer, initiator, polymer or other molecules susceptible to a transfer reaction. This produces a further radical species which can be sufficiently reactive to

SCHEME 2.1

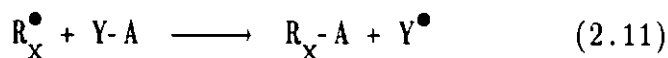
THE MECHANISM OF FREE-RADICAL POLYMERIZATION



(iii) TERMINATION



(iv) CHAIN TRANSFER



where I = Initiator

M = Monomer

R_c^\bullet = Primary radical

R_x^\bullet = Radical containing x monomer units

P_x = Polymer molecule containing x repeating units

Y-A = Chain transfer agent

initiate chain growth. If this occurs then the chain length of the product is reduced. In the presence of very active transfer agents, chain transfer can be a dominant process resulting in the formation of large numbers of short chains with end-groups derived from the chain transfer agent.

2.2.1.1 A comparison of free-radical polymerization processes

Dispersion polymerization is a heterogeneous process. Free-radical polymerization may be carried out by various homogeneous and heterogeneous processes and a brief comparison will serve to emphasize the characteristics of dispersion polymerization.

(i) Homogeneous processes [52].

(a) Bulk Polymerization.

Although bulk (or mass) polymerization of a pure monomer offers the simplest process with minimum product contamination, it requires careful control because of the need to dissipate the heat of reaction and because the viscosity of the reaction system increases rapidly at relatively low conversions. The viscosity and exotherm effects make temperature control difficult. In extreme cases, uncontrolled acceleration of the polymerization can lead to 'runaway' reactions.

(b) Solution Polymerization.

Polymerization of a monomer in a solvent overcomes many of the disadvantages of the bulk process. The solvent acts as a diluent and aids the dissipation of the heat of polymerization resulting in easier thermal control. The viscosity of the reaction mixture is also reduced in comparison to bulk polymerization. However, the solvent may enter into chain transfer reactions and polymers can be contaminated if solvent removal is difficult.

(ii) Heterogeneous Processes [52].

(a) Emulsion Polymerization.

In its simplest form, an emulsion polymerization system consists of water, monomer, surfactant and initiator. The monomer must be only sparingly soluble, the surfactant can be ionic or non-ionic and the initiator is water soluble. Latex particles are produced with a typical size of 0.1-5 μ m. It is possible to obtain a high molar mass polymer at a fast rate as a result of radical isolation within particles.

(b) Suspension Polymerization.

In suspension polymerization, monomer which is relatively insoluble in water is dispersed as liquid droplets by vigorous stirring and the presence of protective colloids. Monomer soluble initiators are added and polymerization occurs to produce polymer particles as a dispersed solid phase. The particles produced are typically greater than 10 μ m, larger than in emulsion polymerization.

(c) Precipitation Polymerization.

Precipitation polymerization is a process in which the monomer and initiator are initially dissolved in a diluent which is a non-solvent for the polymer produced. Therefore, precipitation polymerization commences as a homogeneous process but transforms to heterogeneous on polymerization. This is in contrast to emulsion and suspension processes, where the process is heterogeneous throughout. In precipitation polymerization, the insoluble polymer precipitates in the form of an agglomerate or slurry. This process is usually characterized by an auto-acceleration effect. This is caused by the high viscosity of the system, which restricts the mobility of the growing polymer radicals, thereby reducing the termination rate.

(d) Dispersion polymerization [8,9].

Dispersion polymerization involves the polymerization of a monomer, dissolved in an organic diluent containing a macromolecular stabilizer, to produce an insoluble polymer in the form of a stable colloidal dispersion. This process may be viewed as a special type of precipitation polymerization in which flocculation is prevented and particle size controlled. The particle size obtained by this method is typically in the range 0.05 - 10 μ m. Several features are characteristic of the dispersion polymerization of methyl methacrylate in non-aqueous media. The insoluble polymer precipitates from an initially homogeneous reaction mixture and polymer particles are formed at a very early stage in the polymerization. The rate of dispersion polymerization is also much faster than the corresponding solution polymerization due to an auto-acceleration effect, as seen in precipitation polymerization.

2.2.2 THE ROLE OF THE STABILIZER

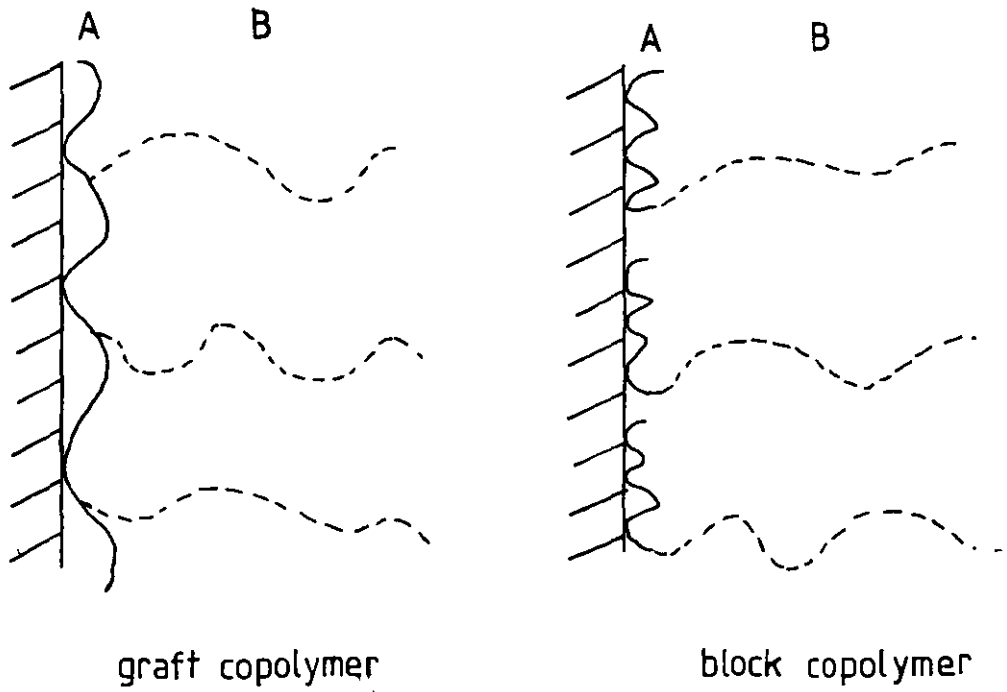
The function of the stabilizer is to provide a layer of material solvated by the dispersion medium on each particle surface. As described in section 2.1.3, the preferred chains for stabilizing colloidal dispersions should not only be firmly anchored but they should also give a thick steric barrier extending into the dispersion medium. Consequently, considerable difficulties arise in selecting effective homopolymers for steric stabilization. Homopolymers containing groups which anchor strongly at the particle surface adopt a flat conformation with most groups in trains. On the other hand, chains containing groups with more affinity for the dispersion medium will generate a thicker steric barrier with most groups existing as loops. However, such chains are easily displaced from the particle surface. It follows that the most effective steric stabilizers are likely to be copolymers. It is possible to use statistical copolymers but it

is difficult to produce such chains which will both anchor strongly and provide a thick enough steric barrier. The most successful stabilizers are those based on graft or block copolymers consisting of two components, one soluble and one insoluble in the dispersion medium [9,53]. The soluble component B is chosen to have no affinity for the particle surface. It provides stabilization against flocculation by protruding into the dispersion medium and providing a steric barrier. The insoluble component or anchor block, A, associates with the dispersed polymer, thereby firmly attaching the soluble component to the surface. The primary requirement for the anchor block is that it is insoluble in the dispersion medium so that it is adsorbed on the particle surface. However, the effectiveness of the stabilizer may be greatly enhanced if the anchor block is also compatible with the dispersed phase [9]. Therefore, the anchoring of such stabilizers is achieved by a physical adsorption mechanism, as illustrated in figure 2.6(a).

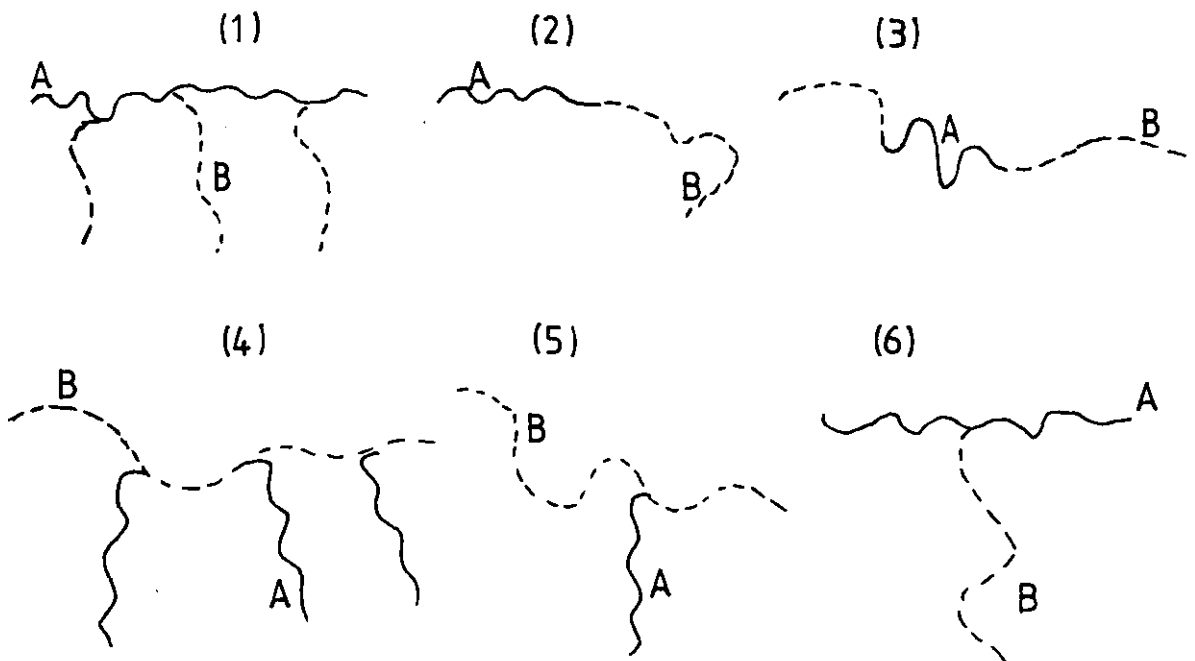
The anchoring of polymeric stabilizers can also be achieved by acid-base interactions or covalent links. Anchoring by acid-base interactions is achieved by the incorporation of complementary acidic and basic groups into the dispersed particle and the anchoring component of the polymeric stabilizer [54]. It is possible for physically anchored stabilizers to be displaced by the action of strong solvents or high temperatures, resulting in the flocculation of dispersions. In order to prevent this, covalent links have been used to attach the anchoring component of the stabilizer more firmly to the dispersed particles. This can be achieved by incorporating copolymerizable groups into the anchor block of the stabilizer [55].

Figure 2.6(b) shows some configurations which might be suitable for use as steric stabilizers by a physical adsorption anchoring mechanism. The present study concerns the use of graft copolymers of the type (1) in figure 2.6(b), where the backbone is the anchor block and the side chains constitute the soluble

FIGURE 2.6(a) GRAFT AND BLOCK COPOLYMERS USED AS STERIC STABILIZERS



(b) SUITABLE COMBINATIONS OF A AND B FOR USE AS COPOLYMER STABILIZERS



component. Such copolymers can be formed 'in situ' during the dispersion polymerization from a precursor or added as a preformed graft copolymer [56]. The present study concerns the use of preformed graft copolymers since the structures of graft copolymers formed 'in situ' can be difficult to control and characterize [57].

2.2.3 THE BEHAVIOUR OF GRAFT COPOLYMERS IN DISPERSION POLYMERIZATION

Amphipathic graft or block copolymers, containing polymer segments with different chemical compositions, are capable of chain segregation in the bulk state or in solvents which are selectively poor for one component and good for the other [58]. The morphology obtained depends upon the concentration and composition of the polymer, the solvent environment and the temperature. In the bulk state or in concentrated solution, microphase separation occurs. Domains of one component are dispersed in a matrix of the other, resulting in regular and periodic mesomorphic structures consisting of spheres, cylinders or alternating lamellae. In dilute solution micellization occurs, where the micelle core is composed of the least soluble component and is surrounded by an outer layer of soluble polymer. At very low concentrations, the graft or block copolymer molecules are unassociated resulting in a conventional polymer solution. Most of the information on chain segregation of amphipathic copolymers refers to block copolymers but graft copolymers behave in the same fashion [58,59].

Dispersion polymerization usually involves graft or block copolymers at a concentration generally less than five per cent by weight. Under such conditions, it is believed that the stabilizer will tend to exist as micelles in equilibrium with single molecules [9]. There will be an equilibrium between adsorbed stabilizer, monomolecular stabilizer and micellized

stabilizer. This is depicted in Figure 2.7 for a graft copolymer stabilizer, where the backbone is the anchor block (A) and the side chains constitute the soluble component (B). The ratio of A to B components is known as the anchor/soluble balance (ASB). When the anchor block is too small, it will not adsorb at the particle/medium interface. If the ASB is too high, the equilibrium will be displaced, favouring micelle formation. This will inhibit dissociation into single molecules, thereby preventing the stabilizer diffusing to the interface. If the ASB is even higher, the stabilizer may not be able to form a stable micelle. This would result in precipitation of the stabilizer. It has been suggested that the ASB should lie in the range 1:3 to 3:1 [60].

2.2.4 THE MECHANISM OF PARTICLE FORMATION

Initially, as in conventional free-radical solution polymerization, the initiator generates free-radicals which react with monomer to form growing oligomeric chains in homogeneous solution. These chains grow in solution until they reach a threshold molar mass at which they precipitate and form particle nuclei. Three different models have been proposed for the formation of particle nuclei from these growing oligomeric radicals [8]. They are self-nucleation, aggregative nucleation and nucleation from micelles which are all illustrated in figure 2.8.

2.2.4.1 Self-nucleation

Each oligomeric radical initially has an extended conformation but then collapses into a condensed state when it reaches a certain threshold molar mass and precipitates. This condensed oligomeric chain constitutes a new particle nucleus. Fitch and Tsai [61] proposed that the behaviour of each oligomer chain is

FIGURE 2.7 THE BEHAVIOUR OF GRAFT COPOLYMERS IN DISPERSION
POLYMERIZATION

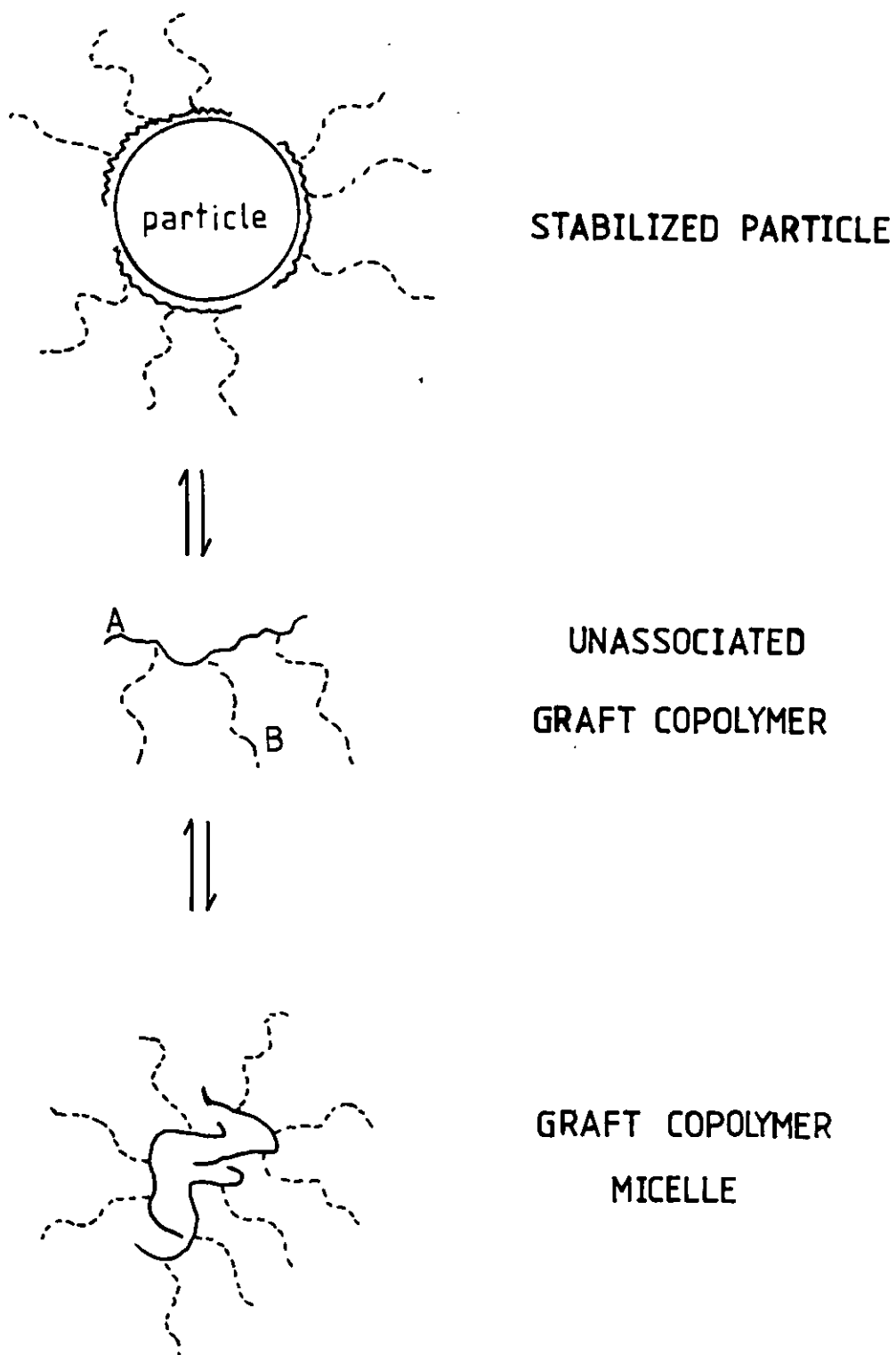
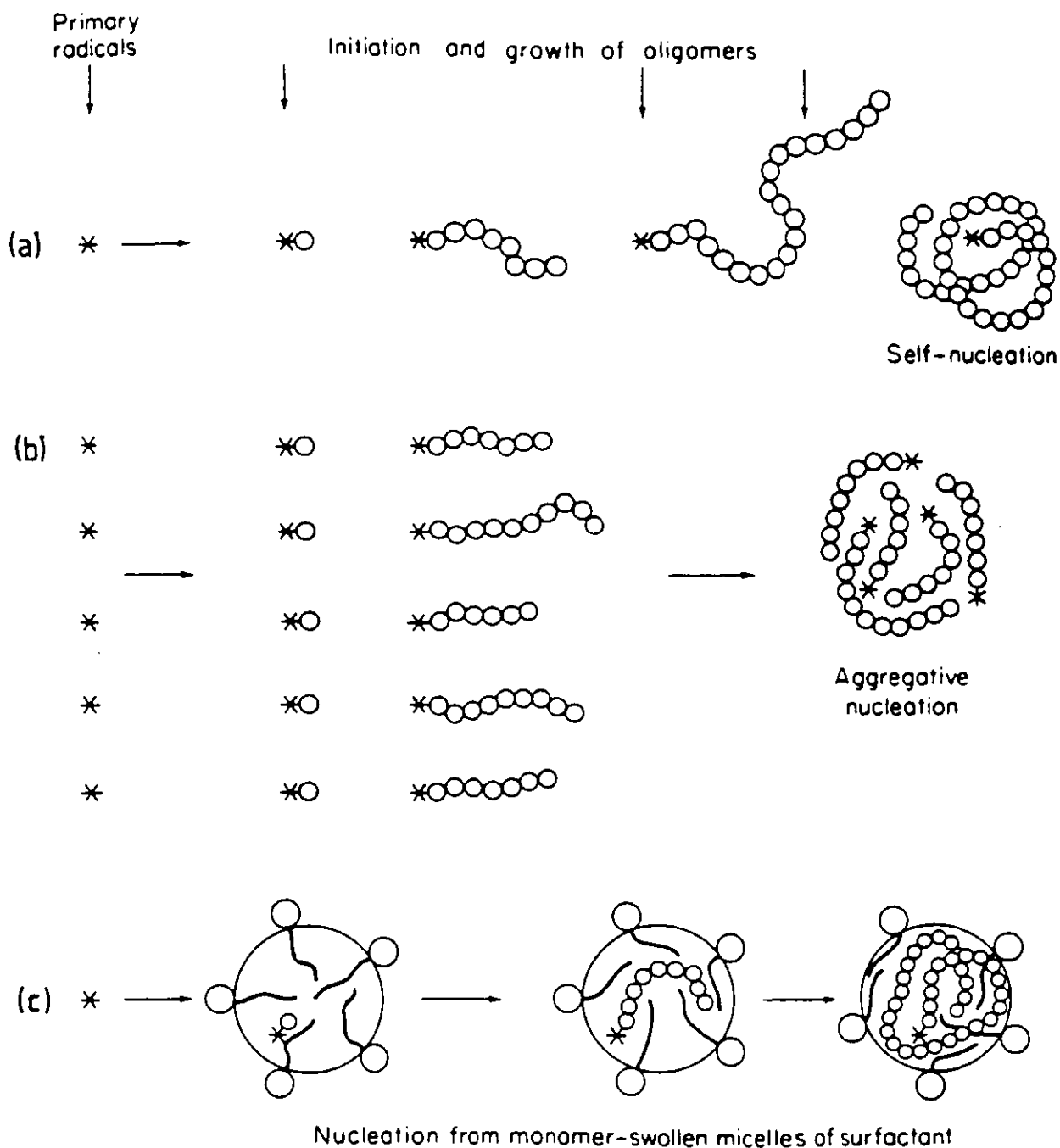


FIGURE 2.8

MODELS FOR PARTICLE NUCLEATION IN DISPERSION
POLYMERIZATION



unaffected by the presence of other oligomer molecules. Therefore, every chain initiated forms a new particle unless it is captured by diffusion to an existing particle before it reaches the threshold molar mass.

2.2.4.2 Aggregative nucleation

In this model, the growing oligomeric radicals associate with each other as their molar mass and concentration rise. Aggregates below a certain critical size are unstable but above this critical size they are stable and constitute new particle nuclei. This model corresponds to the classical theory of homogeneous nucleation developed by Becker and Döring [62]. The rate of nucleation depends on the activation energy required to form an aggregate of critical size. As with the previous model, the capture of oligomers by existing particles competes with nucleation.

2.2.4.3 Nucleation from micelles

This is analogous to the model proposed by Harkins [63] for emulsion polymerization. It is suggested that oligomeric radicals are initiated and grow within monomer swollen micelles of the amphipathic copolymer stabilizers. Nuclei are formed when the oligomeric chains reach a critical molar mass.

Although amphipathic graft and block copolymer stabilizers are capable of forming micelles [58], the monomer used in dispersion polymerization is completely soluble in the medium, unlike emulsion polymerization where the monomer used is only sparingly soluble in the medium. Therefore, this model is unlikely. However, the other two models are complementary. If the polymer solubility is very low, self-nucleation of individual molecules is likely to occur. However, if the polymer solubility is high, the concentration of polymer in solution will be high before precipitation occurs and therefore aggregative nucleation is likely. An intermediate polymer solubility is more probable in

dispersion polymerization [9]. In the absence of a competing process, the formation of particle nuclei might be expected to continue throughout the course of the polymerization providing that free monomer remains. However, unless conditions are altered, the rate of nucleation usually falls to a low level very early in the polymerization. The reason for this is that nearly all of the growing oligomeric radicals are captured by existing particles before they reach their threshold molar mass, i.e. before they precipitate and form new nuclei.

The above models for nucleation neglect the influence of stabilizers. Generally, the presence of a stabilizer enhances nucleation and increases the number of nuclei formed [8]. This is explained by association between the stabilizer and growing oligomers, which raises the probability of nucleation and lowers the probability of capture by existing particles. In the self-nucleation model, the stabilizing graft copolymer associates with a single growing chain, as shown in figure 2.9(a) and this protects it against capture by existing particles. This increases the probability of the chain forming a nucleus and more nuclei are formed. In the aggregative nucleation model (figure 2.9 (b)), the stabilizing copolymer participates in forming incipient nuclei and reduces the interfacial tension. Therefore, smaller nuclei are produced and the total number of nuclei is increased.

2.2.5 THE MECHANISM OF PARTICLE GROWTH

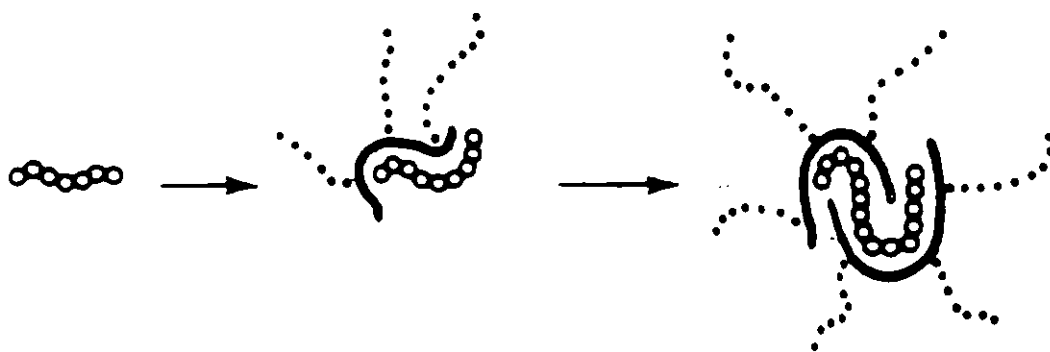
Provided that the conditions remain unchanged, most of the nuclei are formed at an early stage in the polymerization. Following the nucleation stage, subsequent polymerization is confined to further growth of the polymer particles formed initially. Three mechanisms have been postulated to explain particle growth [8]:

- (i) polymerization in solution, followed by precipitation on to the existing polymer particles;

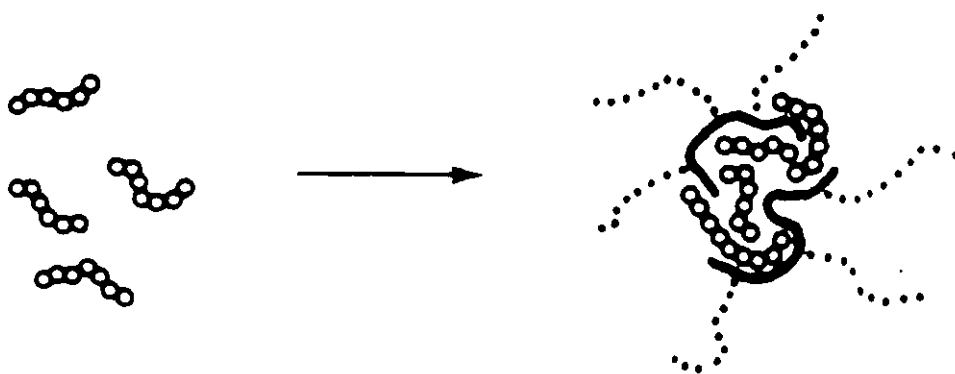
FIGURE 2.9

THE EFFECT OF STABILIZER ON THE MODIFICATION OF
PARTICLE NUCLEATION IN DISPERSION POLYMERIZATION

(a) Self-nucleation



(b) Aggregative-nucleation

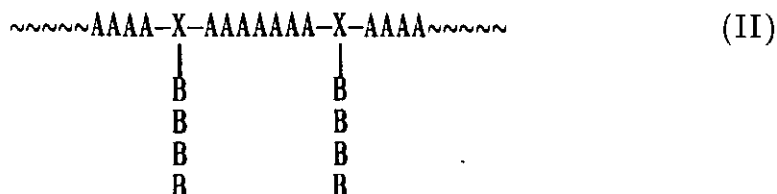


- (ii) polymerization of monomer adsorbed at the surface of the polymer particles;
- (iii) polymerization of monomer absorbed into the interior of the polymer particles.

From a study of the dispersion polymerization of methyl methacrylate in n-dodecane [64], a number of features were apparent. Firstly, the rate of dispersion polymerization was found to be much higher than a solution polymerization under equivalent conditions. This was a result of auto-acceleration and it indicated that the polymer particles were the main site of polymerization. Secondly, the rate of dispersion polymerization was independent of particle size, indicating that a surface polymerization mechanism was improbable. The evidence indicated that mechanism (iii) was the predominant mode of polymerization. The polymer particles were significantly swollen by monomer during the polymerization, resulting in a smooth, spherical particle morphology.

2.3 THE SYNTHESIS OF GRAFT COPOLYMERS

Graft copolymers are copolymers in which one or more side chains or grafts (B) consisting of one polymer, are attached to a backbone (A) of a second polymer at branching sites (X), producing structures of the following type (II):



The chemical composition of the backbone is different to the chemical composition of the side-chains but both can be homopolymers or copolymers. Most of the methods used to synthesize graft copolymers can be classified into three main categories, 'grafting from', grafting onto' and grafting through' techniques, as described in several reviews [12,65]. These are depicted in scheme 2.2.

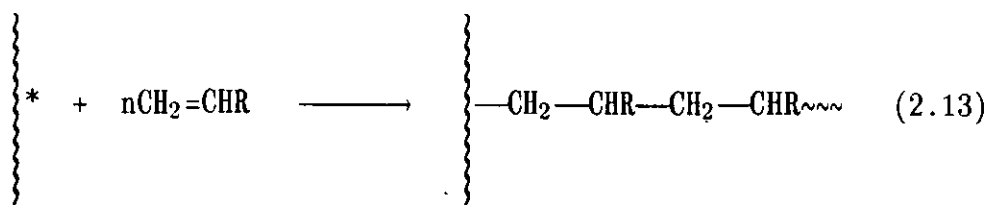
2.3.1 'GRAFTING-FROM' PROCESSES [12,65]

This is where a preformed polymer chain has initiating sites attached to it, or functions capable of generating such sites. The polymerization of a second monomer is initiated from the backbone chain to produce the grafts, as illustrated in equation 2.13. The sites generated on the backbone can be of free-radical, anionic, cationic or Ziegler-Natta type.

Free-radical sites can be generated from a backbone containing labile hydrogen atoms, such as allylic hydrogens. The grafting efficiency can be improved by introducing a small number of very active transfer sites in the preformed polymer, such as trichloromethyl, diethylaminoethyl or thiol functions. Redox radical reactions and irradiation techniques can also be used to generate free-radical sites on a backbone. A polymeric backbone with attached organometallic sites can be used as a multifunctional initiator for the anionic polymerization of a suitable monomer to build the grafts. Such organometallic sites can be generated by the metallation of a polymer from addition reactions, from the substitution of labile hydrogens or from metal-halogen exchange reactions. There are fewer examples of cationic 'grafting from' processes because it is more difficult for carbonium ions to be distributed at random along a polymer backbone as a result of their very high reactivity.

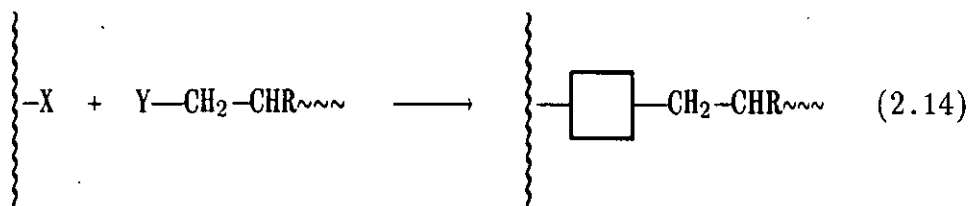
SCHEME 2.2 COMPARISON OF METHODS USED TO SYNTHESIZE GRAFT
COPOLYMERS

(i) "GRAFTING FROM" PROCESS

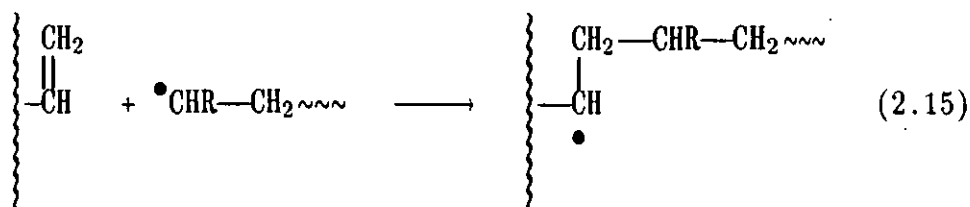


where * = active site

(ii) "GRAFTING ONTO" PROCESS



(iii) "GRAFTING THROUGH" PROCESS



Although 'grafting from' methods can be efficient, it is difficult to characterize the molecular structure of the graft copolymers formed. The processes also suffer from the production of backbone homopolymers and ungrafted side-chain homopolymers.

2.3.2 'GRAFTING ONTO' PROCESSES [12,65]

This is where grafting results from the reaction between a polymer molecule bearing one terminal reactive site and another polymer molecule (the backbone) containing attached antagonist functions distributed along its chain, as illustrated in equation 2.14. 'Grafting onto' processes generally involve ionic or non-ionic methods.

For anionic methods, the backbone chains carry electrophilic functions such as ester, anhydride, epoxide and nitrile groups. The terminally functionalized chains bear nucleophilic carbanions. Cationic 'grafting onto' processes involve the reaction of nucleophilic functions distributed on a polymer backbone with terminally functionalized chains bearing cations. This is restricted to heterocyclic monomers which produce cationic active sites with long lifetimes, i.e. 'living' polymers. In non-ionic 'grafting onto' processes, both the terminally functionalized polymer chains and the polymer backbone contain reactive sites which are antagonist functional groups, i.e. one contains electrophilic functional groups whilst the other contains nucleophilic functional groups.

An advantage of these methods is that the backbone chain and the grafts are made separately and can be characterized individually; this allows a structural characterization of the graft copolymers formed. However, the process involves reactions between functionalized polymers with a different chemical nature. High molar mass precursors may lead to a dramatic reduction in reaction rate due to the reduced reactive site concentration

and/or the incompatibility between the polymer chains of different chemical nature.

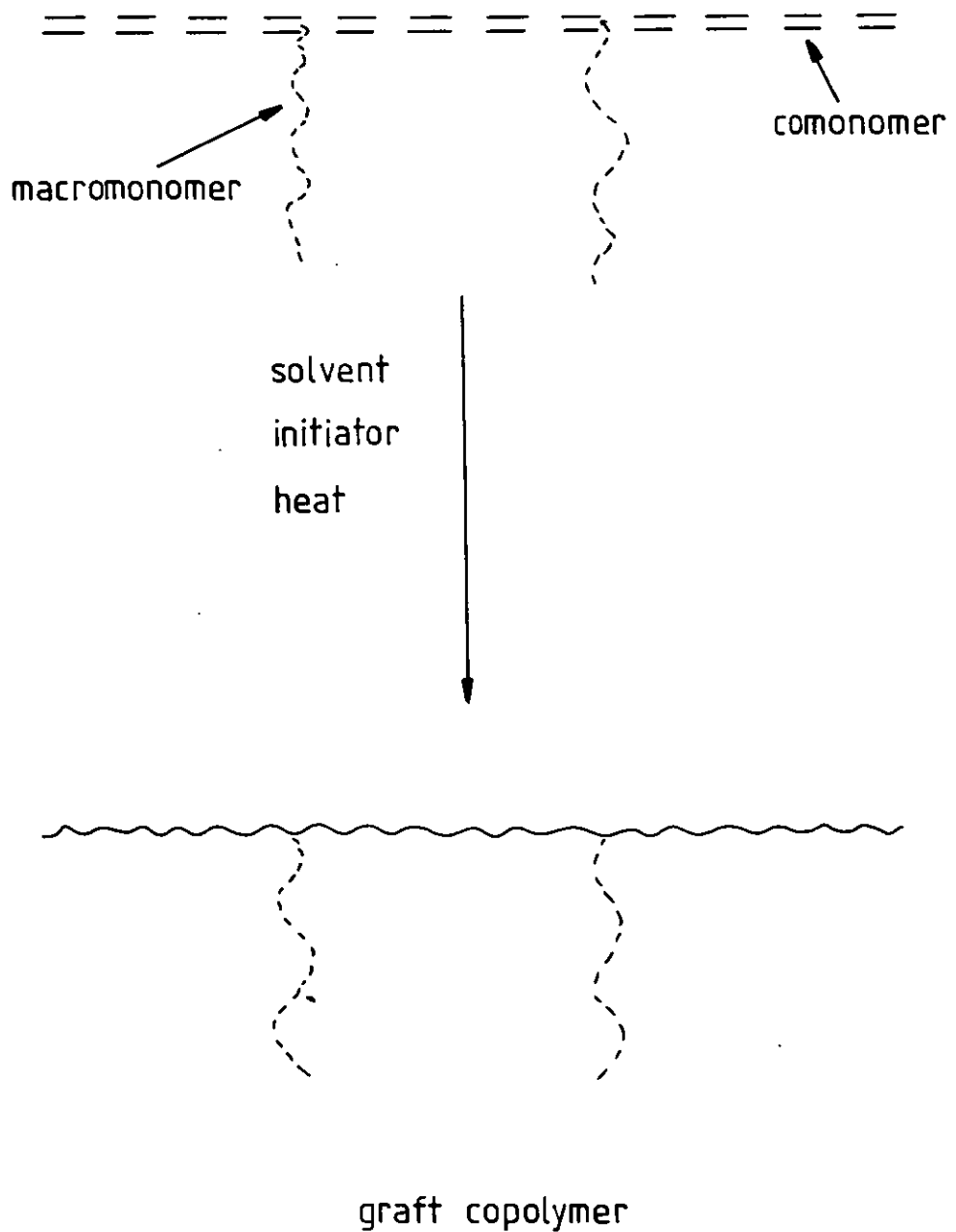
2.3.3 'GRAFTING-THROUGH' PROCESSES [12,65]

In this case, the polymerization of a monomer is performed in the presence of a polymer bearing pendant unsaturations which are capable of copolymerization as depicted in equation 2.15. However, such reactions can involve the formation of links between individual molecules if a growing site incorporates unsaturations belonging to two or more different backbones. Consequently, the process may result in crosslinked material and gel-formation.

2.3.4 THE COPOLYMERIZATION OF MACROMONOMERS

The preparation of graft copolymers from macromonomer precursors is a relatively recent innovation which has attracted much interest in recent years [13,14,65]. A macromonomer is defined as a polymer chain containing a polymerizable end group at one end, generally an unsaturation. Macromonomers provide relatively easy access to graft copolymers by copolymerization with acrylic or vinyl comonomers. This is illustrated in figure 2.10. It can be considered as a type of 'grafting through' process, where the unsaturation is at the terminus of a preformed polymer molecule. Each macromonomer incorporated results in a graft and the comonomer which is incorporated essentially constitutes the backbone. It is possible for the length and number of grafts to be varied by altering the molar mass of the macromonomer and its initial concentration in the copolymerization, respectively. A substantial amount of work has been aimed at finding adequate ways to synthesize macromonomers. Considerable effort has also been made to understand how the polymer chain influences the reactivity of the terminal unsaturation. This point has not yet

FIGURE 2.10 SCHEMATIC REPRESENTATION OF THE FORMATION OF GRAFT
COPOLYMERS FROM THE FREE-RADICAL COPOLYMERIZATION
OF MACROMONOMERS



been settled. Nevertheless, it is possible to prepare a variety of graft copolymers with well-defined structures and compositions containing very little backbone homopolymer contamination by this method. Since the macromonomer is made separately, it can be characterized independently.

2.3.5 MISCELLANEOUS METHODS

Other techniques have also been developed for the production of graft copolymers including radiation, thermal, photochemical and mechanochemical methods. However, the low grafting efficiency and homopolymer contamination are disadvantages. This is covered in more detail elsewhere [66].

2.4 THE SYNTHESIS OF MACROMONOMERS

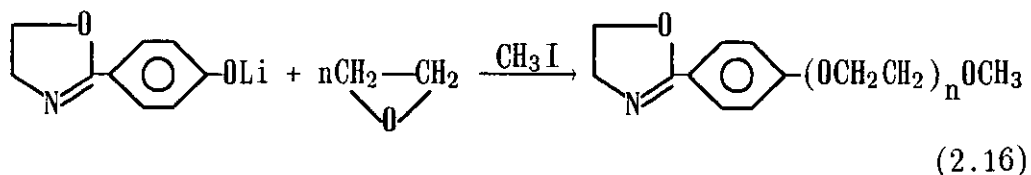
This is well-documented in various reviews [13,14,67]. Anionic, cationic and free-radical polymerization techniques are the most common methods used, with a few examples of polyaddition and group transfer processes.

2.4.1 ANIONIC POLYMERIZATION

The two general methods of producing a terminal unsaturation by anionic polymerization are to either utilize an unsaturated metal organic initiator or, more commonly, to react the 'living' polymer chains produced with an unsaturated electrophile to deactivate the sites.

(i) Use of a polymerizable initiator.

Of the two methods described above, this has the disadvantage that the unsaturation is generally sensitive to attack by carbanions. However, 4-vinylbenzyl lithium has been shown to be effective in the polymerization of styrene to produce monofunctional macromonomers [68]. Also, polymerizations involving oxanionic sites are preferable, since alkoxides do not generally react with carbon-carbon double bonds. Kobayashi et al [69], for example, have described a method of producing poly(ethylene oxide) macromonomers containing a heterocycle at the chain end, which can subsequently undergo cationic ring-opening polymerization. The polymerization of oxirane was initiated by means of an alcoholate and deactivated with methyl iodide, as depicted in equation 2.16.



(ii) Use of a polymerizable deactivator.

The electrophiles most commonly used for the deactivation of 'living' anionic polymers are organic halides and esters. In order to obtain macromonomers, the electrophiles must contain an unsaturation. Therefore, it is important to avoid side reactions of the anions with these unsaturations. For example, Ito et al [70] polymerized styrene anionically with butyl-lithium but found it necessary to react the styryl carbanions with ethylene oxide prior to capping with methacryloyl chloride. Thus, side reactions can be prevented by reducing the nucleophilicity of the carbanions. A wide range of electrophiles can be used to produce polymerizable end-groups, as shown in table 2.1.

TABLE 2.1 THE USE OF POLYMERIZABLE DEACTIVATORS IN ANIONIC
POLYMERIZATION FOR MACROMONOMER SYNTHESIS

<u>INITIATOR</u>	<u>MONOMER</u>	<u>DEACTIVATOR</u>	<u>REFERENCE</u>
sec-butyl lithium	styrene	ethylene oxide/ methacryloyl chloride	[70,71,72,73]
n-butyl lithium	styrene	allyl chloride	[74]
n-butyl lithium	styrene	epichlorohydrin	[75]
n-butyl lithium	styrene	p-vinylbenzylchloride	[76]
1-phenylethyl potassium	styrene	1,1-diphenylethylene/ p-bromomethylstyrene	[77]
n-butyl lithium	styrene	1,1-diphenylethylene/ vinylidimethylchlorosilane	[78]
n-butyl lithium	2-vinyl pyridine	p-bromomethylstyrene	[79]
n-butyl lithium	4-vinyl pyridine	methacryloyl chloride	[80]
potassium 2-methoxyethoxide	ethylene oxide	p-vinylbenzylchloride methacryloyl chloride	[81,82]
triphenylmethyl sodium	t-butyl methacrylate	p-chloromethylstyrene	[83]
triphenylmethyl sodium	methyl methacrylate	p-chloromethylstyrene	[84]
n-butyl lithium	hexamethylcyclotrisiloxane	chlorosilane	[85,86,87,88]

The major advantage of anionic methods is the so-called 'living' character of the polymers, when transfer and termination reactions are negligible [52]. This gives rise to narrow molar mass distributions. The functional purities of macromonomers prepared by anionic polymerization in the literature are high, usually >0.90. However, there are a number of disadvantages to anionic polymerization [12]. Low temperatures are often required and a high vacuum or an inert gas blanket is necessary. Scrupulous care must be taken to produce ultra-pure reagents and solvents in order to prevent side reactions of the 'living' sites. Also, the number of monomers which polymerize anionically is limited [89].

2.4.2 CATIONIC POLYMERIZATION

(i) Heterocyclic monomers.

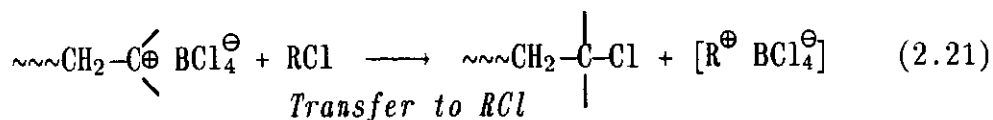
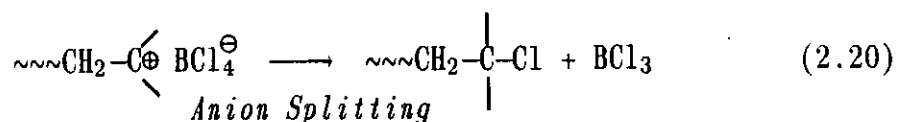
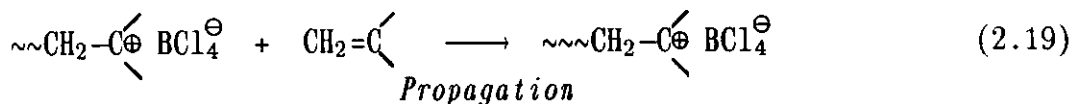
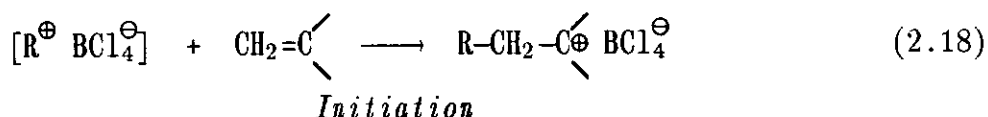
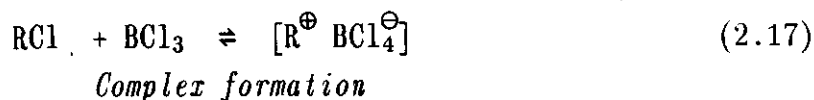
The cationic polymerization of some heterocycles, such as tetrahydrofuran, proceeds without spontaneous termination or chain transfer, i.e. 'living' polymers are produced [52,89]. In this case, similar principles apply as to anionic polymerizations. Macromonomers can be produced by using either an unsaturated initiator to initiate the polymerization or an unsaturated nucleophile to end-cap the 'living' cations. Whereas there are only a few examples of the use of an unsaturated initiator, the use of unsaturated nucleophiles predominates. Tetrahydrofuran is the obvious choice of a substrate to undergo cationic polymerization. Poly(tetrahydrofuran) macromonomers have been prepared with methacrylate [90], acrylate [91], p-vinylphenoxy [92] and p-vinylbenzyloxy [93] polymerizable end-groups.

(ii) Vinyl monomers.

The problem with the cationic polymerization of vinyl monomers is that transfer processes occur. However, Kennedy [94] developed a

method for producing macromonomers by the so-called 'inifer' technique which favours transfer to the initiating species (since the same species acts as initiator and chain transfer agent, this is called the 'inifer' technique). In the simplest case, monofunctional prepolymer can be obtained from a monofunctional inifer (see scheme 2.3). Kennedy has mainly applied this technique to isobutene. For example, isobutene has been polymerized using p-(β-bromoethyl) cumyl chloride and aluminium chloride, followed by dehydrobromination to produce a styryl end group [94].

SCHEME 2.3 THE SYNTHESIS OF MACROMONOMERS BY THE 'INIFER' TECHNIQUE



where R Cl = initiator and chain transfer agent

B Cl₃ = coinitiator

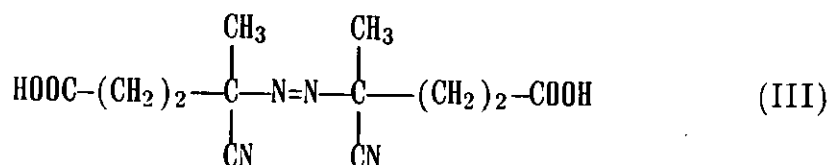
2.4.3 FREE-RADICAL POLYMERIZATION

Although this method has some drawbacks compared to anionic polymerization, such as broad molar mass distributions and mean functionality [13], it can be applied to a much wider range of monomers [52,89]. Also, the experimental difficulties encountered with ionic polymerizations do not occur with free-radical polymerization, so that the method is easier to apply. It does not appear that the drawbacks of free-radical polymerization adversely affect the final properties of the graft copolymers, after the macromonomers have been copolymerized [13].

Since the lifetime of growing radicals is very short, functionalization can only arise from the use of functional initiators or transfer processes [13,14]. Generally, monofunctional prepolymers are prepared, typically with carboxyl or hydroxyl groups, which are then converted to macromonomers by further reaction.

(i) Functional initiators.

A typical functional initiator is 4,4'-azobis(4-cyanovaleric acid) (ACVA, III)

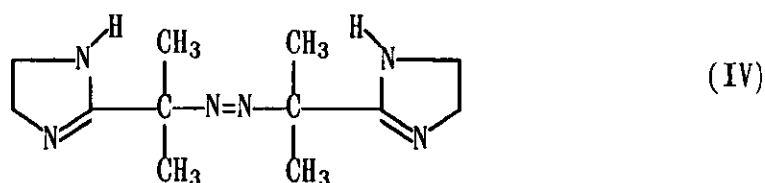


This behaves like a typical azo initiator. On homolytic cleavage of ACVA, radicals are formed which can then add to a monomer, thereby producing a polymer molecule with a functional group.

However, the following problems arise:-

- (a) Functionalization at only one end requires that termination occurs exclusively by disproportionation and that transfer reactions of the radical to monomer and solvent are negligible. If the first condition is not fulfilled, bifunctional chains can result from combination. If the second condition is not valid, only those macromolecules arising from primary radicals are functionalized.
- (b) It is difficult to control the molar mass, since conventional chain transfer agents will only give rise to a fraction of the resulting polymer molecules being functionalized.

However, Ishizu et al [95,96,97] have recently synthesized polystyrene and poly(vinyl acetate) prepolymers by using 2,2'-azobis(N,N'-di-methyleneisobutyramidine) (ADIB, IV) as functional initiator in the presence of diethyl(2-allylmalonate) as degradative chain transfer agent.



They claimed that approximately one imidazol group per chain was produced. This group was then reacted with an excess of various reagents, such as chloromethylstyrene [96,97], glycidyl methacrylate [95] or allyl glycidyl ether [95] to produce macromonomers. Also, poly(*t*-butyl methacrylate) macromonomers have been prepared by a similar procedure [83] using ADIB as

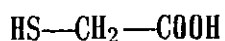
initiator and 1-buten-3-ol as a degradative chain transfer agent, followed by end-capping with chloromethylstyrene.

(ii) Functionalization by transfer reactions.

Functionalization at one end can be achieved by means of efficient functionalized transfer agents [52]. By controlling the molar ratio of monomer to transfer agent it is facile to control the molar mass of polymer formed. The efficiency of a chain transfer agent X for a given monomer is measured by its chain transfer constant C_x . In order to prevent the formation of polymer molecules lacking a functional group (arising from primary radicals originating from the initiator), a large value of C_x is essential; this increases the probability of transfer reactions occurring. There are many examples of the use of functionalized chain transfer agents. Some of these are shown in table 2.2.

(iii) Functionalization by matched initiator and chain transfer agent.

In general, the synthesis of well-defined functionalized polymers by means of functional free-radical initiators alone is far from satisfactory. Generally, large proportions of bifunctional polymers are produced [56]. Thompson and Waite [98] found that the yield of monofunctional chains could be increased by using an initiator and a chain transfer agent, both containing the same functional group. The chain transfer agent was used in such an amount to minimize chain disproportionation or combination occurring, i.e. to maximize the occurrence of chain transfer. Scheme 2.4 illustrates the formation of monofunctional carboxyl-terminated prepolymers using a combination of ACVA as initiator and thioglycollic acid (TGA, V) as chain transfer agent [56].



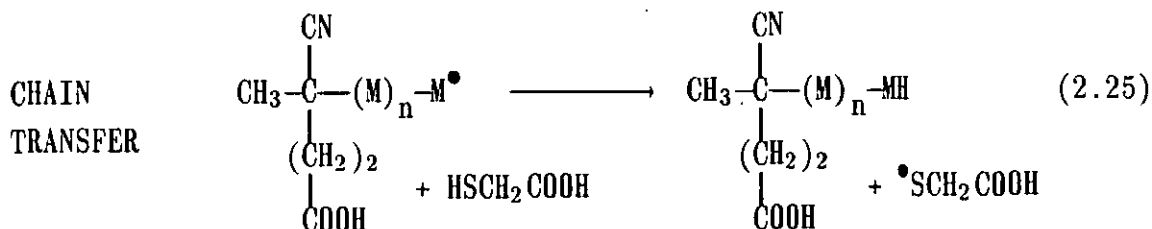
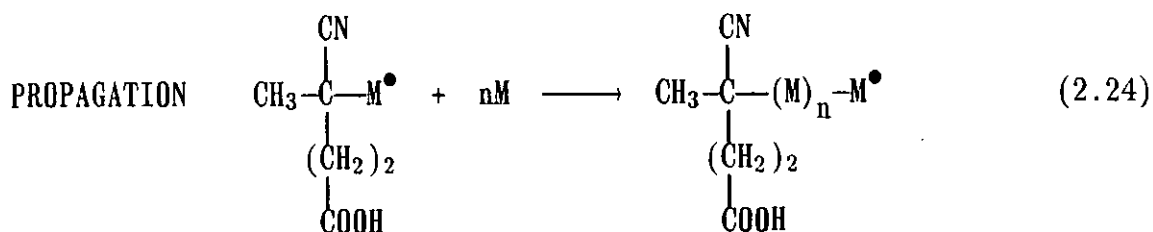
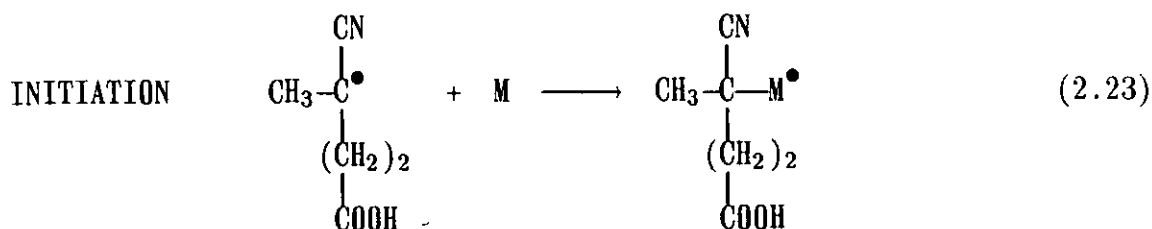
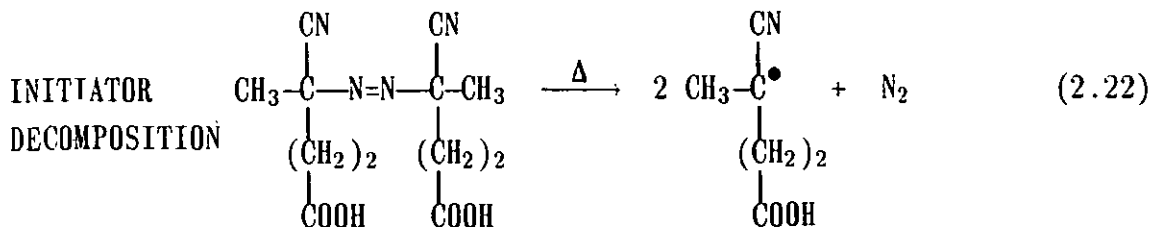
(V)

TABLE 2.2 MACROMONOMER SYNTHESIS USING FUNCTIONALIZATION BY
TRANSFER REACTIONS IN FREE-RADICAL POLYMERIZATION

<u>MONOMER</u>	<u>CHAIN TRANSFER AGENT</u>	<u>CAPPING AGENT</u>	<u>REFERENCE</u>
methyl methacrylate	thioglycollic acid	glycidyl methacrylate	[99,100,101,102]
stearyl methacrylate	thioglycollic acid	glycidyl methacrylate	[103]
methacrylic acid	} thioglycollic acid	glycidyl methacrylate	[102]
ethyl methacrylate			
butyl methacrylate			
lauryl methacrylate			
vinyl pyrrolidone	mercaptopropionic acid	chloromethylstyrene + phase transfer catalyst	[104,105]
dodecyl acrylate	mercaptoethanol	acryloyl chloride	[106]

SCHEME 2.4

FUNCTIONALIZATION USING A MATCHED FREE-RADICAL
INITIATOR AND CHAIN TRANSFER AGENT



Thompson and Waite [98] used various initiators and chain transfer agents to produce monofunctional carboxyl and hydroxyl terminated chains which could be transformed to macromonomers. They claimed that suitable monomers included esters, amides and nitriles of acrylic and methacrylic acids; styrene and alkyl styrenes; vinyl esters and heterocyclic compounds. Carboxyl-terminated poly(methyl methacrylate) and poly(2-acetoxyethyl methacrylate) have also been prepared by Niwa et al [107] using the matched initiator and chain transfer agent method. However, Corner [108] found difficulty in polymerizing vinyl acetate, styrene and N-vinyl pyrrolidone using ACVA in combination with TGA. This prompted him to perform a kinetic analysis of the matched chain transfer polymerization route. He found that care must be taken in the choice of reactants, experimental conditions and polymerization method in order to reduce the fraction of chains with unwanted functionality to negligible proportions. By defining w_t as the number of chains with unwanted functionality produced by termination reactions and w_{tr} as the number of chains with unwanted functionality produced by transfer reactions, he concluded the following:

- (i) w_t is smaller for low molar mass polymers; the use of a functionalized initiator and a functionalized chain transfer agent causes a decrease in w_t for monomers which terminate by disproportionation but an increase in w_t for monomers which terminate by combination. Thus, w_t depends upon the dominant mode of termination and the particular combination of initiator and chain transfer agent.
- (ii) In order to minimize w_t and w_{tr} , one should prepare a polymer with a low degree of polymerization, carefully choose reagents and restrict polymerizations to low conversions.
- (iii) The use of low standing concentrations of reactants by using a continuous feed results in an increase in w_t

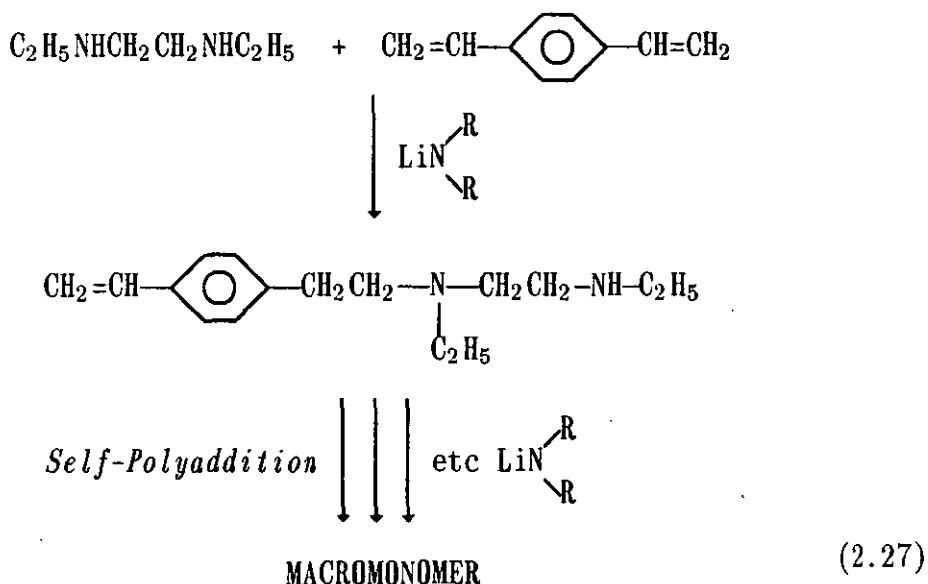
and w_{tR} .

(iv) The magnitude of w_t and w_{tR} can be reduced by polymerizing at a lower temperature.

Nevertheless, there is no doubt that monofunctional chains can be obtained under the correct conditions. The degree of functionalization can be as high as that obtained by ionic polymerization methods.

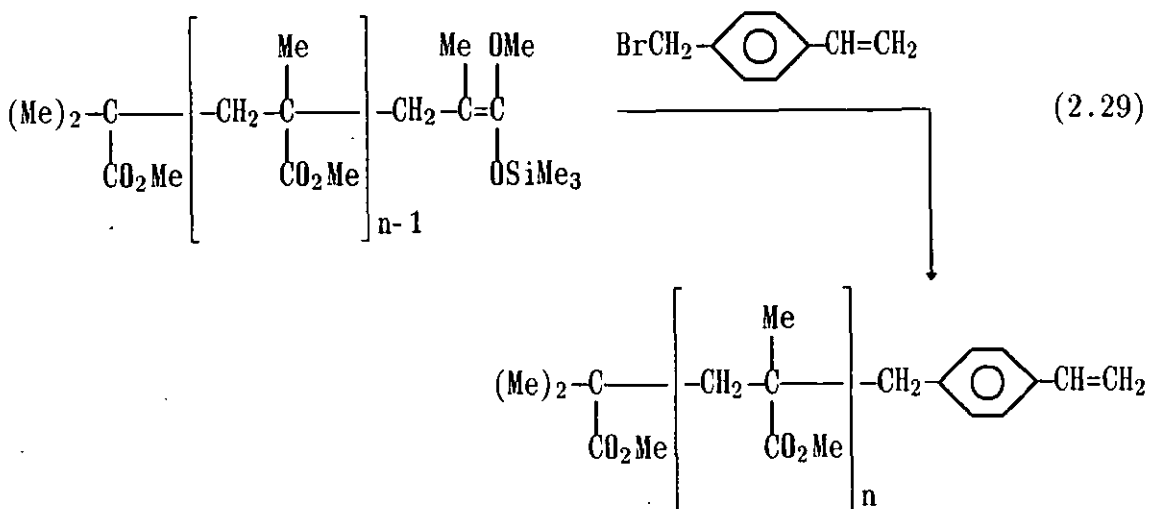
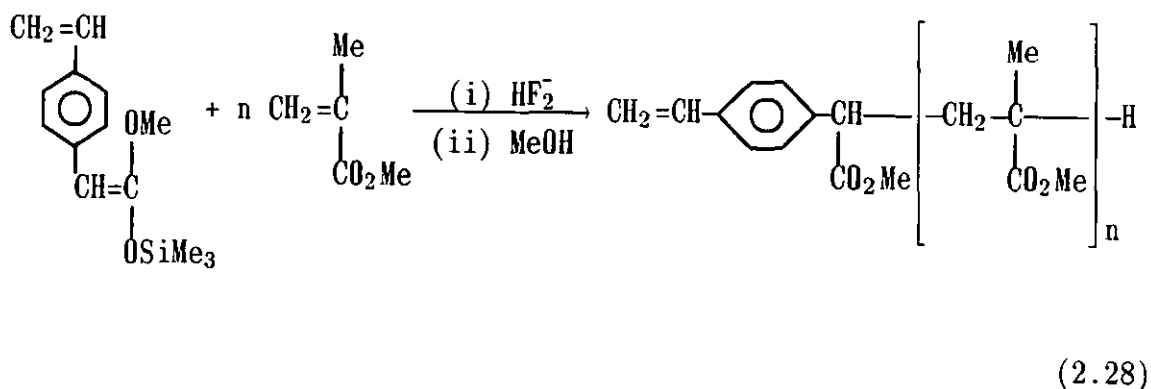
2.4.4 POLYADDITION PROCESSES

There are very few examples of these, the most noteworthy being the polyamine macromonomers prepared by Tsuruta et al [109,110]. Lithium diisopropylamide catalyses the reactions of N,N-diethylethylenediamine or piperazine with 1,4-divinylbenzene. The reaction is fast providing that stoichiometric proportions of the two reactants are used. The reaction is depicted in equation 2.27.



2.4.5 GROUP-TRANSFER POLYMERIZATION (GTP)

Group transfer polymerization is a relatively new concept [111]. A silyl ketene acetal initiator reacts with a monomer by a Michael addition. During the addition, the silyl group transfers to the monomer generating a new ketene acetal function which reacts with additional monomer in a repeated fashion. Group transfer polymerization works best with methacrylates, acrylates and acrylamides. It is similar to anionic polymerization in that 'living' polymers are produced, resulting in narrow molar mass distributions. Active hydrogens interfere with GTP, so that reagents and solvents must be dry and pure. The polymerization must also be conducted in a dry atmosphere. Two GTP techniques can be used to prepare macromonomers, as illustrated by Asami et al for the synthesis of poly(methyl methacrylate) macromonomers [112]. The first technique involved the use of a silyl ketene



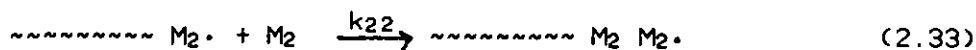
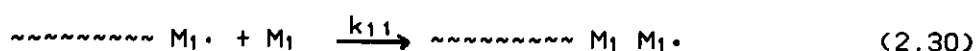
acetal initiator containing a vinylphenyl unsaturated group (see equation 2.28). The other method of producing a polymerizable end-group involved reacting the living silyl ketene end-group with p-vinylbenzylbromide, an electrophilic reagent (equation 2.29).

2.5 THE COPOLYMERIZATION OF CONVENTIONAL MONOMERS

Copolymerization involves the simultaneous polymerization of two or more monomers to form products which contain two or more different structures in the chain. Copolymerization may be achieved using various active centres including free-radical, ionic and coordination processes. The four basic copolymer structures are statistical, alternating, block and graft. The copolymerization of conventional monomers has been discussed in several excellent reviews. General references for sections 2.5.1 to 2.5.6 are [51,52,89,113].

2.5.1 THE TERMINAL MODEL AND REACTIVITY RATIOS

The copolymer composition and microstructure depend upon the relative concentrations of a variety of species and their relative reactivities towards each other. A number of models have been developed. The most universally applicable model is the terminal model, which can adequately represent many copolymerization systems. This was introduced in 1944, in papers contributed independently by Mayo and Lewis [114], Alfrey and Goldfinger [115] and Wall [116]. The basic assumption in the terminal model is that the reactivity of a propagating chain depends only upon the monomer unit in the copolymer chain on which the active centre is located. By considering the free-radical copolymerization of two monomers M_1 and M_2 , there are four possible propagation steps:



where k_{11} is the rate constant for a propagating chain ending in M_1 adding monomer M_1 , etc. The rates of disappearance of the two monomers, which are synonymous with their rates of entry into the copolymer, are given by the following equations:

$$\frac{-d[M_1]}{dt} = k_{11}[M_1 \cdot][M_1] + k_{21}[M_2 \cdot][M_1] \quad (2.34)$$

$$\frac{-d[M_2]}{dt} = k_{12}[M_1 \cdot][M_2] + k_{22}[M_2 \cdot][M_2] \quad (2.35)$$

Dividing equation 2.34 by 2.35 produces the ratio of the rates at which the two monomers enter the copolymer, ie.

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1 \cdot][M_1] + k_{21}[M_2 \cdot][M_1]}{k_{12}[M_1 \cdot][M_2] + k_{22}[M_2 \cdot][M_2]} \quad (2.36)$$

Assuming that a steady-state concentration of radicals exists, then

$$k_{21}[M_2 \cdot][M_1] = k_{12}[M_1 \cdot][M_2] \quad (2.37)$$

By substituting equation 2.37 into 2.36 and defining monomer reactivity ratios

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}} \quad (2.38)$$

one obtains the so-called copolymerization equation or the copolymer composition equation,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] (r_1[M_1] + [M_2])}{[M_2] ([M_1] + r_2[M_2])} \quad (2.39)$$

The terminal model also assumes that the copolymer chains have large molar masses and that the amount of monomer consumed in reactions other than propagation is negligible.

The monomer reactivity ratios, r_1 and r_2 , are the ratios of the rate constant for a given reactive species adding its own monomer to the rate constant for it adding the other monomer. The tendency of the two monomers to copolymerize is defined by their r values. An r_1 value greater than one means that the reactive species preferentially adds M_1 instead of M_2 , whereas an r_1 value less than unity means that the reactive species prefers to add M_2 .

2.5.2 TYPES OF COPOLYMERIZATION

Different types of copolymerization behaviour are observed depending on the values of the monomer reactivity ratios.

2.5.2.1 Ideal copolymerization

This occurs when the product $r_1 r_2$ is unity. In this case, the reactivities of both propagating chains are the same,

$$\text{i.e.} \quad \frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} \quad (2.40)$$

and the copolymerization equation becomes

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \quad (2.41)$$

The relative rate of incorporation of the two monomers is independent of the unit at the end of the propagating chain.

2.5.2.2 Alternating copolymerization

This occurs when $r_1 = r_2 = 0$ and the two monomers enter the copolymer in an alternating fashion. In this case, each reactive species preferentially reacts with the other monomer. The copolymerization equation reduces to

$$\frac{d[M_1]}{d[M_2]} = 1 \quad (2.42)$$

Therefore, the copolymer has an alternating structure irrespective of the feed composition.

2.5.2.3. Copolymerization in which $0 < r_1, r_2 < 1$

Most systems lie between the ideal and alternating cases. Obviously, as the $r_1 r_2$ product decreases towards zero, the tendency towards alternation increases. For cases in which both r_1 and r_2 are less than unity, there is a certain feed composition which produces an identical copolymer composition. This is known as an azeotropic copolymerization and proceeds without a change in composition of the feed or copolymer. For this condition,

$$\frac{[M_1]}{[M_2]} = \frac{(1 - r_2)}{(1 - r_1)} \quad (2.43)$$

2.5.2.4 Block copolymerization

If both r_1 and r_2 are greater than one, each propagating species prefers to react with its own monomer tending to form a blocky copolymer in which there are blocks of both monomers in the chain.

2.5.3 COPOLYMER COMPOSITION VARIATION

2.5.3.1 Statistical chemical heterogeneity

The copolymerization equation describes the instantaneous copolymer composition on a macroscopic scale and defines the overall composition. However, since the copolymer molar mass is finite, the compositions (as well as the chain lengths) of the individual copolymer molecules produced instantaneously are not identical. Therefore, there is a distribution in composition due to statistical fluctuations, known as statistical chemical heterogeneity.

2.5.3.2 Conversion chemical heterogeneity

The copolymerization equation strictly only gives the instantaneous composition formed at low degrees of conversion or when the change in comonomer feed is small as copolymerization proceeds. Except for azeotropic copolymerizations, the comonomer feed changes in composition as one of the monomers preferentially enters the copolymer. Therefore, as the degree of conversion increases, there is a drift in the comonomer (and hence copolymer) composition towards the less reactive monomer, resulting in conversion chemical heterogeneity. In order to determine the instantaneous copolymer composition as a function of conversion for any given comonomer feed, an integrated form of the copolymerization equation should be used.

Attaining a copolymer with a narrow composition distribution is desirable, since copolymer properties often depend on composition. The conversion chemical heterogeneity in the copolymer composition can be minimized by:

- (i) restricting the degree of conversion;
- (ii) choosing two comonomers whose copolymerization behaviour results in copolymer compositions similar to

the feed;

- (iii) the batchwise or continuous addition of the more reactive monomer, thereby maintaining the feed approximately constant.

2.5.4 EXPERIMENTAL DETERMINATION OF REACTIVITY RATIOS

For many systems, reactivity ratios have been calculated assuming that the terminal model is valid. If copolymerizations are performed at low conversion, then the instantaneous copolymerization equation applies but for high conversion copolymerizations, an integrated form of this equation is required. Many reactivity ratios have often been evaluated by determining the copolymer compositions for several feed compositions. The copolymer compositions can be measured directly or they can be determined by measuring concentrations of unreacted monomers, with the use of mass balances to calculate the mole fractions of monomers in the copolymer produced.

2.5.4.1 Linear least-squares techniques at low conversion

These techniques involve transferring the instantaneous copolymerization equation into a form which is linear in the parameters r_1 and r_2 and then estimating the reactivity ratios by linear least squares.

- (i) Finemann-Ross method [117].

By defining $f = d[M_1]/d[M_2]$ and $F = [M_1]/[M_2]$ then equation 2.39 can be rearranged to

$$\frac{F(f-1)}{f} = r_1 \frac{F^2}{f} - r_2 \quad (2.44)$$

Therefore, a plot of $F(f-1)/f$ versus F^2/f yields a straight line with slope r_1 and intercept r_2 .

(ii) Kelen-Tüdös method [118].

This is an extension of the Finemann-Ross method which spreads the data on the axes, thereby avoiding excessive weighting by extreme points. By defining $G = F(f-1)/f$ and $H = F^2/f$, they proposed the following linear equation,

$$\frac{G}{(\alpha + H)} = \left[r_1 + \frac{r_2}{\alpha} \right] \frac{H}{(\alpha + H)} - \frac{r_2}{\alpha} \quad (2.45)$$

where $\alpha = \sqrt{H_{\min} \cdot H_{\max}}$

H_{\min} and H_{\max} are the minimum and maximum values of H calculated from experiment.

Alternatively, equation 2.45 can be rearranged to

$$\frac{G}{(\alpha + H)} = r_1 \frac{H}{(\alpha + H)} - \frac{r_2}{\alpha} \left[1 - \frac{H}{(\alpha + H)} \right] \quad (2.46)$$

Therefore, by plotting $G/(\alpha + H)$ versus $H/(\alpha + H)$, r_1 and r_2 can be calculated from linear least squares analysis.

2.5.4.2 Non-linear least squares techniques at low conversion

Tidwell and Mortimer [119] pointed out that reactivity ratios should be determined by a non-linear regression technique and that the error associated with the estimates of r_1 and r_2 was a joint error which should be expressed as a joint confidence region. Many reactivity ratios are determined by a set of experiments where the monomer feed ratios are varied. However, Tidwell and Mortimer [120] used a different approach based on the statistical design of experiments using the instantaneous copolymer composition equation and non-linear least squares

estimation. They recommended an experimental design which involved doing a number of experiments at two compositions of monomer only defined by

$$F_a = \frac{2}{(2 + r_1)} \quad (2.47)$$

and

$$F_b = \frac{r_2}{(2 + r_2)} \quad (2.48)$$

where F_a and F_b are the comonomer feed ratios.

The r_1 and r_2 values used to define these feed compositions were estimates based on preliminary experiments and chemical intuition.

2.5.4.3 Estimating reactivity ratios when composition drifts

Apart from azeotropic copolymerizations, there is a drift in both monomer and copolymer composition as copolymerization proceeds. If the copolymer composition is analysed, the observed composition is an average of all the polymer made up to that conversion. However, if the monomer composition is being analysed, an integrated form of the copolymer composition equation can be used.

The error in variables method (EVM) has been used on composition data taken over a range of conversion [121]. EVM is a statistical approach to the general problem of estimating parameters in mathematical models which takes into account all sources of experimental error from all the measured variables. This is in contrast to least squares methods in which errors are assumed to exist only in the dependent variable, ie. copolymer composition. O'Driscoll and Reilly [122] have recommended that the EVM method should be used even at low conversion instead of least squares methods if there is a significant error in the

comonomer feed composition.

2.5.5 ALTERNATIVE COPOLYMERIZATION MODELS

Deviations from the terminal copolymerization model have been noted for various comonomer pairs and for various polymerization systems. Alternative copolymerization models are more complicated and require more parameters to describe them. The choice of experimental design and statistical estimation for reactivity ratio determination are likely to be more crucial for these models.

2.5.5.1 Penultimate model

The fundamental assumption of the terminal model, ie. that the reactivity of a growing radical chain is determined only by the identity of the terminal monomer unit, is equivalent to the assumption that the relative rates of monomer addition are insensitive to substitution at positions more remote than β to the radical centre. In order to explain some deviations from the terminal model in free-radical copolymerization, Merz Alfrey and Goldfinger [123] introduced the concept of the penultimate effect. They suggested that the reactivity of a growing polymer radical is determined by the identity of the penultimate as well as the terminal unit in the chain. This results in four distinct propagating radicals, eight possible propagation reactions and four reactivity ratios. The penultimate effect has been observed in free-radical copolymerizations where the monomers contain highly bulky or polar substituents. For example, Hill et al [124] have shown that the penultimate model most accurately describes the copolymerization of styrene and acrylonitrile.

2.5.5.2 Complex-participation model

Copolymerizations of monomers containing electron-donating substituents with monomers containing electron-withdrawing substituents have a marked tendency to produce alternating copolymers. The complex-participation model has been used to describe this behaviour and Seiner and Litt [125] were the first to report a mathematical analysis for this model. It is proposed that the 1:1 monomeric donor-acceptor complexes participate in propagation and compete with monomers for the growing chain ends. The complex-participation model can be described by eight propagation reactions and an equilibrium reaction forming the complex from the monomers.

2.5.5.3 Complex-dissociation model

This is similar to the complex-participation model in that donor-acceptor complexes participate in copolymerization. However, the complexes do not add to propagating chains in a concerted fashion but deliver only one of the two complexed monomers [113].

2.5.5.4 Depropagation during copolymerization

In all of the models described previously, the copolymerizations are effectively treated as being irreversible. However, near the ceiling temperature, the influence of depropagation must be considered. Lowry [126] has treated deviations from the copolymerization equation by developing a theory in which the addition of one of the two monomers is reversible.

2.5.5.5 Model discrimination

Most of the models can adequately fit copolymer composition data.

Composition data alone is inadequate for discriminating between models but comonomer sequence distributions are used for this purpose because they are more sensitive to the details of the chain growth process [113]. Hill et al [124] showed that the terminal, penultimate and complex-participation models all reproduced the compositional data for copolymerizations of styrene and acrylonitrile quite well. However, the sequence distribution predictions were quite different and allowed a clear distinction between the models. Information on the comonomer sequence distribution can be provided by ^{13}C Nuclear Magnetic Resonance spectroscopy [124]. It is also possible to calculate the comonomer sequence distributions for the various models from a knowledge of reactivity ratios and comonomer feed ratios. For example, the conditional probability P_{11} that a propagating chain terminated in M_1 adds monomer M_1 for the terminal model is given by

$$P_{11} = \frac{k_{11}[M_1\cdot][M_1]}{(k_{11}[M_1\cdot][M_1] + k_{12}[M_1\cdot][M_2])} = \frac{r_1}{(r_1 + [M_2]/[M_1])} \quad (2.49)$$

The number of various sequences depends on such probabilities. Complex algebraic expressions can be avoided if a matrix multiplication method is used to generate the probabilities [127]. Another method is the Monte Carlo approach [127] which involves generating copolymer chains in the computer memory using conditional probabilities to set the conditions for choices based on random number selections. By comparing the experimentally determined comonomer sequence distributions with those predicted by the various models, one can identify the most appropriate model for the copolymerization under study.

2.5.6 RADICAL AND MONOMER REACTIVITIES IN FREE-RADICAL COPOLYMERIZATION

The reactivity of a monomer towards a radical depends upon the

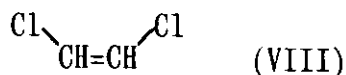
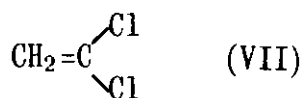
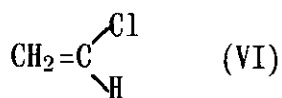
reactivities of both the monomer and the radical. The relative reactivities of monomers and their corresponding radicals can be obtained from monomer reactivity ratio data. The nature of substituents can influence reactivity through resonance, polar and steric effects.

2.5.6.1 Resonance effects

Mayo and Walling [128] originally showed that different reference radicals give essentially similar sequences of monomer reactivities. They found that the effectiveness of substituents in enhancing the reactivity of monomers depends on the resonance stabilization of the radical produced from the monomer. Substituents composed of unsaturated linkages are most effective in stabilizing the radicals due to the π -electrons which are available for delocalization. As with monomer reactivities, the order of radical reactivities is essentially the same irrespective of the monomer used as a reference. However, the order of substituents in enhancing radical reactivity is opposite to that for monomer reactivity. A substituent that increases monomer reactivity does so because it stabilizes and decreases the reactivity of the corresponding radical.

2.5.6.2 Steric effects

The rates of radical-monomer reactions also depend on steric effects. For example, compared to vinyl chloride (VI), the reactivity of vinylidene chloride (VII) increases, whereas the reactivity of 1,2-dichloroethene (VIII) decreases [52]. The former effect is due to increased stabilization of the resulting radicals due to two Cl substituents, whereas the latter effect is a result of steric hindrance between the monomer and the radical to which it is adding.



2.5.6.3 Polar effects

Tendency towards alternation increases as the difference in polarity between two monomers increases. Monomers with electron-donating or electron-withdrawing groups have widely differing polarities and, when copolymerized with one another, can produce highly alternating copolymers [129]. There is strong evidence from a number of systems to suggest that this results from the homopolymerization of 1:1 complexes formed [130,131]. The addition of a Lewis acid, such as trialkylaluminium, can increase the tendency to form alternating copolymers, even between monomers which do not normally copolymerize in an alternating fashion [130,131].

Various attempts have been made to correlate polymer radical and monomer reactivities in copolymerization. One of the earliest semi-theoretical attempts was the 'Q-e' scheme developed by Alfrey and Price [132] which took into account resonance stabilization and polar effects but not steric factors. This is still widely used, despite its shortcomings. This is dealt with more extensively elsewhere [133].

2.5.6.4 Solvent effects

Many free-radical copolymerizations are carried out in solution.

Copolymerizations of non-polar monomers with monomers containing ionizable groups, groups capable of hydrogen-bonding interactions or even just polar groups have been shown to be influenced strongly by the nature of the solvent [134]. The effects have been attributed to electrostatic repulsion of charged monomers and radicals, changes in monomer polarity, the participation of monomer complexes, hydrogen-bonding of monomer with solvent or solvent dielectric effects. Such effects give rise to changes in measured reactivity ratios, depending on the solvent. However, Harwood [127] has found that, although the reactivity ratios of a number of copolymerization systems varied considerably as the reaction solvent was varied, copolymers with identical compositions had the same microstructure irrespective of the solvent (ie. the monomer sequence length distributions were the same). Harwood suggested that partitioning of monomers between solvent and growing radicals is very significant. He proposed that reactivity ratios determined for polar monomers were probably artefacts which were the products of true reactivity ratios and partition coefficients. He suggested that reactivity ratios were independent of solvent and the role of the solvent was to influence the relative concentrations of comonomers available to the growing chain end.

2.6 THE COPOLYMERIZATION OF MACROMONOMERS WITH COMONOMERS

2.6.1 GENERAL FEATURES

The copolymerization of macromonomers with vinyl or acrylic comonomers to yield graft copolymers with well-defined compositions is the major field of application for macromonomers. The ability of macromonomers to copolymerize differs from conventional monomers due to the following reasons [14,135,136].

- (i) The molar concentration of macromonomer is low as a result of its molar mass ($\bar{M}_n = 1 \times 10^3 - 3 \times 10^4 \text{g.mol}^{-1}$)

in most cases).

- (ii) The reactivity of the terminal unsaturation may be lower than that of a conventional monomer exhibiting the same type of unsaturation, due to the influence of the bulky chain to which it is attached.
- (iii) When the macromonomer chain can give rise to transfer reactions, the probability for such reactions is enhanced because the number of chain segments per unsaturation is high.

Macromonomer copolymerizations have been generally performed using free-radical methods, although there are a few examples of anionic [137], group transfer [73], and coordination copolymerization [74,138]. Macromonomers with different chemical structures have been copolymerized with a range of different comonomers to produce graft copolymers with a variety of chemical compositions. The macromonomer molar mass used in these copolymerizations varied from approximately 5.0×10^2 to $3.0 \times 10^4 \text{g.mol}^{-1}$ (\bar{M}_n). The free-radical copolymerizations are generally carried out in solution and the molar masses of the graft copolymers produced are generally low [78,85,87,88,139] ($\bar{M}_n < 8 \times 10^4 \text{g.mol}^{-1}$). This low molar mass is explained to be a consequence of one of the following:

- (a) the low concentration of double bonds [85,92,135,139];
- (b) the low mobility of the macromonomer and lack of access to the reactive site [85];
- (c) transfer reactions [85,90].

In any case, the lifetime of a radical is too short to allow the sufficient number of growth steps necessary for high molar masses. Further evidence of this has been obtained by studying macromonomer homopolymerizations. Generally for free-radical solution homopolymerizations of macromonomers, the degrees of

polymerization are very low and only oligomers are formed [85,90,136]. In some cases, no polymerization has occurred at all [80,140,141]. Several authors have observed that, although the end group concentration decreased, there was no increase in molar mass [140,141]. Kennedy and Hiza [141] and Takaki et al [142] have homopolymerized macromonomers in bulk, despite not being able to homopolymerize them in solution. Recently, Tsukahara et al [143], in a study of the free-radical solution homopolymerization behaviour of a polystyrene macromonomer, found that the degree of polymerization depended strongly on concentration as a result of a pronounced gel effect. It is believed that if the macromonomer concentration is too low, the rates of propagation and termination are suppressed by (a) or (b) above, whereas the rate of chain transfer is unaffected. Therefore, the radical has little chance to propagate. However, the viscosity of the system is increased if the macromonomer concentration is high enough, thereby increasing the rate of propagation and reducing the rate of termination. This results in a product with a higher molar mass.

2.6.2 THE TERMINAL MODEL AND REACTIVITY RATIOS

As with conventional monomers, the ability of macromonomers and comonomers to participate in a copolymerization is determined by their reactivity ratios. If it is assumed that the terminal model is valid, then the instantaneous copolymer composition is given by the copolymerization equation described in section 2.5.1. The most outstanding characteristic feature in a macromonomer copolymerization is the large difference between the molar masses of the macromonomer and the comonomer. This results in a large difference between their molar concentrations in the feed. Under such circumstances, the copolymerization equation can be simplified, as originally described by Jaacks[144]. In the case of copolymerizations of macromonomer (M_2) with comonomer

(M₁),

$$[M_2] \ll r_1[M_1] \text{ and } r_2[M_2] \ll [M_1].$$

As a result, the copolymerization equation (equation 2.39) reduces to

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]} \quad (2.50)$$

This implies that the value of r_2 is insignificant to the process, provided that the molar concentration of macromonomer in the feed is small. Essentially, the copolymer is almost pure poly(comonomer) containing only a few macromonomer units (in molar quantities). Therefore, chain propagation takes place almost exclusively by addition to polymer radicals with a terminal M₁ unit and the propagation of radicals with a terminal M₂ unit may be neglected on a statistical basis. Equation 2.50 provides a method of determining the reactivity ratio r_1 in macromonomer copolymerizations. In principle, reactivity ratios can also be obtained from methods applicable to the copolymerization of conventional monomers, previously outlined in section 2.5.4.

2.6.3 GRAFT COPOLYMER COMPOSITION VARIATION

2.6.3.1 Statistical chemical heterogeneity

As with conventional copolymers, the compositions of individual graft copolymer molecules produced instantaneously are not identical. The chemical composition distributions (CCD) of graft copolymers, arising from statistical chemical heterogeneity in the copolymerizations of macromonomers, have been predicted by Stejskal et al [145-147] as follows. The CCD is much broader than copolymers prepared by the copolymerization of conventional monomers [147]. The CCD becomes broader and more asymmetrical

when macromonomers with higher molar masses are copolymerized [146]. However, the graft copolymer CCD decreases as the degree of grafting (ie. higher macromonomer incorporation) increases [145,147]. The chemical heterogeneity also decreases when the backbone molar mass increases [146], similar to the prediction in the copolymerization of conventional monomers.

2.6.3.2 Conversion chemical heterogeneity

In contrast to the statistical chemical heterogeneity, the conversion chemical heterogeneity is not predicted to be affected by the macromonomer molar mass. Stejskal and Kratochvíl [148] have predicted that the graft copolymer CCD resulting from conversion chemical heterogeneity is similar to statistical copolymers. Also, owing to the low molar concentrations of macromonomer, there is little change in the comonomer feed as the copolymerization proceeds. Therefore, it is thought that fluctuation in composition due to conversion chemical heterogeneity will be low up to 50-70% conversion [135,136].

2.6.4 MACROMONOMER REACTIVITY

The copolymerization of macromonomers raises an important question: will the polymerizable unsaturation attached to a polymer chain react with the same predictability as a typical low molar mass monomer? The general copolymerization behaviour of macromonomers is disputed in the literature. Opinions differ as to whether the polymer chain affects the reactivity of the terminal unsaturation. Reports dealing with both r_1 and r_2 values for the copolymerization of comonomer M_1 with a macromonomer M_2 have been limited as a result of the low molar concentration of macromonomer. However, values for the comonomer reactivity ratio r_1 have been quite extensively reported and most of the information available has been gained from such

determinations.

2.6.4.1 Macromonomer end-group

There are many reports showing that the copolymerization reactivity of a macromonomer is similar to that of a conventional monomer corresponding to the polymerizable end-group. In these cases, the reactivity is governed by the chemical structure of the end-group and it is independent of the macromonomer molar mass [77,87,94,97,99,102,103,149,150,151,152]. Therefore, the macromonomer reactivity is governed by the resonance, steric and polar effects associated with the end-group, as for conventional monomers in free-radical copolymerization.

2.6.4.2 Macromonomer chain length

There are also reports showing that macromonomer reactivity is lower than the respective low molar mass monomers and that it decreases as the macromonomer molar mass increases. Generally, three factors have been reported to be responsible for this.

(i) Kinetic excluded volume effect.

This is essentially an enhanced diffusion control effect associated with the size of the macromonomer chain. The macromonomer molar mass reduces its translational diffusivity and it increases the topological resistance against the segmental diffusion of the reactive end-group. This results in a reduction of the relative propagation rate of the macromonomer compared to the small monomer. As a result of the kinetic excluded volume effect, it has been reported that the macromonomer reactivity decreases as its molar mass increases [18,74,75,81,91,110]. Parameters affecting the macromonomer mobility have also been found to affect the copolymerization. For example, the rate of polymerization decreases with an increase in macromonomer molar mass [153]; conversion decreases as the macromonomer molar mass increases due to increased viscosity [138] and the reactivity decrease is more pronounced at higher conversion due to increased

viscosity [141].

(ii) Incompatibility between unlike polymers.

This is due to the thermodynamic repulsive interaction between a macromonomer and a propagating comonomer chain which results in a non-homogeneous distribution of the polymerizable end-group in the reaction medium. As a result, it has been reported that the macromonomer reactivity decreases as its molar mass increases [81,82,104,150,154]. Other consequences are that macromonomer reactivity decreases with conversion [150], incomplete macromonomer conversion due to phase separation [71], and decreased conversion with a higher macromonomer molar mass [71,104]. In such systems, it is likely that the factors determining polymer-polymer-solvent compatibility will influence the macromonomer reactivity. These include [155]:

- (a) the relative amounts of the two polymer chains;
- (b) the interaction parameter χ between the two chains, which is molar mass dependent;
- (c) the nature of the solvent.

(iii) The effect of the copolymerization solvent.

Repulsive interactions arising from the asymmetrical nature of the copolymerization solvent for the macromonomer and the propagating comonomer chain have been found to affect the macromonomer reactivity in a number of systems [81,105,152,154,156,157]. In such cases, the difference in expansion or swelling of the polymer coils can change the degree of interpenetration and the volume fraction of solvent will be an important factor. One of the more interesting works covering solvent effects in macromonomer copolymerizations has been produced recently by Tsukahara et al [157]. They copolymerized methacrylate-terminated poly(dimethylsiloxane) macromonomers with methyl methacrylate in benzene (a good solvent for both

components) and phenetol (a poor solvent for the macromonomers). They found that the reactivity of a macromonomer with a molar mass of $\bar{M}_n = 1020\text{g.mol}^{-1}$ was identical to a conventional methacrylate in both solvents. However, although a macromonomer with a higher molar mass ($\bar{M}_n = 8670\text{g.mol}^{-1}$) also had the same reactivity in benzene, its reactivity was markedly reduced in phenetol.

It is also possible for the copolymerization solvent, rather than the macromonomer chain length, to affect the reactivity of the terminal unsaturation in a similar manner to its effect in the copolymerization of conventional monomers as already discussed in section 2.5.6.4.

CHAPTER THREE

EXPERIMENTAL

3.1 CHEMICALS USED

3.1.1 ALPHABETICAL LIST INCLUDING ABBREVIATIONS

4,4'-Azobis(4-cyanovaleric acid) (ACVA) was used as supplied by Aldrich Chemical Company Ltd, 98% pure.

2,2'-Azobis(isobutyronitrile) (AIBN) was used as supplied by Fluka Chemie AG.

Benzoic acid, 99+% purity, was used as supplied by Aldrich Chemical Company Ltd.

Tetrabutylammonium hydroxide (TBAH) was used as supplied by Aldrich Chemical Company Ltd, 1.0M solution in methanol.

n-Butyl methacrylate (BMA) was supplied by Koch Light Laboratories, stabilized with 0.01% hydroquinone. This was purified by vacuum distillation (section 3.1.2).

Calcium hydride, 95% (CaH_2) was used as supplied by Aldrich Chemical Company Ltd as a coarse ground powder.

Carbon tetrachloride (CCl_4), Standard Laboratory Reagent (SLR) grade, was used as supplied by Carless Solvents.

Chloroform (CHCl_3), SLR grade, was used as supplied by Carless Solvents.

2-Ethoxyethanol, 99% pure, was used as supplied by Aldrich Chemical Company Ltd.

Ethyl acetate, SLR grade, was used as supplied by Carless Solvents.

2-Ethyl hexyl acrylate (EHA) was supplied by Harlow Chemical Co. Ltd. This was dried over anhydrous magnesium sulphate, filtered and destabilized by passing through an inhibitor remover column (see section 3.1.2).

n-Heptane, 99+% HPLC grade, was used as supplied by Aldrich Chemical Company Ltd.

n-Hexane, Analytical Reagent (AR) grade, was used as supplied by Fisons PLC.

2-Hydroxyethyl methacrylate (HEMA) was supplied by Aldrich Chemical Company Ltd, in 97% purity and inhibited with 300 ppm hydroquinone monomethyl ether. This was dried over anhydrous magnesium sulphate before use.

Propan-2-ol(isopropanol), AR grade, was used as supplied by Fisons PLC.

Anhydrous Magnesium sulphate ($MgSO_4$) was used as supplied by Fisons PLC.

Methanol, SLR grade, was used as supplied by Carless Solvents.

4-Methyl pentan-2-one (methyl isobutyl ketone MIBK), AR grade, was used as supplied by Fisons PLC.

Methyl methacrylate (MMA) was obtained from Aldrich Chemical Company Ltd, 99% pure and inhibited with 10 ppm hydroquinone monomethyl ether. This was purified by vacuum distillation before use (see section 3.1.2).

Oxalyl chloride, 98% pure, was supplied by Aldrich Chemical Company Ltd. This was also purified by vacuum distillation before use.

Phenolphthalein, primary standard reagent, was used as supplied by Aldrich Chemical Company Ltd.

Potassium hydrogen phthalate, primary standard grade, was used as supplied by Aldrich Chemical Company Ltd.

Silica gel, self-indicating granules, was used as supplied by Fisons PLC.

Sodium hydroxide pellets, 97+% pure, were used as supplied by BDH Chemicals Ltd.

Styrene was obtained from Aldrich Chemical Company Ltd, 99% pure and inhibited with 10-15ppm 4-tert-butylcatechol. This was purified by vacuum distillation before use (see section 3.1.2).

Tetrahydrofuran (THF), unstabilized AR grade was used as supplied by Fisons PLC.

Mercaptoacetic acid (Thioglycolic acid, TGA), 95% pure, was used as supplied by Aldrich Chemical Company Ltd.

Thymol Blue, ACS reagent, was supplied by Aldrich Chemical Company Ltd. This was used as a 2%(w/v) solution in methanol.

Toluene, SLR grade, was supplied by Carless Solvents. For polymer purification purposes, it was used as supplied. For macromonomer and graft copolymer synthesis it was dried over calcium hydride before use and then filtered.

Triethylamine, 98% pure SLR grade, was used as supplied by Fisons PLC.

3.1.2 MONOMER PURIFICATION

BMA, MMA and styrene monomers were purified by high vacuum distillation on a purpose built vacuum frame as used by Taylor [17]. The pumping system consisted of a rotating oil pump and a mercury diffusion pump. Greaseless PTFE O-ring taps and joints were used throughout the frame. Monomers were degassed using the familiar freeze/degas/thaw cycles to remove dissolved oxygen and then distilled immediately before use.

EHA could not be purified by distillation as a result of its high boiling point. This monomer was purified by passing through a column containing a hydroquinone monomethyl ether inhibitor

remover. This method was recommended by Harlow Chemical Company Ltd and the inhibitor remover column was supplied by Aldrich Chemical Company Ltd.

3.2 THE SYNTHESIS OF METHACRYLATE-TERMINATED MACROMONOMERS

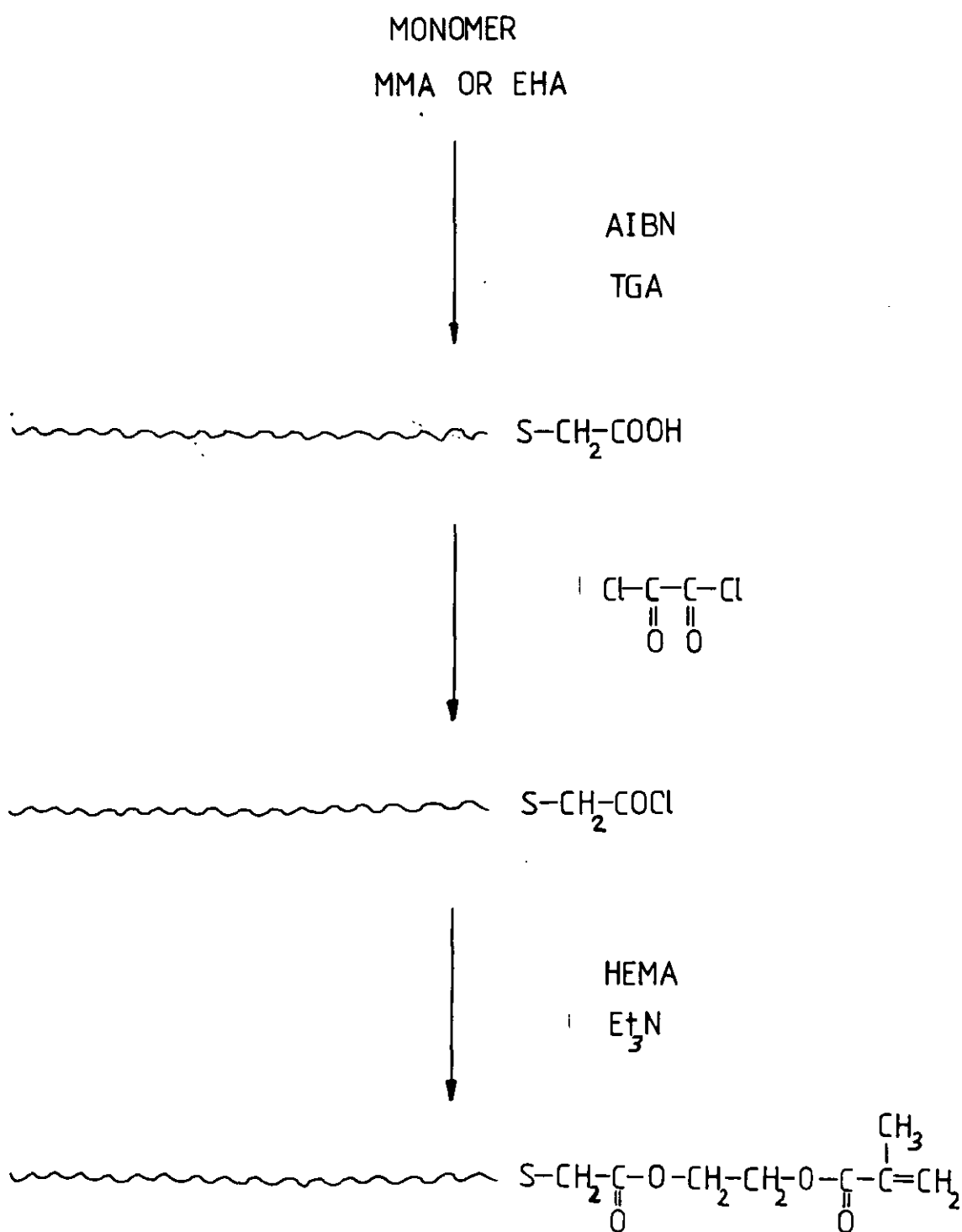
Methacrylate-terminated macromonomers of PMMA and PEHA were synthesized using the same procedure. This involved three steps, as illustrated in scheme 3.1. Initially, a carboxyl-terminated prepolymer was prepared by free-radical polymerization. The carboxyl group was then converted to the methacrylate polymerizable end-group via an acyl-chloride intermediate.

3.2.1 THE SYNTHESIS OF CARBOXYL-TERMINATED PREPOLYMERS

This was achieved by the free-radical solution polymerization of monomer using ACVA and TGA as matched free-radical initiator and chain transfer agent, respectively. MMA or EHA were mixed with polymerization solvent and TGA in a three-necked flask containing a nitrogen inlet and condenser. After purging the solution with nitrogen for 20 minutes, the initiator ACVA was added and the flask was transferred to a thermostatic water bath set at 353 ± 0.1 K. Polymerization was then allowed to continue for 1.5-2 hours. The flask was then removed and the polymer solution was allowed to cool. For MMA polymerizations, 2-ethoxyethanol was originally used as the polymerization solvent but this was subsequently changed to ethyl acetate, which was used exclusively as a solvent for the polymerizations of EHA.

The procedure for isolating and purifying the polymers produced varied, depending on the nature of the polymer and the polymerization solvent in which it was synthesized.

SCHEME 3.1 THE SYNTHESIS OF METHACRYLATE-TERMINATED
MACROMONOMERS



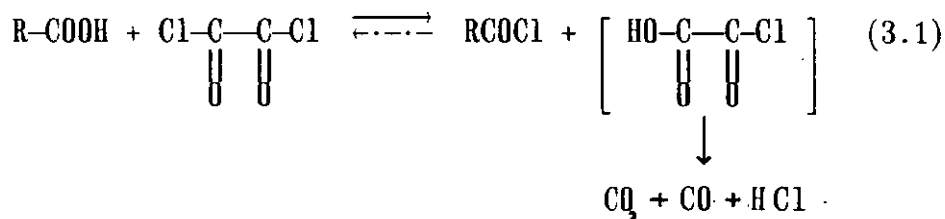
- (i) For PMMA prepared in 2-ethoxyethanol, the polymer was initially precipitated in water. This was then heated in order to coagulate the PMMA so that it could be readily isolated. Purification was then performed by redissolving the polymer in fresh hot methanol followed by precipitation in water which was then heated to coagulate the PMMA as above. This procedure was carried out three times.
- (ii) For PMMA prepared in ethyl acetate, the solvent was initially evaporated to isolate the polymer. This was then purified in an identical manner to (i) by repeatedly redissolving in hot methanol and precipitating in water.
- (iii) For PEHA prepared in ethyl acetate, the polymer was isolated in cold methanol as an oil which settled under gravity. After decanting the ethyl acetate/methanol mixture, purification was achieved by redissolving the PEHA in fresh ethyl acetate followed by reisolation in cold methanol. This procedure was also carried out several times.

After purification, all polymers were dried at 353 K for several hours in a vacuum oven containing a solvent trap. Poly(methyl methacrylate) was obtained as a white powder, whereas poly(2-ethyl hexyl acrylate) was obtained as a colourless, viscous oil. These carboxyl-terminated prepolymers were characterized by EGA, IR, ¹H NMR and GPC, details of which are given in section 3.5.

3.2.2 THE CONVERSION OF CARBOXYL END-GROUP TO ACYL CHLORIDE

This was accomplished using oxalyl chloride. The reaction is

essentially an equilibrium exchange reaction which is thought to involve an anhydride intermediate [158]. The oxalic acid derivative is unstable producing carbon dioxide, carbon monoxide and hydrochloric acid thereby driving the equilibrium to the right, as depicted in equation 3.1. Oxalyl chloride was preferred to thionyl chloride since it is less reactive [159].

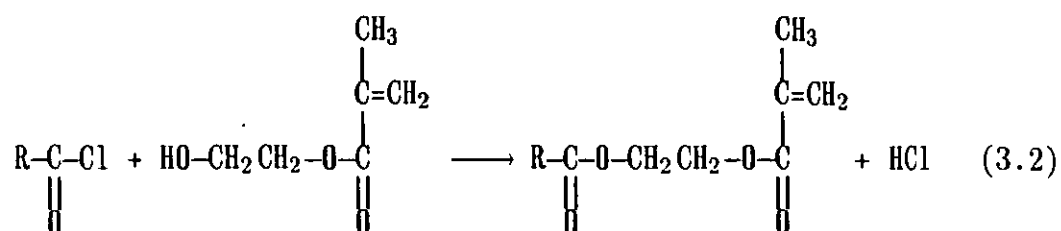


The procedure which was used for this reaction was similar for both carboxyl-terminated PMMA and PEHA prepolymers, irrespective of their methods of preparation. A 5% (w/w) solution of carboxyl-terminated PMMA was prepared in dry toluene. For PEHA prepolymers this concentration was 10% (w/w) as a result of its higher solubility. This solution was transferred to a three-necked flask equipped with a nitrogen inlet and condenser containing a silica-gel drying tube. The flask was placed in an ice-bath and the solution was purged with nitrogen for 30 minutes. The nitrogen supply passed through a silica-gel drying tube before entering the solution in order to remove any moisture. Oxalyl chloride was then added and the reaction was carried out for 24 hours, during which the solution attained room temperature. Double the molar quantity of oxalyl chloride necessary for stoichiometric reaction was used. After reaction, the unreacted oxalyl chloride and the toluene were removed by distillation under reduced pressure using the same procedure given in section 3.1.2 for monomer purification using this method. When distillation had ceased, the polymer was redissolved and this was again removed to extract any last traces of oxalyl chloride. The acyl chloride terminated polymers were characterized by IR (see

section 3.5.2.1).

3.2.3 THE CONVERSION OF ACYL CHLORIDE END-GROUP TO METHACRYLATE

This was achieved by reacting the acyl chloride-terminated polymers with HEMA using triethylamine as a catalyst according to equations 3.2 and 3.3.



The acyl chloride terminated polymers were dissolved in dry toluene. As for the previous step, the concentrations of PMMA polymers were 5% (w/w) while the concentrations of PEHA polymers were 10% (w/w). As before, each solution was placed in a three-necked flask containing a nitrogen inlet and a condenser equipped with a silica-gel drying tube. After placing the flask in an ice bath and purging the solution with N₂ for 30 minutes, HEMA was added in 0.3 molar excess. Triethylamine was finally added as catalyst. The reaction was carried out for 24 hours, over which room temperature was attained. After reaction, the mixture was filtered in order to remove the salt produced. The remaining triethylamine and toluene were then removed by distillation under reduced pressure. Both methacrylate-terminated PMMA and PEHA macromonomers were purified by dissolving in acetone followed by isolation in water to remove unreacted HEMA. The PMMA macromonomers were filtered off as a solid and the PEHA

macromonomers were isolated in a separating funnel as an oil. This procedure was then repeated. Finally, all macromonomers were redissolved in acetone. The solutions were transferred to distillation flasks and distilled under reduced pressure at room temperature in order to remove water resulting from the purification process.

3.3 THE SYNTHESIS OF GRAFT COPOLYMERS

3.3.1 POLY STYRENE-graft-POLY(METHYL METHACRYLATE) AND POLYSTYRENE-graft-POLY(2-ETHYL HEXYL ACRYLATE) COPOLYMERS

PS-graft-PMMA and PS-graft-PEHA copolymers were synthesized by the free-radical solution batch copolymerization of styrene with methacrylate-terminated PMMA and PEHA macromonomers respectively. This was depicted in figure 2.10. Purified styrene and PMMA or PEHA macromonomer were weighed accurately into a three-necked flask containing a magnetic follower. The required volume of toluene was added and the flask was equipped with a stopper, a nitrogen inlet and a condenser. After allowing the components to mix via magnetic stirring, the solution was purged with nitrogen for 20 minutes. AIBN was weighed accurately and added as a free-radical initiator. The flask was immediately transferred to a water bath thermostatic at 333 ± 0.1 K, where the copolymerization was performed with nitrogen continuing to bubble through the solution. Two series of copolymerizations were performed for each macromonomer copolymerized. Firstly, a copolymerization time of 10 hours was used to give a fairly low conversion of macromonomer (<20%) in order to study macromonomer reactivities. Secondly, a copolymerization time of 31 hours was

used to produce an intermediate macromonomer conversion (approximately 40%) in order to monitor any drifts in composition. Copolymers prepared under the latter conditions were subsequently used as steric stabilizers in dispersion polymerization (see sections 3.4 and 4.3). In each series of copolymerizations, the feed ratio of styrene to macromonomer was varied but the overall monomer and the initiator concentrations were kept constant. Conditions were chosen to produce copolymers with molar masses of approximately $40 \times 10^3 \text{g.mol}^{-1}$ (\bar{M}_{peak} by GPC) at a reasonable rate of polymerization. After copolymerization, the flasks were removed and the solutions were allowed to cool. Unpurified products were initially characterized by GPC using dual detectors in order to determine macromonomer conversions (see sections 3.5.4.2 and 4.2.1). Unreacted macromonomer was removed by redissolving the impure products in toluene followed by precipitation in hot methanol. This procedure was repeated (3-6 times). The purification was also monitored by GPC. Purified products were then dried in a vacuum oven at 353 K and initially characterized by TLC in order to estimate homopolymer contamination (see section 3.5.5). The products were then characterized by GPC, IR spectroscopy and ^1H NMR spectroscopy, as described in section 3.5.

3.3.2 DETERMINATION OF REACTIVITY RATIOS

Reactivity ratios were determined for the copolymerizations of PMMA and PEHA macromonomers with styrene by evaluating the data obtained at low conversion. The Finemann-Ross [117] and Kelen-Tüdös [118] linear least squares methods and Jaacks simplification [144], as described in sections 2.5.4 and 2.6.2, were all used for each series of copolymerizations of different macromonomers to obtain estimates of reactivity ratios.

3.3.3 "BLANK" EXPERIMENTS INVOLVING THE POLYMERIZATION OF STYRENE

A number of "blank" experiments were performed where styrene was polymerized in the presence of PMMA or PEHA carboxyl-terminated prepolymers, ie. PMMA/PEHA chains with non-copolymerizable end-groups. The reaction conditions used were identical to those for macromonomer copolymerizations except that the methacrylate-terminated PMMA or PEHA chains were replaced by their carboxyl-terminated prepolymers. Products were analysed by GPC using dual detectors and compared to the graft copolymers produced as described in section 3.3.1. This was achieved in order to monitor any macromonomer incorporation resulting from transfer grafting reactions to the PMMA or PEHA chain segments, rather than by copolymerization of the terminal unsaturation.

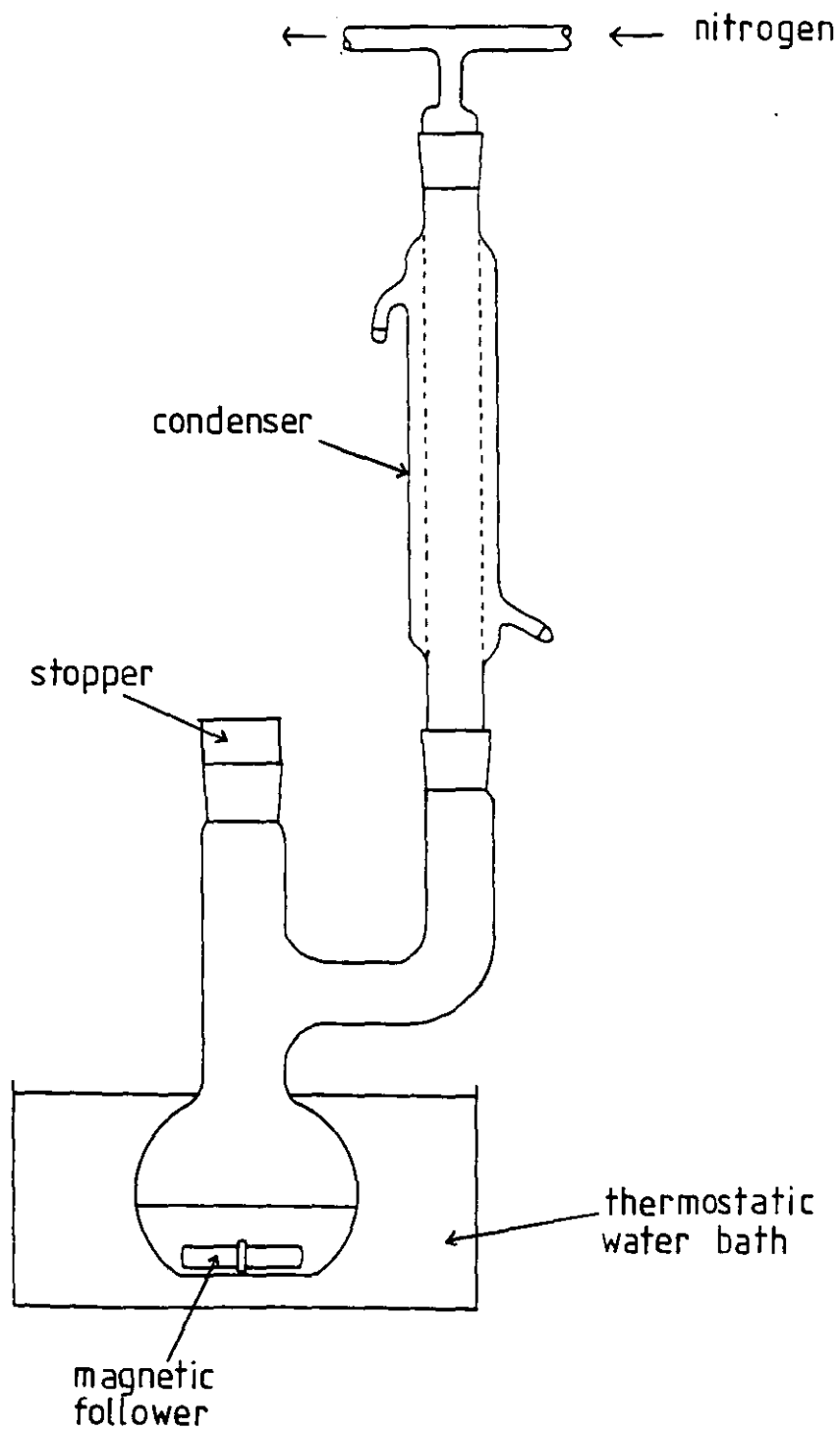
In addition, PS homopolymers were synthesized by polymerizing styrene under the same conditions as for the macromonomer copolymerizations, ie. identical total monomer and initiator concentrations and the same polymerization times. Such products were also characterized by GPC in order to compare their molar masses with those of the graft copolymers produced under similar conditions.

3.4 THE SYNTHESIS OF NON-AQUEOUS DISPERSIONS

Dispersions of PMMA in aliphatic hydrocarbon media were prepared using PS-graft-PEHA copolymers as stabilizers. The dispersion polymerizations were performed using the apparatus illustrated in figure 3.1. Purified MMA monomer, AIBN initiator and PS-graft-PEHA stabilizer were dissolved in hexane contained in a round-bottomed flask with a side-arm and equipped with a magnetic follower, a stopper and a condenser. There was a nitrogen blanket throughout the experiment and the polymerization temperature was controlled to $342^{\circ}\text{K} \pm 0.1^{\circ}\text{K}$ by immersing the reactor in a

FIGURE 3.1

APPARATUS USED FOR NON-AQUEOUS DISPERSION
POLYMERIZATION EXPERIMENTS



thermostatic water bath. The stirring mechanism was provided by the magnetic bar inside the flask which was stirred using a magnetic stirrer placed underneath the water bath. Various polymerization techniques were used. These differed in the manner in which the monomer, initiator and stabilizer were added to the polymerization. In all cases, the MMA and AIBN concentrations were constant, at 20% (w/w) and 1% (w/w) of the total reagents. The effects of varying the stabilizer composition and concentration were investigated in addition to the polymerization method.

3.4.1 ONE-STAGE POLYMERIZATION TECHNIQUE

The stabilizer was dissolved in the monomer in a separate vessel at room temperature. n-Hexane was placed in the polymerization vessel at room temperature and purged with nitrogen for 30 minutes in order to remove air, after which the purge was converted to a nitrogen blanket. This was then transferred to the water bath and the hexane was stirred and allowed to reach the polymerization temperature. The stopper was rapidly removed and the solution of stabilizer in monomer was added to the flask using a syringe. After a further 5 minutes, the initiator was added. The solution soon became cloudy and then opaque white as the dispersion was produced. After 2 hours, the flask was removed, the dispersion was cooled and transferred to a storage bottle at room temperature.

3.4.2 SEED/FEED POLYMERIZATION TECHNIQUES

These techniques consisted of two stages, a seed stage and a growth stage. The methods varied depending on which components were partitioned between the seed and feed and also on the method of feed addition.

3.4.2.1 Seed/feed method 1

The stabilizer and initiator were dissolved in the monomer in a separate flask. n-Hexane was placed in the polymerization flask, purged with nitrogen at room temperature and transferred to the water bath. After allowing the n-hexane to reach the polymerization temperature, the seed stage was performed by adding 20% (w/w) of the stabilizer/initiator/ monomer solution to the dispersion medium. The seed dispersion was allowed to form for 1 hour, following which the growth stage was achieved by adding the remaining stabilizer/initiator/monomer solution incrementally in four separate, equal shots at 30 minute intervals over a 90 minute period. After the last feed addition, the polymerization was allowed to continue for a further 2 hours. The flask was then removed, the dispersion was cooled and transferred to a storage bottle at room temperature. The total polymerization time was 4.5 hours.

3.4.2.2 Seed/feed method 2

In this case only monomer and initiator were partitioned between the seed and the feed. The stabilizer was initially dispersed in the hexane contained in the flask overnight at room temperature. The seed monomer, constituting 40% (w/w) of the total monomer, was then added and this was stirred and purged with nitrogen for 30 minutes at room temperature. After converting the purge to a N₂ blanket, the flask was transferred to the water bath and the solution was stirred for 10 minutes, allowing it to reach the polymerization temperature. The seed initiator (also 40% (w/w) of the total initiator) was then added and the seed stage was allowed to continue for 1 hour. Meanwhile, the remaining feed initiator was dissolved in the feed monomer at room temperature. The growth stage was achieved by adding this remaining initiator/monomer solution in one shot. Polymerization was allowed to continue for a further 2 hours resulting in a total polymerization time of 3 hours.

3.4.2.3 Seed/feed method 3

This method was identical to 2 apart from the feed addition. In this case, the growth stage was accomplished by adding the remaining monomer/initiator solution incrementally in 6 equivalent shots at 30 minute intervals over a period of 2.5 hours. After the final shot, polymerization was allowed to continue for a further 1.5 hours resulting in a total polymerization time of 5 hours.

3.4.3 DETERMINATION OF THE EXTENT OF CONVERSION

Monomer conversion was determined at the end of the polymerization for each of the dispersion polymerization systems. Samples of dispersion (0.5cm³) were removed using a graduated 1 cm³ pipette into a pre-weighed small vessel. Unpolymerized monomer and diluent were then allowed to evaporate under vacuum at room temperature to a constant weight. Therefore, the solids content of the final dispersion was determined (w/v). By comparing this to the solids content of the system before polymerization had commenced, and taking account of the small loss of material which had evaporated during the polymerization (approximately 5% of the total mass), the monomer conversion was determined.

3.4.4 PURIFICATION OF NON-AQUEOUS DISPERSIONS BY REDISPERSION

In order to remove the unconverted monomer, unadsorbed stabilizer and initiator residues from the dispersions prepared, each dispersion was subjected to several redispersion cycles. The dispersions were centrifuged at 15000 rpm for 20 minutes and the supernatant above the sedimented particles was replaced by fresh dispersion medium. This was chosen to be n-heptane as a result

of the evaporation of some n-hexane during the centrifuge process. The particles were redispersed by vigorous shaking followed by continuous stirring (by means of a magnetic stirrer bar) and the redispersion cycle was repeated. Analysis of the supernatant by IR spectroscopy showed that 3-4 such redispersion cycles were sufficient to reduce the excess stabilizer content to negligible proportions.

3.4.5 PARTICLE CHARACTERIZATION AND SURFACE COVERAGE

Particles were characterized after the dispersions were purified, as described above. A rough estimate of the order of particle size was made by observing the settling of particles under gravity. Approximately, polymer particles in n-heptane with a particle size $>1\mu\text{m}$ settled out in less than 30 minutes, whereas particles of size 0.2-0.75 μm settled out within a few days. TEM was used extensively to determine particle shape, size, size distribution and to monitor particle aggregation (see section 3.5.6.). Dried dispersion samples were analysed for graft copolymer content using UV spectroscopy (see section 3.5.7). The surface coverage of the PEHA stabilizing chains on the particle surfaces was calculated by comparing the graft copolymer contents obtained by UV to the average particle diameters obtained by TEM.

3.5 CHARACTERIZATION TECHNIQUES

3.5.1 END-GROUP ANALYSIS (EGA)

Carboxyl-terminated prepolymers were titrated with standardized base in order to obtain molar masses. With all titrations, experiments were repeated to obtain titrated volumes within 0.05cm³ and the average titre was taken.

3.5.1.1 Aqueous titrations

A standard solution of sodium hydroxide was prepared in distilled water (approximately 0.05M) and this was added to a 50cm³ burette. A solution of potassium hydrogen phthalate was then prepared (0.03M). 20cm³ of this solution was transferred by pipette to a conical flask, a few drops of phenolphthalein indicator were added and this was titrated to standardize the sodium hydroxide. The end-point was detected visually as a colour change from colourless to pink. 0.5-1.0g of prepolymer was accurately weighed, dissolved in 50cm³ of hot methanol and titrated with the standardized sodium hydroxide, again using phenolphthalein as indicator. 50cm³ of methanol was also titrated as a "blank" experiment and the titrated volume of standardized base was subtracted from that required for the polymer solution titration. The number average molar masses of the prepolymers were calculated assuming one carboxyl end-group per chain. This method was only used for PMMA prepolymers prepared in 2-ethoxyethanol.

3.5.1.2 Non-aqueous titrations

10ml of TBAH, supplied as approximately 1.0M solution in methanol, was diluted with isopropanol producing an approximate 0.02M solution, which was transferred to a 50cm³ burette. A 2.5 × 10⁻³M solution of benzoic acid was then prepared accurately in MIBK. 10cm³ of this solution were then transferred by pipette into a conical flask, a few drops of Thymol blue indicator were added and this was titrated to standardize the TBAH. The end-point was detected visually as a colour change from yellow to blue which was significantly easier to detect than the end-point in the aqueous titrations. 0.5-1.0g of carboxyl-terminated prepolymer were then accurately weighed, dissolved in 20cm³ of MIBK and titrated with the standardized TBAH, again using thymol blue as indicator. 20cm³ of MIBK was also titrated separately as a "blank" experiment and the volume of standardized base solution required was subtracted from the volumes required to titrate the

polymer solutions. As before, the number average molar masses of the prepolymers were calculated assuming one carboxyl end-group per chain. This method was used for both PMMA and PEHA carboxyl-terminated prepolymers prepared in ethyl acetate.

3.5.2 INFRA-RED SPECTROSCOPY (IR)

IR spectra were measured using a Nicolet 20-DXC Fourier Transform Infra-Red spectrometer using the bench optics in transmission mode. The spectrometer had a resolution limit of 0.5cm^{-1} . The spectra were recorded using a Nicolet Series 600 computer console.

3.5.2.1 Characterization of polymers isolated during macromonomer synthesis

Carboxyl-terminated, acyl chloride-terminated and methacrylate-terminated PMMA and PEHA polymers were characterized using this method. For each sample, a sodium chloride disk was firstly placed in the sample holder, scanned and the spectrum was stored in the background file of the software. Typically, 20 scans were recorded over the range $4000\text{-}400\text{cm}^{-1}$ at a resolution of 2cm^{-1} . The sodium chloride disk was removed and for PMMA polymers, concentrated toluene solutions were smeared over the disk using a glass rod and the toluene was allowed to evaporate, thereby forming a polymer film. This disk was replaced in the sample compartment and scanned as above but the spectrum was stored in the sample file of the software. This automatically subtracted data in the background file, thereby producing the spectrum of the polymer film. The sodium chloride disk was washed thoroughly with chloroform and the above procedure was repeated for each sample. PEHA polymer samples were easier to prepare since neat polymer samples could be smeared over the disk. PEHA polymer samples were analysed in an identical manner to PMMA samples as described above. The IR spectra measured were used for the

qualitative determination of the various functional end-groups present in the different samples isolated during each macromonomer synthesis.

3.5.2.2 Characterization of graft copolymers

From a suitable calibration of the infra-red absorbance of a group in a compound, the concentration of groups can be determined quantitatively. Absorbance is given by Beer's law [160]

$$A = \epsilon bc \quad (3.4)$$

where A is the absorbance, b is the path length, c is the concentration and ϵ is the extinction coefficient.

The chemical compositions of PS-graft-PMMA and PS-graft-PEHA copolymers were quantitatively determined from the carbonyl absorbance of methacrylate units and acrylate units, respectively at 1728cm^{-1} . The constant (ϵb) in equation 3.4 was determined in each case by setting up a calibration curve of Absorbance versus concentration with solutions of PMMA and PEHA homopolymers, respectively. Solutions of PMMA or PEHA macromonomers were prepared in CHCl_3 in volumetric flasks, varying from $0\text{-}40\text{mg}\cdot\text{cm}^{-3}$. In order to obtain the spectrum for each solution, a sodium chloride solution cell (obtained from Perkin Elmer) was firstly filled with neat CHCl_3 . The cell was placed in the sample compartment, 20 scans were taken from $4000\text{-}400\text{cm}^{-1}$ at a resolution of 4cm^{-1} and the spectrum was stored in the background file of the software. The cell was then removed, cleaned and filled with sample solution. The spectrum was determined as above but stored in the sample file of software. The software automatically subtracted the background file from the sample file, thereby producing the spectrum of the polymer. Spectra were recorded as absorbance versus wavenumber. Peak absorbances at 1728 cm^{-1} for PMMA and PEHA samples were determined by subtracting the average baseline absorbance at either side of the

peak. This procedure was repeated for each sample and care was taken to clean the cell thoroughly between each determination by washing with chloroform. Figure 3.2 shows typical calibration curves for PMMA and PEHA macromonomer samples. Solutions of graft copolymers in CHCl_3 were then accurately prepared (typically 40 mg.cm^{-3}) and spectra were measured in the same manner as above. The absorbances of the carbonyl peaks in the copolymer samples were then compared to the respective calibration curves in order to determine the concentration of methacrylate or acrylate units.

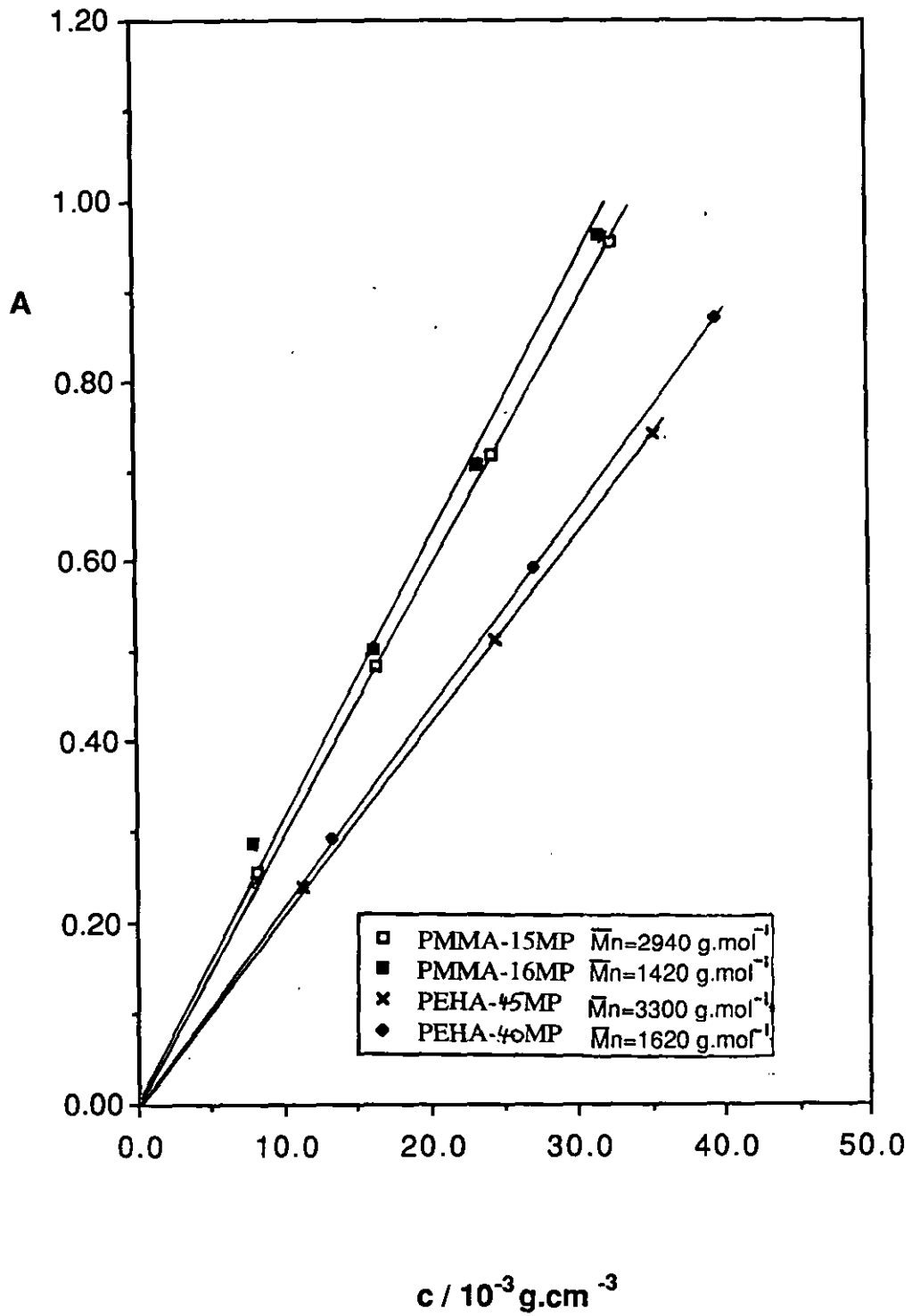
3.5.3 ^1H NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY (^1H NMR)

^1H NMR spectroscopy was used to determine polymer compositions for PMMA and PEHA carboxyl-terminated prepolymers, methacrylate-terminated macromonomers and PS-graft-PMMA or PS-graft-PEHA copolymers.

The characterization of low molar mass carboxyl-terminated prepolymers and methacrylate-terminated macromonomers was achieved using a Bruker AM-250 250 MHz ^1H NMR spectrometer. This work was performed under the supervision of Dr. Brian Taylor at the Chemistry Department, Sheffield University. Typically, 30 mg of each sample was supplied. This was dissolved in 0.7 cm^3 deuterated chloroform containing tetramethylsilane (TMS) at a concentration of $15 \mu\text{l}/100 \text{ ml}$. A spectrometer with such a field strength was required in order to determine the end-group concentration in the low molar mass polymers. Spectra were analysed by comparing the integration of end-group protons to that of the PMMA or PEHA constitutional repeating unit (CRU) in order to determine the polymer molar masses. This is described in more detail in sections 4.1.1 and 4.1.3.

The characterization of graft copolymers was performed using an EM-360 60MHz spectrometer. Samples were prepared by dissolving 0.1-0.15g of polymer in 1-2 cm^3 of deuterated chloroform

FIGURE 3.2 IR CALIBRATION CURVES OF THE CARBONYL GROUP
 ABSORBANCE AT 1728 cm^{-1} IN PMMA AND PEHA
 MACROMONOMERS



containing approximately 1% (w/w) TMS. Spectra were analysed by comparing the integration of protons in styrene CRU to the integration of protons in the methacrylate or acrylate units. This is discussed further in section 4.2.3.2 and 4.2.3.3.

3.5.4 GEL-PERMEATION CHROMATOGRAPHY (GPC)

GPC was used to characterize the molar masses and polydispersities of various samples, including carboxyl-terminated prepolymers, methacrylate-terminated macromonomers and graft copolymers. It was also used to estimate macromonomer conversions in graft copolymer synthesis. GPC was performed using THF as the mobile phase and lightly crosslinked polystyrene beads as stationary phase.

3.5.4.1 Characterization of carboxyl-terminated prepolymers and methacrylate-terminated macromonomers

These low molar mass samples were initially dissolved in THF at a concentration of approximately 0.25% (w/v). Approximately 3 μ l of toluene were added as internal standard. The solutions were filtered and loaded into a 6-port injection valve containing a 50 μ l loop using a syringe, ensuring that air bubbles were expelled before loading. The separation of the polymer samples were then achieved by injecting on to a stainless steel column (60cm long, internal diameter 7.5mm), fitted with a 2 μ m prefilter. The column was obtained from Polymer Laboratories Ltd and contained crosslinked PS beads with a particle size of 5 μ m and a pore size of 500 Å . The column was maintained at room temperature throughout the analyses and samples were eluted with THF using a Knauer High Performance Liquid Chromatography (HPLC) pump 64 at a flow rate of 1.0 cm³ per minute. Detection of separated analyte was performed by continuously monitoring the effluent stream from the end of the column using a Knauer differential refractometer refractive index (RI) detector

connected to a JJ chart recorder. This was a 2-channel recorder fitted with an event marker which was used to show the injection point. The normal chart speed was 20mm per minute. The column was regularly calibrated with PS standards and chromatograms were analysed as described in section 3.5.4.3.

3.5.4.2 Characterization of graft copolymers

A similar method was used to that described above, but there were some notable differences. For graft copolymers, samples were initially dissolved in THF at a concentration of 0.20% (w/v) with approximately 3 μ l of toluene as internal standard. Solutions were loaded on to a 6-port injection valve containing a 100 μ l loop. Separation was achieved using a different stainless steel column obtained from Polymer Laboratories Ltd. This was a mixed gel column (60cm long, internal diameter 7.5mm) containing lightly crosslinked PS beads with a larger particle size (10 μ m). As before, the column was maintained at room temperature throughout the analyses and samples were eluted with THF using a Knauer HPLC pump 64 at a flow rate of 1.0cm³ per minute. Detection of separated sample was performed by monitoring the effluent using both an RI detector and a UV detector placed in series. The RI detector was that previously described and the UV detector was a Pye-Unicam LC UV detector operating at a fixed wavelength of 267nm. The RI and UV detector outputs were connected to separate channels of the same JJ 2-channel chart recorder, operating using a chart speed of 20mm per minute. In this way, GPC traces of RI and UV detector responses versus elution time were obtained simultaneously. Both impure and purified graft copolymers were analysed by this method. Impure graft copolymers containing unreacted macromonomers were characterized in order to estimate the macromonomer conversion. This is described in detail in section 4.2.1. Purified graft copolymers were analysed in order to obtain average molar masses and polydispersities from the RI detector response. The column was regularly calibrated with PS standards, as described below.

3.5.4.3 Calibration and determination of average molar masses

Each column was calibrated with a series of polystyrene standards with narrow molar mass distributions, also supplied by Polymer Laboratories Ltd. The "500Å" column was calibrated using a series of standards with molar masses varying from $\bar{M}_p=164$ to $22.0 \times 10^3 \text{g.mol}^{-1}$ whereas the "mixed gel" column was calibrated using a series of standards with molar masses varying from $\bar{M}_p=1.25 \times 10^3$ – $2.1 \times 10^6 \text{g.mol}^{-1}$. All PS standards had molar mass distributions $\bar{M}_w/\bar{M}_n < 1.10$. A calibration curve is a plot of \log (peak molar mass) against elution volume. By taking the injection point as zero elution volume and the toluene peak as complete elution, the polymer standard elution volumes were expressed as a percentage of the internal standard elution volume. Such calibration curves for the 500Å and mixed gel columns are illustrated in figures 3.3 and 3.4, respectively.

The refractive index chromatograms of polymer samples were analysed by dividing the chromatographic curves into a series of trace heights and elution volumes at 1% intervals, again expressed as a percentage of the total elution volume of the internal standard. This is illustrated in figure 3.5. By comparing the elution volumes with the appropriate calibration curve, a list of trace heights and molar masses were obtained. This information was analysed by a computer program as used by Croucher [161] in order to obtain the number average molar mass (\bar{M}_n), the weight average molar mass (\bar{M}_w), the peak average molar mass (\bar{M}_p) and the polydispersity (\bar{M}_w/\bar{M}_n). No attempts were made to correct chromatograms for line broadening. The molar mass at the peak of the chromatogram (\bar{M}_{peak}) was also determined directly from the chromatogram by comparing to the appropriate calibration curve.

FIGURE 3.3 GPC CALIBRATION CURVE FOR POLYSTYRENE STANDARDS IN THF FOR THE "500Å" COLUMN

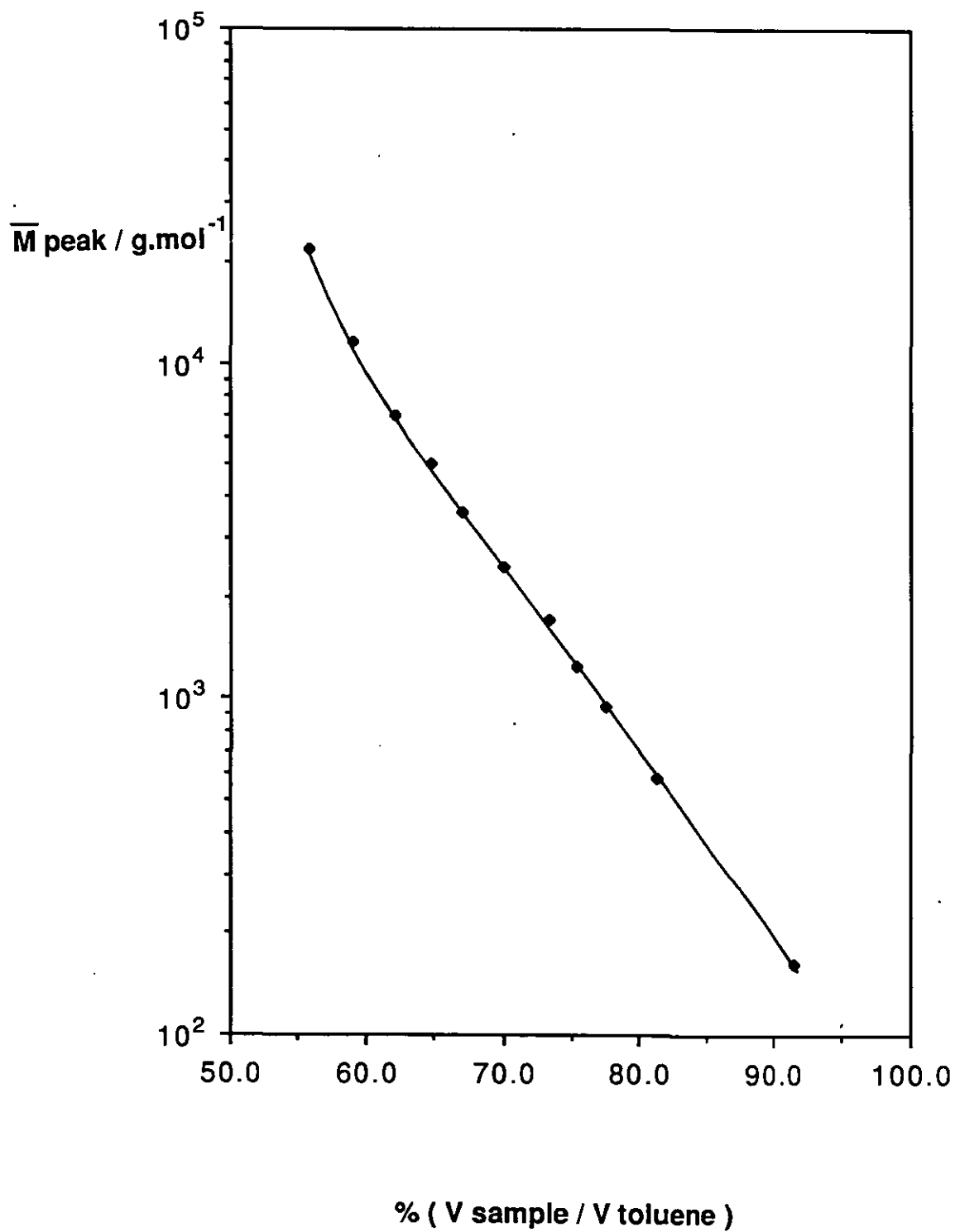


FIGURE 3.4

GPC CALIBRATION CURVE FOR POLYSTYRENE STANDARDS IN THF FOR THE "MIXED GEL" COLUMN

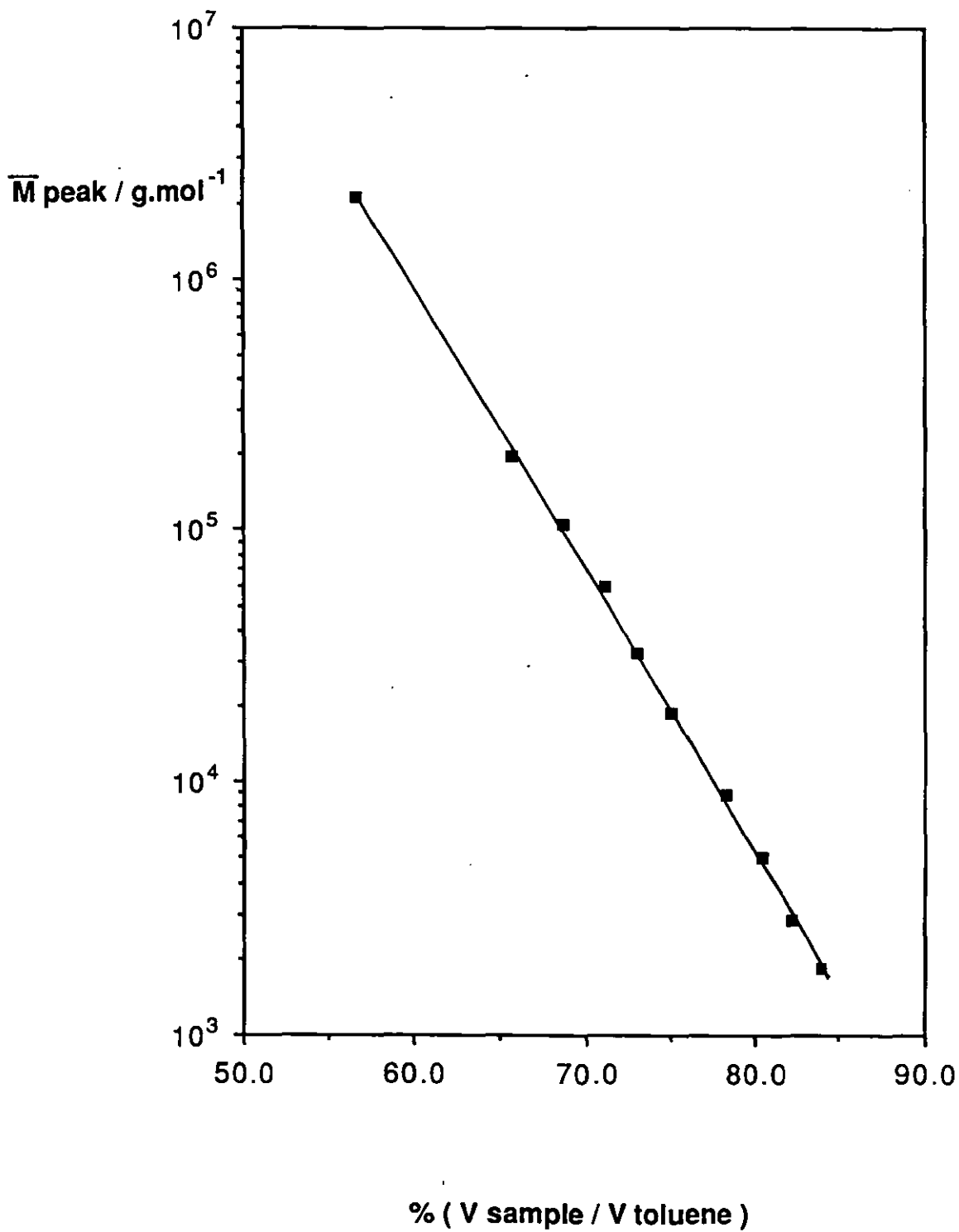
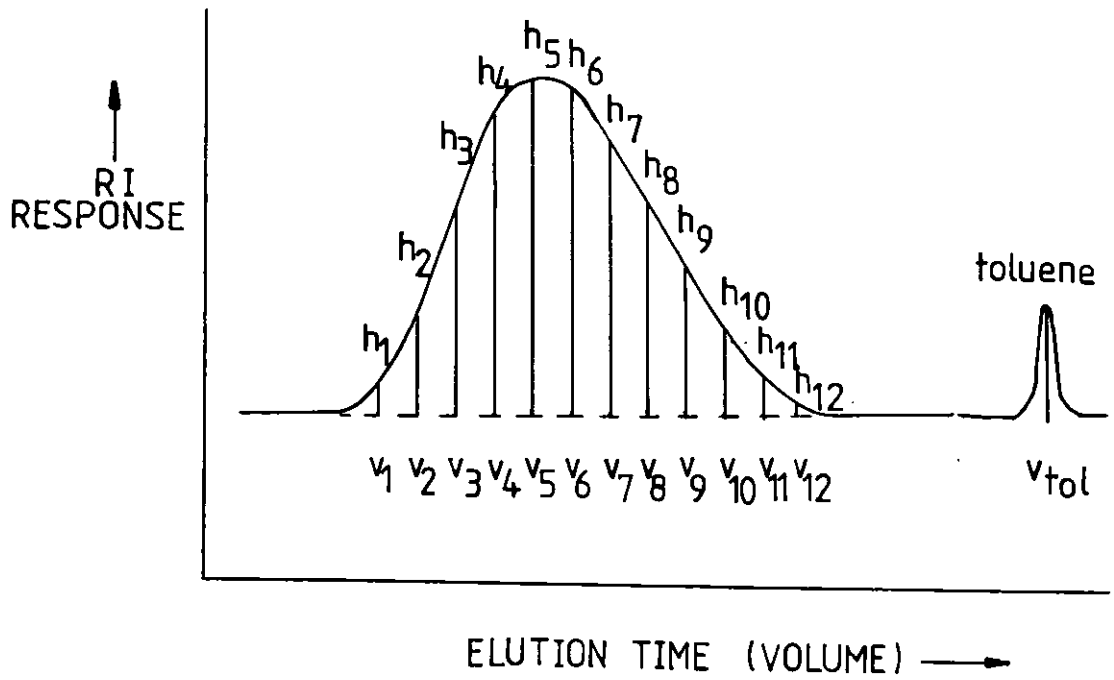


FIGURE 3.5

ANALYSIS OF GPC CHROMATOGRAMS



3.5.5 THIN-LAYER CHROMATOGRAPHY (TLC)

In TLC, the separation of components in a mixture is carried out on thin layers of a solid adsorbent stationary phase by a liquid mobile phase (the developer) which flows over it. The basic principle is that the migration rate of each component in a mixture relative to the developer is retarded preferentially by the stationary phase. Migration of components is defined by the rate of flow (R_f) [160] where

$$R_f = \frac{\text{distance travelled by sample}}{\text{distance travelled by developer}} \quad (3.5)$$

For polymeric samples, R_f is independent of molar mass when the developer is a good solvent for the components. Under such circumstances, an adsorption mechanism will predominate and separation is achieved by differences in polarity between the developer and the components to be separated [162,163,164,165]. Therefore, separation of components can be achieved due to differences in chemical composition. TLC was used in order to determine the extent of any PS homopolymer contamination in PS-graft-PMMA and PS-graft-PEHA copolymers (from which unreacted macromonomer had already been removed).

Significant effort was placed into devising the correct experimental method. This was performed on Merck silica-gel 60F254 precoated sheets, 0.2mm thick on aluminium, containing an immobile fluorescent compound. Initially, these were activated by placing in an oven at 373K for 5 minutes. 1.0%(w/v) solutions of polymer sample were accurately prepared in CHCl_3 . 5 μl of this solution (equivalent to 50 μg of polymer) were deposited in a vertical band on the silica-gel sheets, 30mm long with the lower limit of the band being 10mm from the bottom edge of the plate. Figure 3.6 shows a representation of a typical plate prior to development. The CHCl_3 solvent was then removed by blowing with a hot hair-dryer. Development was then achieved using various solvents by placing the bottom edge of the plate in the mobile

FIGURE 3.6 SCHEMATIC REPRESENTATION OF A TLC PLATE BEFORE
VERTICAL DEVELOPMENT

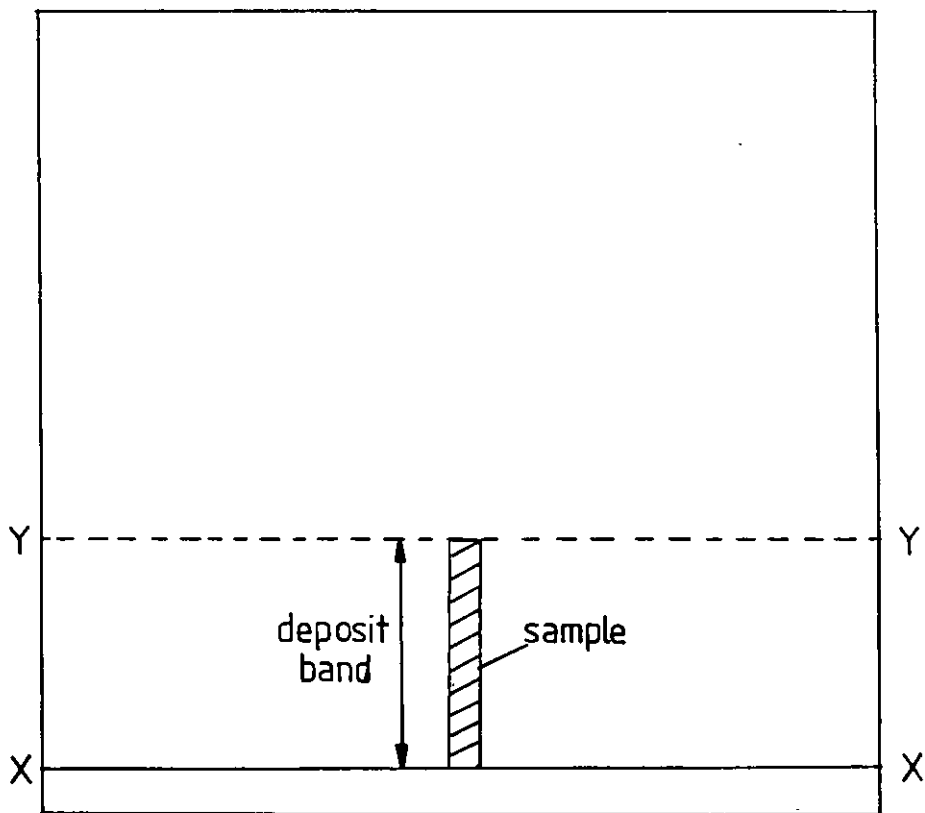
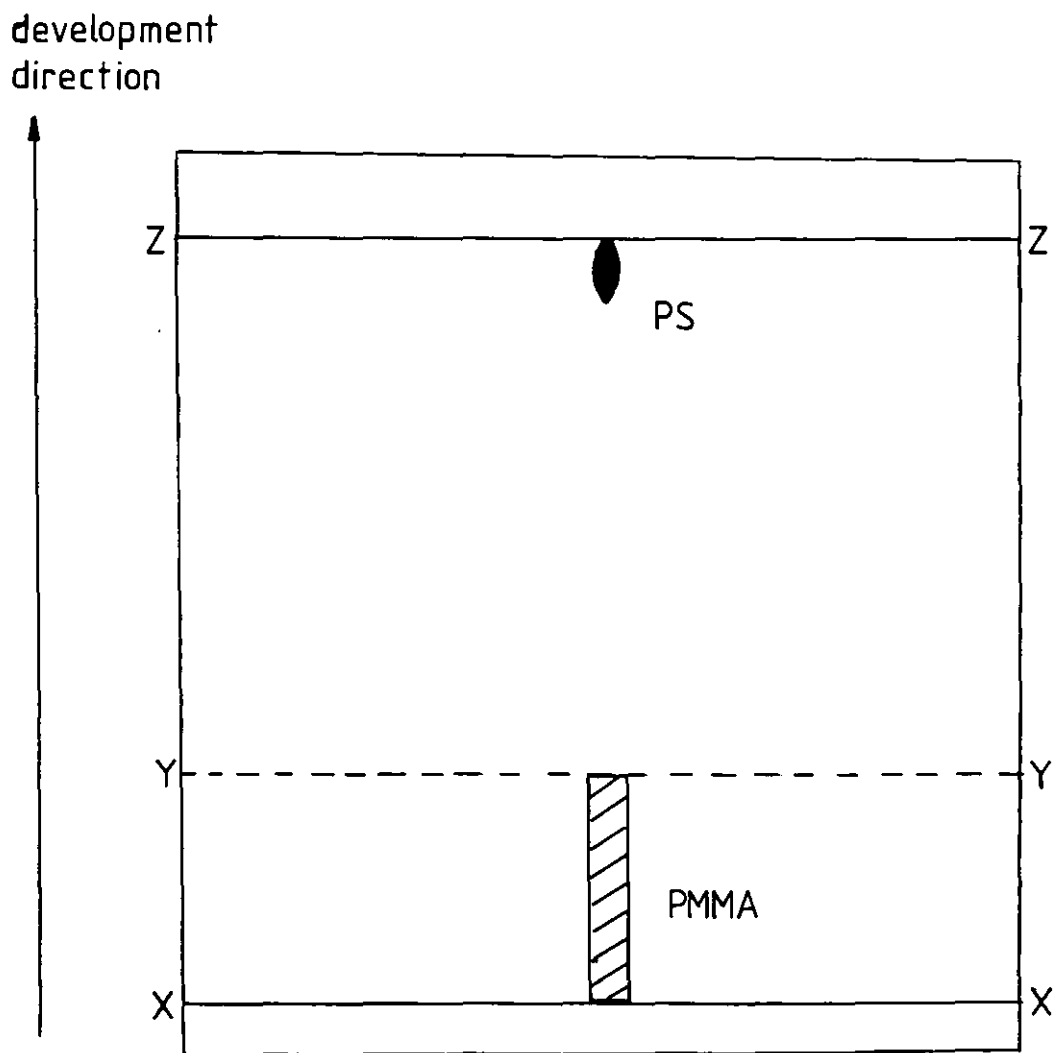


plate placed vertically in developer up to X

FIGURE 3.7 PRINCIPLES OF TLC SEPARATION OF PS FROM PMMA USING
CHCl₃ AS DEVELOPER



Z = solvent front
XY = deposit band

phase contained in an enclosed glass tank. After vertical development, typically to a solvent front height of 100mm from the lower limit of the band, the plate was removed, the solvent front was marked and the sheet was dried. Detection was achieved by viewing the plate under a UV lamp set at 254nm. The polymers were shown as dark spots or bands against a fluorescing background because of their quenching effect on the fluorescence. In the experiments performed, the polymer solutions were applied in bands rather than spots, similar to experiments carried out by Horii et al [166] and Inagaki [163]. This is necessary in order to prevent overload effects owing to the high loading of polymer used (50µg, necessary to detect impurities down to 1%) [166].

The R_f value of PS is unity using CHCl_3 as a developer and silica-gel as stationary phase [165]. Under the same conditions, R_f for poly(meth)acrylates is zero [165]. Therefore, in principle, chloroform can be used to distinguish polystyrene from poly[styrene-co-(meth)acrylate] copolymers due to differences in their polarity. Figure 3.7 illustrates the principles of separation. This has been achieved by Inagaki et al [167] for the separation of PS from polystyrene-block-poly(methyl methacrylate) copolymers. However, it is uncertain as to how selective chloroform is between the development of PS homopolymer and poly[styrene-co-(meth)acrylate] copolymers with high styrene contents. Since the R_f value of PS is zero using CCl_4 as developer and silica-gel as stationary phase [165] (compared to $R_f=1$ for CHCl_3), various $\text{CCl}_4/\text{CHCl}_3$ mixtures were used in order to determine the developer composition which produced the optimum selectivity between polystyrene and styrene-rich copolymers. This was investigated using various PS homopolymers and poly[styrene-stat-(n-butyl methacrylate)] copolymers, where the styrene content varied from 53-95% (w/w). The copolymers are listed in table 3.1. These were synthesized by the free-radical batch copolymerization of styrene and n-butyl methacrylate in toluene using AIBN as initiator. The experimental procedure for

TABLE 3.1 POLY[STYRENE-stat-(n-BUTYL METHACRYLATE)]
COPOLYMERS PREPARED FOR USE IN THIN-LAYER
CHROMATOGRAPHY^{1, 2}

<u>SAMPLE</u>	<u>wt-% STYRENE³</u>
SB-1	94.9
SB-2	89.2
SB-3	85.5
SB-4	79.0
SB-5	53.0

- NB (1) Prepared by free-radical solution copolymerization of styrene with n-butyl methacrylate in toluene solvent using AIBN initiator at 333°K. [M] = 16% (w/v). [AIBN] = 0.5% (w/w) on monomer.
- (2) Copolymers purified by repeated precipitation in methanol from toluene solutions.
- (3) Copolymer compositions determined by IR spectroscopy, as described in section 3.5.2.2 but using solutions of poly(n-butyl methacrylate) for calibration.

these syntheses was similar to that described in section 3.3.1 for the synthesis of graft copolymers. Copolymers were purified by reprecipitation in methanol from toluene, followed by drying under vacuum at 353 K. Table 3.2 illustrates the R_f values for the various copolymers using the experimental technique described earlier but with different mixtures of CCl_4 and CHCl_3 as the developing mobile phase. CHCl_3 is more polar than CCl_4 and so the polarity of the developer increases from left to right in the table. The table shows that as the polarity of the developer increased, copolymers with a higher methacrylate content migrated with the mobile phase. Therefore, whereas a 65/35 (v/v) $\text{CCl}_4/\text{CHCl}_3$ mixture only caused PS to migrate with the solvent front, CHCl_3 developed polystyrene and copolymers containing $\leq 15\%$ (w/w) of n-butyl methacrylate. Therefore, the selectivity of the developer increased as its polarity decreased. However, the developer polarity must not be so low as to prevent the migration of polystyrene. Solution mixtures of the poly[styrene-stat-(n-butyl methacrylate)] copolymers and polystyrene homopolymer (90/10(w/w) copolymer/PS) were then prepared and characterized by TLC in exactly the same manner as described previously. The results are shown in table 3.3. When CHCl_3 was used as developer, copolymers containing $\leq 15\text{--}20\%$ (w/w) butyl methacrylate were developed in addition to PS. However, when the polarity of the developer was reduced, there was an increased selectivity for the development of PS. A 60/40 (v/v) $\text{CCl}_4/\text{CHCl}_3$ mixture discriminated between PS and copolymers containing $>5\%$ (w/w) butyl methacrylate.

In summary, care must be taken in the choice of developer used to measure PS homopolymer contamination in poly[styrene-co-(meth)acrylate] copolymer samples. As a result of the optimum selectivity, a 60/40 (v/v) $\text{CCl}_4/\text{CHCl}_3$ solvent mixture was preferred as the developer in order to prevent the overestimation of homopolymer contamination. This developer was chosen using exactly the same experimental technique described earlier, in

TABLE 3.2 CHARACTERIZATION OF POLYSTYRENE AND POLY[STYRENE-
stat-(n-BUTYL METHACRYLATE)] COPOLYMERS BY THIN-
LAYER CHROMATOGRAPHY

SAMPLE	% (w/w) STYRENE		R _f VALUES USING DEVELOPER MIXTURE: CCl ₄ /CHCl ₃ (v/v)						
	IN COPOLYMER	100/0	65/35	60/40	50/50	40/60	25/75	0/100	
PS	100.0	0	1	1	1	1	1	1	
SB-1	94.9	0	0-1	1	1	1	1	1	
SB-2	92.1	0	0	0-1	0-1	1	1	1	
SB-3	85.5	0	0	0	0	0	0-1	0-1	
SB-4	79.0	0	0	0	0	0	0	0	
SB-5	53.0	0	0	0	0	0	0	0	

NB: R_f = 0 = no vertical development of sample

R_f = 1 = full vertical development, sample migrates with the solvent front.

R_f = 0-1 = partial vertical development, sample is deposited across the whole vertical range.

TABLE 3.3 SEPARATION OF POLYSTYRENE HOMOPOLYMER FROM
POLY[STYRENE-stat-(n-BUTYL METHACRYLATE)]
COPOLYMERS USING THIN-LAYER CHROMATOGRAPHY

SAMPLE	% (w/w) STYRENE		SEPARATION USING DEVELOPER MIXTURE CCl ₄ /CHCl ₃ (v/v)						
	IN COPOLYMER	70/30	60/40	50/50	40/60	25/75	0/100		
SB-1	94.9	SEP	SEP	X	X	X	X		
SB-2	92.1	SEP	SEP	SEP	X	X	X		
SB-3	85.5	SEP	SEP	SEP	SEP	X	X		
SB-4	79.0	SEP	SEP	SEP	SEP	SEP	SEP		

NB: (1) This table refers to the separation of mixtures of 90/10 (w/w) copolymer/PS

(2) SEP = separation of the 2 components, with only PS migrating with the solvent front.

(3) X = no separation, with both PS and copolymer migrating with the solvent front.

order to determine PS homopolymer contamination in the PS-graft-PMMA and PS-graft-PEHA copolymers prepared from the copolymerization of methacrylate-terminated macromonomers. Only purified copolymer samples, where unreacted macromonomers had been removed, were characterized by this technique.

3.5.6 TRANSMISSION ELECTRON MICROSCOPY (TEM)

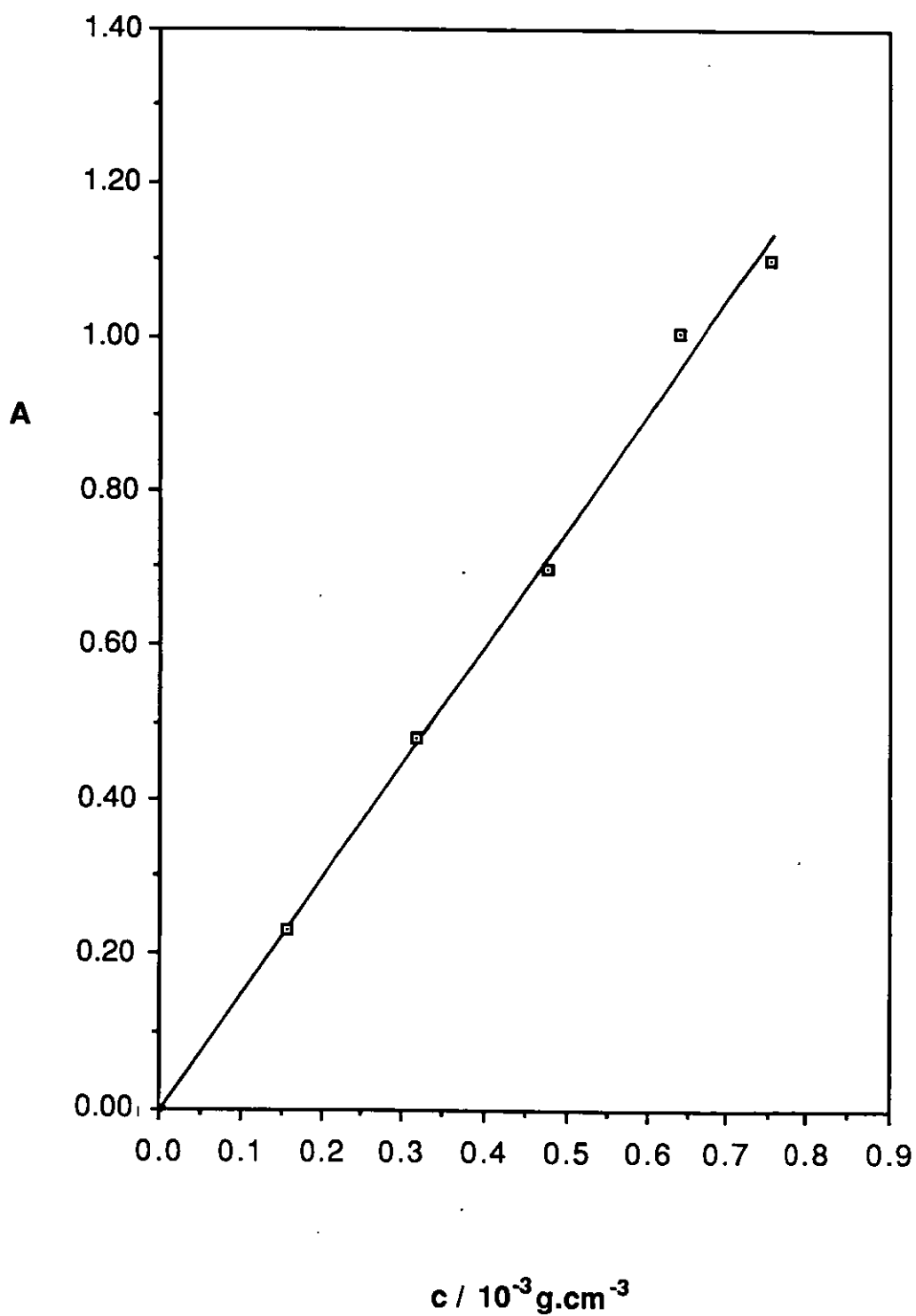
TEM was used extensively to characterize polymer dispersions which had been previously purified by redispersion. Samples were prepared by placing a few drops of dilute, redispersed dispersion (approximately 0.1% (w/v) polymer content) directly on to a carbon-coated copper grid and evaporating to dryness. Samples were examined at magnifications of $2.5-20 \times 10^3$ times using a JEOL JEM 100CX electron microscope calibrated with a replica of a 2160 lines mm^{-1} grating and operating with a 60kV accelerating voltage. The microscope was operated by Mr. John Bates in the Institute of Polymer Technology and Materials Engineering, Loughborough University of Technology. Typically 4-5 micrographs were taken for each sample from different parts of the grid. In particular, particle aggregation was monitored and particle shapes, sizes and size distributions were determined from the direct measurement of individual particles on micrographs.

3.5.7 ULTRA-VIOLET SPECTROSCOPY (UV)

From a suitable calibration of the UV absorbance of a group in a compound, the concentration of groups can be determined quantitatively according to equation 3.4, as previously described in section 3.5.2.2. Purified and dried PMMA dispersion samples were analysed for PS-graft-PEHA copolymer stabilizer content from the UV absorption of the styrene units in the copolymer using a Shimadzu UV 160 UV/visible spectrometer. The constant (ϵb) in equation 3.4 was determined by setting up a calibration curve of

Absorbance versus concentration with solutions of standard PS homopolymer, obtained from Polymer Laboratories Ltd ($\bar{M}_p=22.0 \times 10^3 \text{g.mol}^{-1}$ $\bar{M}_w/\bar{M}_n = 1.05$), with a similar molar mass to the graft copolymer stabilizers. Initially, several standard solutions of the PS homopolymer were accurately prepared in chloroform with concentrations varying from 0-0.8mg.cm⁻³. Absorbance values were obtained over the wavelength range 200-400nm at 1nm intervals and a calibration curve of Absorbance at 268nm against PS concentration was obtained, as illustrated in figure 3.8. Solutions of dried dispersion were then prepared accurately in chloroform (typically 4.0mg.cm⁻³) and the UV spectra were measured as above. The concentration of styrene units in the sample were determined from the absorbance at 268nm by interpolation from the calibration curve. Then, from a knowledge of the graft copolymer stabilizer composition (previously determined by IR spectroscopy, see section 3.5.2.2), the percentage of copolymer in the sample was determined.

FIGURE 3.8 UV CALIBRATION CURVE OF THE ABSORBANCE OF
POLYSTYRENE AT 268nm



CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 THE PREPARATION OF METHACRYLATE-TERMINATED MACROMONOMERS

4.1.1 THE PREPARATION OF CARBOXYL-TERMINATED PREPOLYMERS

4.1.1.1 Poly(methyl methacrylate) prepolymers

(a) Polymerizations in ethyl acetate.

Examples of unpurified carboxyl-terminated prepolymers prepared from the free-radical solution polymerization of MMA in ethyl acetate at 353 K are shown in table 4.1. A polymerization time of 1.5-2 hours was used to give approximately 60% conversion of monomer to polymer. As explained in section 1, conditions were altered to produce prepolymers with molar masses of $\bar{M}_n=1500$ and $3000\text{g}\cdot\text{mol}^{-1}$. PMMA-1 and PMMA-2 are syntheses where no chain transfer agent was used. As expected, the addition of thioglycollic acid markedly reduced the molar mass of the polymers produced and an increased TGA concentration resulted in a lower molar mass. This is illustrated by figure 4.1, which shows the relationship between the reciprocal \bar{M}_{Peak} value obtained from GPC and the chain transfer agent concentration used. \bar{M}_{Peak} was used for this relationship rather than \bar{M}_n because the polymers listed in table 4.1 were isolated but not purified. As a result of low molar mass impurities present, the number average molar masses calculated are likely to be lower than the values for purified polymers and different concentrations of impurities will produce varying errors in \bar{M}_n from one sample to another. Nevertheless, the \bar{M}_{Peak} values are relative and give an approximate guide to the molar masses being produced. A typical GPC chromatogram of an impure sample is illustrated in figure 4.2.(a). The impurities are noticeable at the low molar mass tail of the PMMA molar mass distribution. These are likely to be initiator and chain transfer agent fragments. As a result of these impurities, the polydispersities quoted in table 4.1 are probably overestimated. Figure 4.2(b) illustrates the profile of the same polymer after repeated purification by dissolving in hot

TABLE 4.1 GPC CHARACTERIZATION OF UNPURIFIED CARBOXYL-TERMINATED PMMA PREPOLYMERS PREPARED IN ETHYL ACETATE

REFERENCE	[ACVA]	[TGA]	$\bar{M}_{Peak}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n
	$/10^{-3}\text{mol}\cdot\text{dm}^{-3}$	$/10^{-1}\text{mol}\cdot\text{dm}^{-3}$	←-----units $\text{g}\cdot\text{mol}^{-1}$ -----→				
PMMA-1	21.6	-	33.1	14.7	29.2	20.7	1.99
PMMA-2	8.11	-	46.7	27.0	51.2	37.2	1.90
PMMA-3	8.11	1.2	5.07	3.38	5.28	4.22	1.56
PMMA-4	7.7	1.6	3.76	2.25	3.88	2.96	1.73
PMMA-10	8.11	2.0	3.09	2.13	3.45	2.71	1.62
PMMA-5	21.6	4.0	1.72	1.16	1.76	1.43	1.52

NB (i) [MMA] = 33% (w/w) = $3.0 \text{ mol}\cdot\text{dm}^{-3}$.

(ii) PMMA-1 and PMMA-2 characterized using mixed gel column.

(iii) Remaining samples characterized using column with 500Å pore size.

TABLE 4.2 GPC CHARACTERIZATION SHOWING THE EFFECT OF PURIFICATION ON THE MOLAR MASSES OF CARBOXYL-TERMINATED PMMA PREPOLYMERS

REFERENCE	[ACVA]	[TGA]	$\bar{M}_{Peak}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n
	$/10^{-3}\text{mol}\cdot\text{dm}^{-3}$	$/10^{-1}\text{mol}\cdot\text{dm}^{-3}$	←-----units $\text{g}\cdot\text{mol}^{-1}$ -----→				
PMMA-15	8.11	1.8	3.43	2.17	3.69	2.83	1.70
PMMA-15C	-	-	3.63	2.56	3.85	3.14	1.50
PMMA-16	16.2	3.9	1.72	1.04	1.73	1.34	1.66
PMMA-16C	-	-	1.78	1.29	1.87	1.55	1.45

NB (i) GPC performed using 500Å pore size column.

(ii) The suffix C denotes a purified prepolymer.

FIGURE 4.1 THE EFFECT OF CHAIN TRANSFER AGENT CONCENTRATION ON THE MOLAR MASSES OF CARBOXYL-TERMINATED PMMA PREPOLYMERS

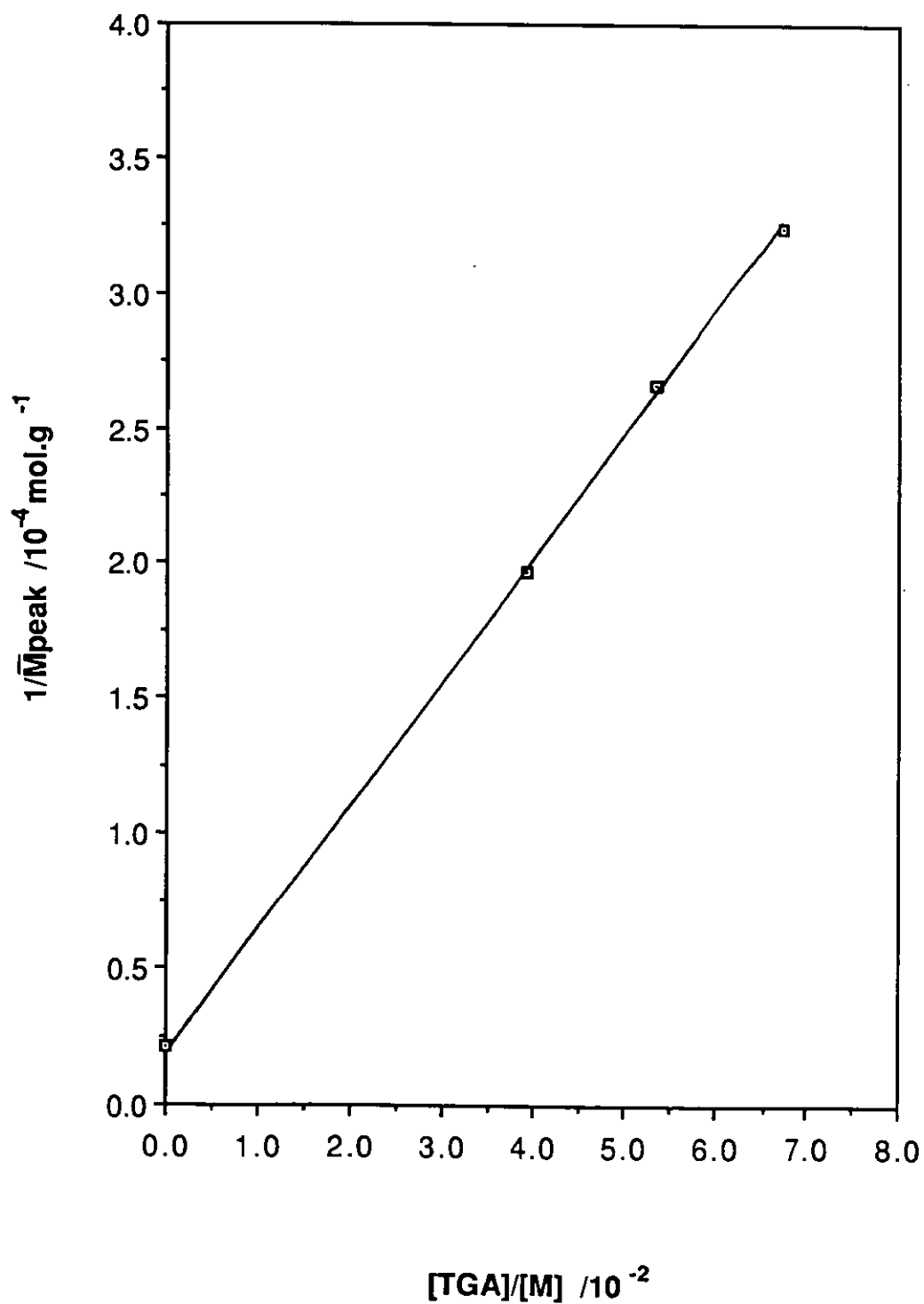
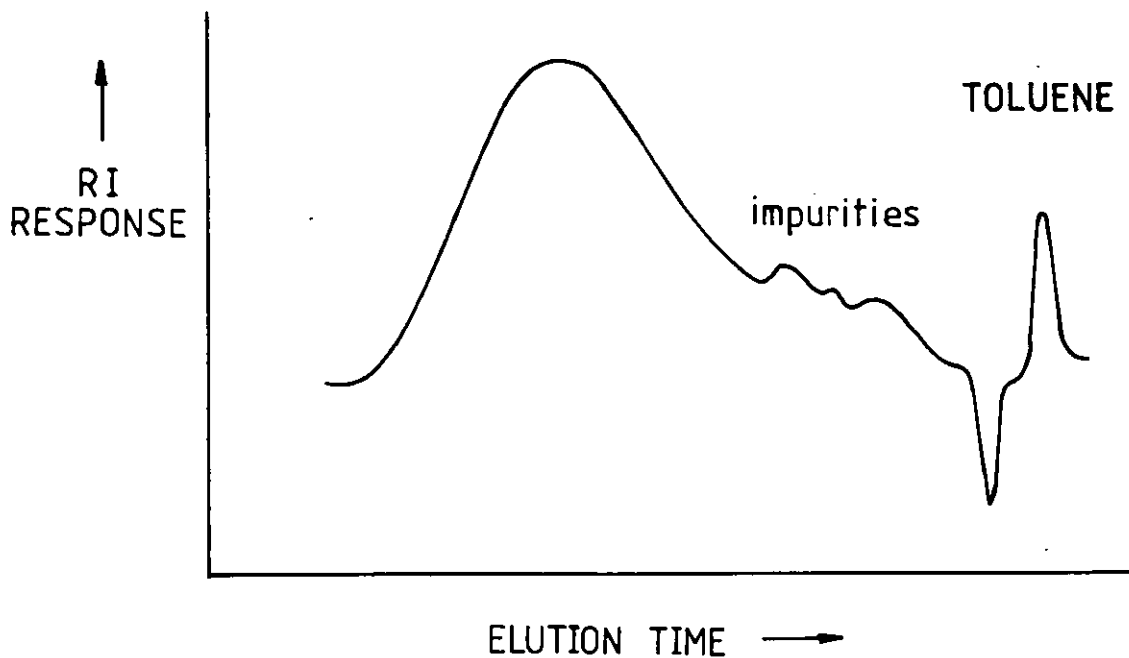


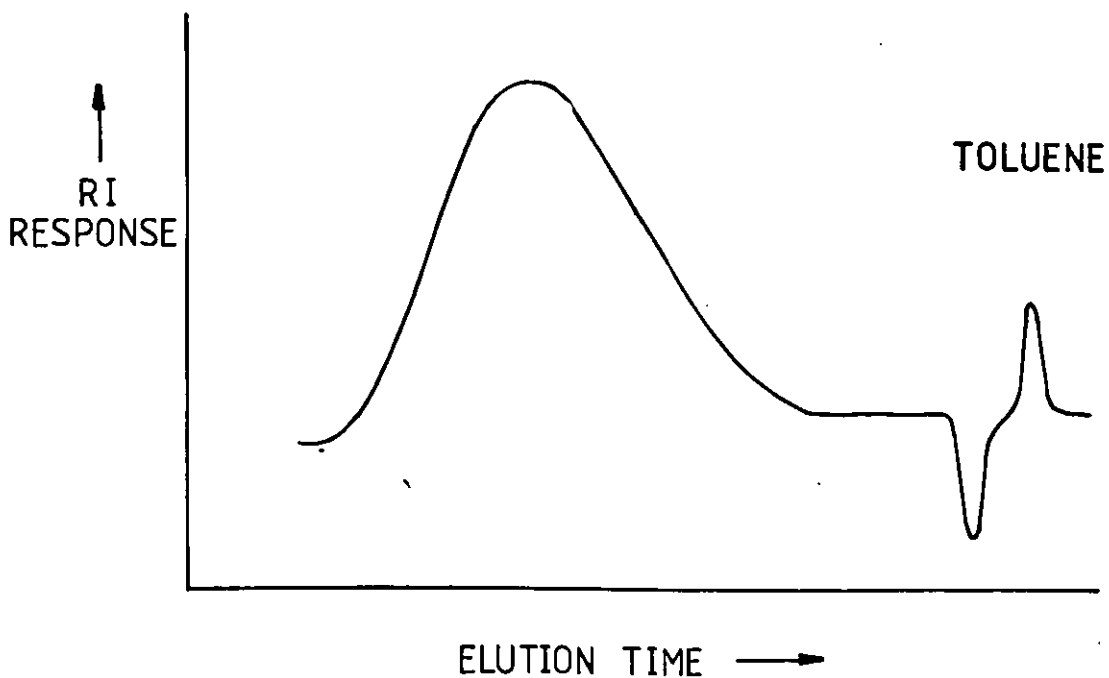
FIGURE 4.2

THE PURIFICATION OF CARBOXYL-TERMINATED PMMA
PREPOLYMERS

(a) GPC CHROMATOGRAM OF UNPURIFIED PREPOLYMER



(b) GPC CHROMATOGRAM OF PURIFIED PREPOLYMER
(3xMeOH/H₂O)



methanol and precipitating in water. It is apparent from this that the purification procedure is effective in removing the low molar mass by-products of the reaction. However, the \bar{M}_{Peak} value shifts to a slightly higher molar mass after purification. Table 4.2 illustrates the changes in molar masses for samples PMMA-15 and PMMA-16 after purification. It can be seen that all molar masses increase after purification with the greatest effect on \bar{M}_n . Therefore, in addition to removing impurities, a small fraction of low molar mass polymer is also removed during purification. This fractionation during purification is also reflected by the resulting narrower molar mass distributions. However, the fact that the peak molar masses are only slightly affected suggests that the fractionation of the PMMA carboxyl-terminated prepolymers during purification is not serious.

A complete characterization was performed on purified carboxyl-terminated prepolymers PMMA-15C and PMMA-16C. Figure 4.3 illustrates the GPC profiles of both prepolymers from which the data given in table 4.2 were determined. The molar mass of PMMA-15C is too high to allow the separation of oligomers with the system used. However, the oligomers for PMMA-16C are quite well resolved on the low molar mass tail of the molar mass distribution and the dimer, trimer, tetramer etc. are labelled 2, 3, 4 etc. in figure 4.3(b). Despite this, oligomers longer than the heptamer remain unresolved and the prepolymer molar mass cannot be determined from oligomer analysis.

Figure 4.4 illustrates the IR spectrum of PMMA-16C. The most important structural features giving rise to absorption above $\sigma = 1500\text{cm}^{-1}$ are labelled in figure 4.4. The strongest absorption is at 1732cm^{-1} due to the PMMA ester carbonyl group. The presence of a carboxyl group is confirmed by the broad O-H stretch at 3254cm^{-1} . The IR spectrum of PMMA-15C was qualitatively identical to figure 4.4. However, the O-H absorption was weaker for PMMA-15C which had a higher molar mass. This molar mass dependence indicates that the carboxyl group is at the terminus of the PMMA

FIGURE 4.3 GPC CHARACTERIZATION OF PURIFIED CARBOXYL-TERMINATED PMMA PREPOLYMERS

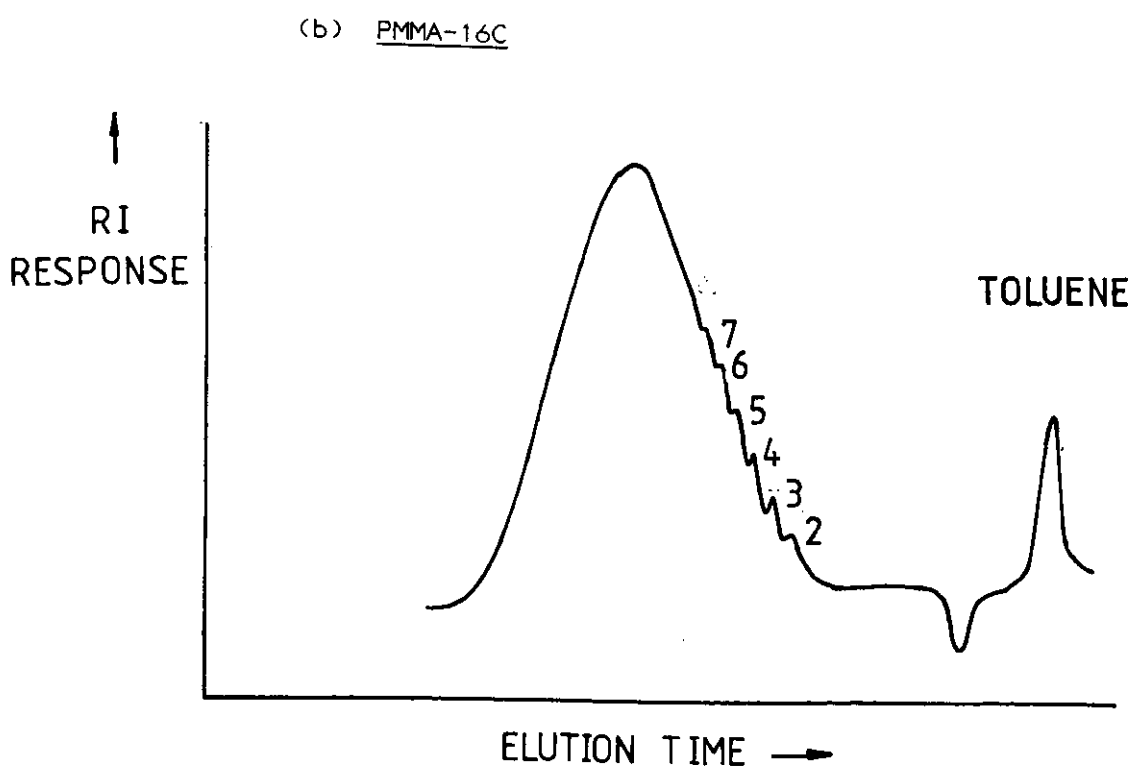
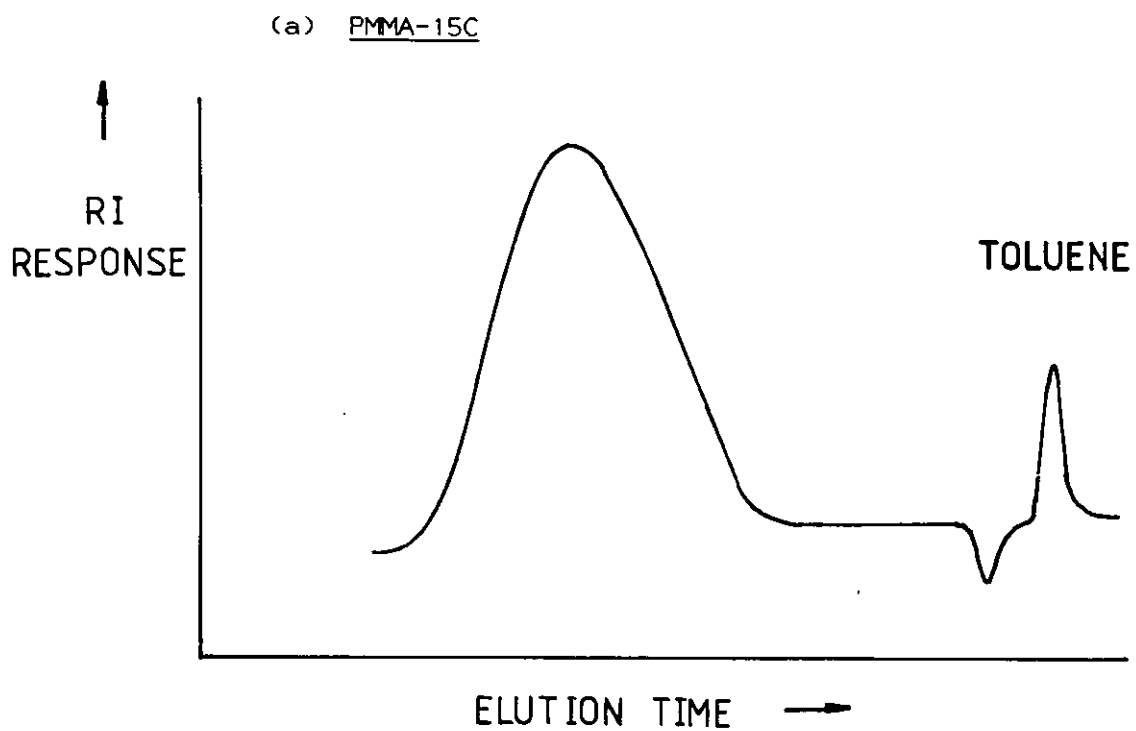
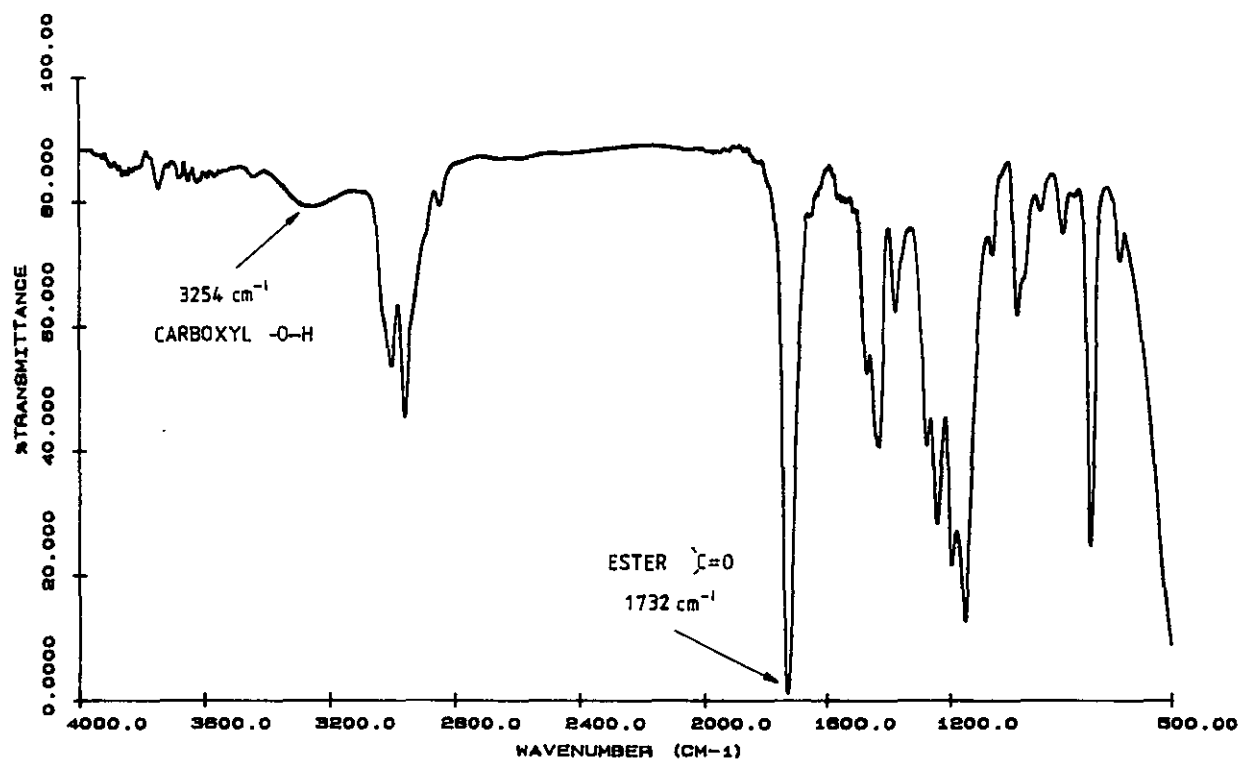


FIGURE 4.4 THE IR SPECTRUM OF CARBOXYL-TERMINATED PREPOLYMER
PMMA-16C



chain.

Purified carboxyl-terminated prepolymers were also characterized by ^1H NMR spectroscopy. As an example, the ^1H NMR spectrum of PMMA-16C is illustrated in figure 4.5. The assignments of the chemical shifts (δ) of the various proton resonances are given in table 4.3 and these correspond to the protons labelled in the structure of the carboxyl-terminated prepolymer (IX). Both the main chain methylene (c) and the α -methyl group (b) of the PMMA CRU are split into three peaks as a result of their different stereoregular environments. Although the ^1H NMR spectrum shows the presence of the thioglycollic acid residue, it does not indicate the carboxyl O-H proton. Although figure 4.5 only illustrates the spectrum from $\delta = 0-5$ ppm, spectra were obtained from $\delta = 0-13$ ppm. The only proton resonance above $\delta = 3.6$ ppm occurred at $\delta = 7.28$ ppm due to residual protons in the deuterated chloroform which was used as the solvent. However, the presence of the carboxyl group was confirmed by IR spectroscopy as previously illustrated. By comparison of the integration H_a of the PMMA ester methyl group (a) at $\delta = 3.6$ ppm to the integration H_d of the end-group protons (d) at $\delta = 3.2$ ppm, it is possible to obtain the ratio of PMMA repeating units to end-groups. This produces the average number of PMMA repeating units per chain (x in structure IX) which then allows the number average molar mass to be calculated from structure IX.

Therefore,

$$x = \frac{\text{number of PMMA repeating units}}{\text{number of end-groups}} = \frac{\text{H}_a/3}{\text{H}_d/2} \quad (4.1)$$

and values of x were calculated to the nearest integer. The number average molar masses obtained by ^1H NMR spectroscopy for PMMA-15C and PMMA-16C are shown in table 4.4 in comparison to those obtained by EGA. The functionality value f is the average number of carboxyl groups per molecule obtained by comparing the molar mass obtained by ^1H NMR and EGA.

FIGURE 4.5 THE ^1H NMR SPECTRUM OF CARBOXYL-TERMINATED
PREPOLYMER PMMA-16C

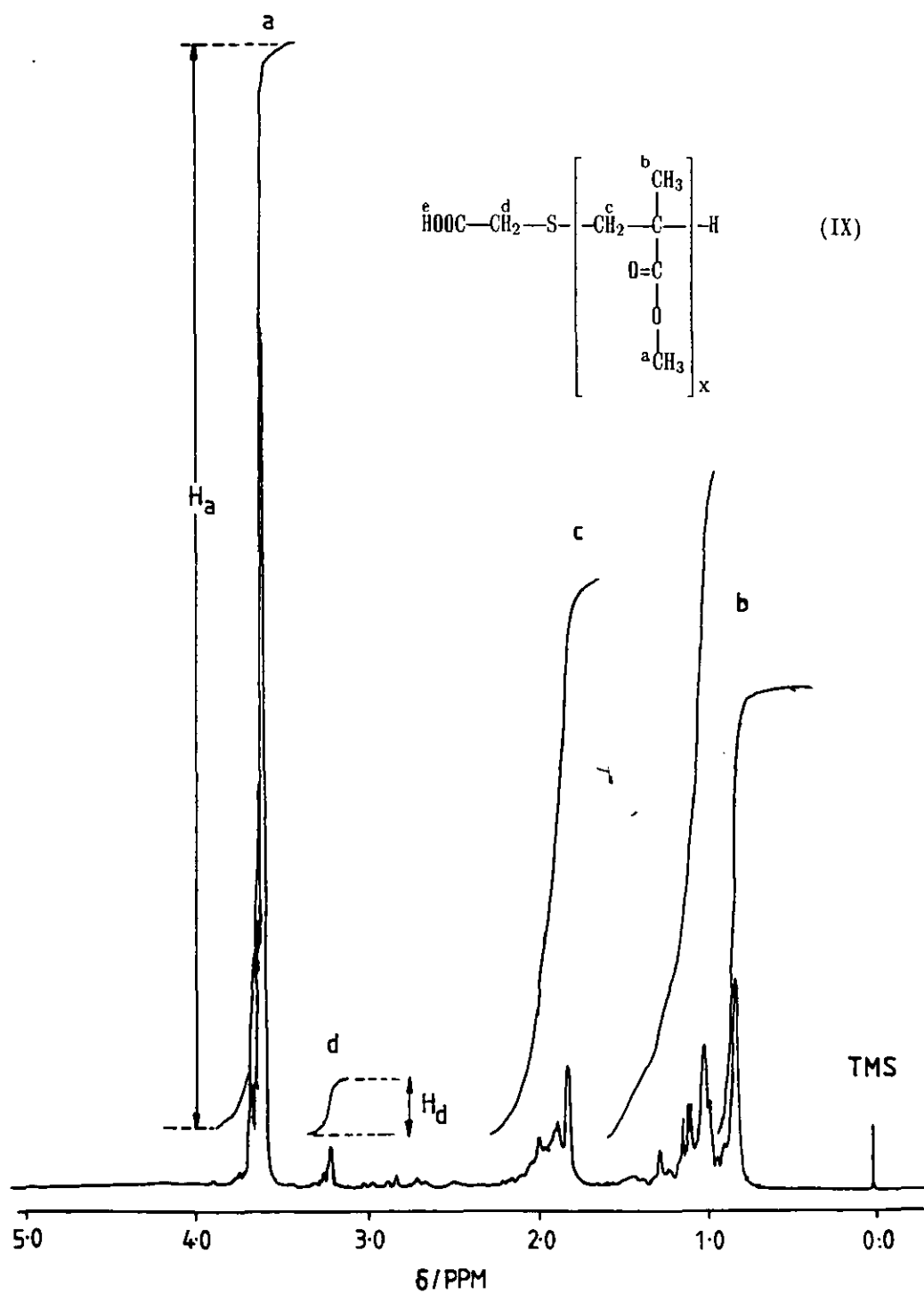
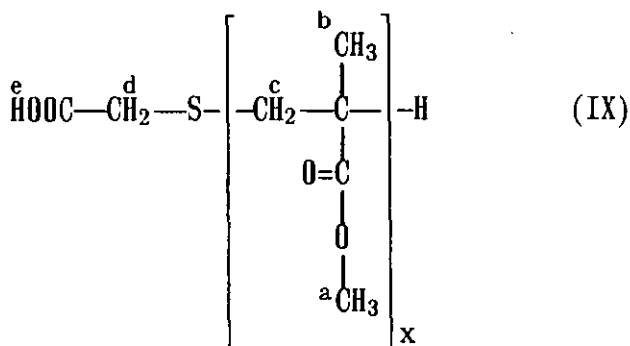


TABLE 4.3 THE ASSIGNMENT OF CHEMICAL SHIFTS IN THE ¹H NMR
SPECTRUM OF CARBOXYL-TERMINATED PREPOLYMER PMMA-
16C

CHEMICAL SHIFT	ASSIGNMENT	LABEL IN STRUCTURE IX
δ/PPM		
0.83	Syndiotactic } Heterotactic } Isotactic }	PMMA α-CH ₃ b
1.02		
1.25		
1.81-1.98	PMMA -CH ₂ - in syndiotactic, heterotactic and isotactic environments	c
3.2	TGA residue -S-CH ₂ -COOH	d
3.60	PMMA -O-CH ₃ methylester	a



Therefore

$$f = \frac{\bar{M}_n(1H\ NMR)}{\bar{M}_n(EGA)} \quad (4.2)$$

It is evident from the f values in table 4.4 that the polymer chains are approximately monofunctional.

(b) Polymerizations in 2-ethoxyethanol.

As mentioned in experimental section 3.2.1, 2-ethoxyethanol was originally used as the solvent for the MMA polymerizations following the method used by Margetts [168]. The purification method was identical to the prepolymers prepared in ethyl acetate and similar observations were noted for the fractionation of polymers during purification. However, only \bar{M}_{Peak} values were analysed from GPC and a full description of the various molar masses and the molar mass distributions were not obtained. EGA and 1H NMR spectroscopy were used to gain information about the molar masses and functionalities of carboxyl-terminated PMMA prepolymers in an identical fashion to that reported in the previous section. The appearance of the 1H NMR spectra of the PMMA prepolymers prepared in 2-ethoxyethanol were qualitatively identical to those prepared in ethyl acetate and previously illustrated for PMMA-16C in figure 4.5. Table 4.5 shows the concentrations of reagents used and the characterization of purified PMMA prepolymers prepared in 2-ethoxyethanol. A polymerization time of 1.5-2 hours at 353 K was used to give approximately 60% conversion of monomer to polymer. As for polymerizations in ethyl acetate, increasing the concentration of transfer agent resulted in a polymer with a lower molar mass, although an insufficient number of experiments were performed to obtain the relationship between molar mass and TGA concentration as previously shown in figure 4.1 for ethyl acetate polymerizations. Apart from sample PMMA-80/1C, the functionalities obtained are approximately 1.0, ie. the carboxyl-terminated chains are approximately monofunctional. Ethyl acetate was

TABLE 4.4 THE COMPARISON OF \bar{M}_n VALUES OBTAINED BY ^1H NMR AND
END-GROUP ANALYSIS FOR CARBOXYL-TERMINATED PMMA
PREPOLYMERS

SAMPLE	$\bar{M}_n(^1\text{H NMR})/10^3$ g.mol ⁻¹	$\bar{M}_n(\text{EGA})/10^3$ g.mol ⁻¹	f
PMMA-15C	2.60	2.80	0.93
PMMA-16C	1.49	1.31	1.13

NB End-group analysis performed using non-aqueous titration

TABLE 4.5 \bar{M}_n VALUES FOR PURIFIED CARBOXYL-TERMINATED PMMA
PREPOLYMERS PREPARED IN 2-ETHOXYETHANOL

SAMPLE	[ACVA] /10 ⁻³ mol.dm ⁻³	[TGA] /10 ⁻¹ mol.dm ⁻³	$\bar{M}_n(^1\text{H NMR})/10^3$ g.mol ⁻¹	$\bar{M}_n(\text{EGA})/10^3$ g.mol ⁻¹	f
PMMA-80/1C	9.5	1.1	2.89	2.40	1.20
PMMA-80/5C	1.9	1.0	2.89	2.97	0.97
PMMA-80/6C	9.5	2.9	1.69	1.60	1.05
PMMA-80/8C	9.5	2.9	1.69	1.70	0.99

NB (i) MMA concentration = 28.5% (w/w).

(ii) end group analysis performed using aqueous titration

subsequently preferred to 2-ethoxyethanol as a polymerization solvent for two reasons. Firstly, it has a much lower boiling point, which enables it to be removed more easily. Secondly, any 2-ethoxyethanol remaining in purified samples would interfere with the conversion of carboxyl end-group to acyl chloride as a result of its hydroxyl content.

4.1.1.2 Poly(2-ethyl hexyl acrylate) prepolymers

Carboxyl-terminated PEHA prepolymers were prepared from the free-radical solution polymerization of EHA in ethyl acetate at 353 K. A polymerization time of 1.5-2 hours was used to give approximately 60% conversion of monomer to polymer. Once again, the concentrations of ACVA and TGA were varied to obtain molar masses (\bar{M}_n) of approximately 1500 and 3000g.mol⁻¹. Examples of unpurified prepolymers which were characterized by GPC are shown in table 4.6. PEHA-3 and PEHA-6 are syntheses where no chain transfer agent was used. As with PMMA prepolymers, the addition of thioglycollic acid reduced the molar mass of the polymers produced and an increased concentration of TGA resulted in a polymer with a lower molar mass. This is illustrated in figure 4.6 which shows the relationship between the reciprocal \bar{M}_{Peak} value and the initial TGA concentration. As for impure PMMA prepolymers, the GPC chromatograms indicated the presence of impurities at the low molar mass tail of the molar mass distribution, likely to be initiator and chain transfer agent fragments. These impurities are likely to produce errors in the \bar{M}_n values and, therefore, \bar{M}_{Peak} values were used for the relationship shown in figure 4.6. In order to remove the impurities, PEHA carboxyl-terminated prepolymers were dissolved in ethyl acetate and then isolated as oils in methanol. However, as table 4.7 indicates for sample PEHA-14, the temperature of the methanol used for isolation was crucial in determining the fractionation of polymers during purification. The sample

TABLE 4.6 GPC CHARACTERIZATION OF UNPURIFIED CARBOXYL-TERMINATED PEHA PREPOLYMERS PREPARED IN ETHYL ACETATE

SAMPLE	[ACVA]	[TGA]	$\bar{M}_{Peak}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n
	$/10^{-3}\text{mol}\cdot\text{dm}^{-3}$	$/10^{-1}\text{mol}\cdot\text{dm}^{-3}$	←—————units $\text{g}\cdot\text{mol}^{-1}$ ————→				
PEHA-3	21.3	-	75.0	-	-	-	-
PEHA-14	21.3	2.0	1.55	1.15	1.80	1.44	1.57
PEHA-26	21.3	2.7	1.45	-	-	-	-
PEHA-6	11.0	-	83.0	-	-	-	-
PEHA-17	11.0	1.0	2.75	1.93	3.25	2.50	1.68
PEHA-16	11.0	1.3	2.19	1.67	2.64	2.10	1.58
PEHA-15	11.0	1.6	1.82	1.51	2.36	1.89	1.57
PEHA-27	8.8	1.1	2.69	-	-	-	-

NB (i) EHA Concentration = $33\%(\text{w/w}) = 1.61 \text{ mol}\cdot\text{dm}^{-3}$

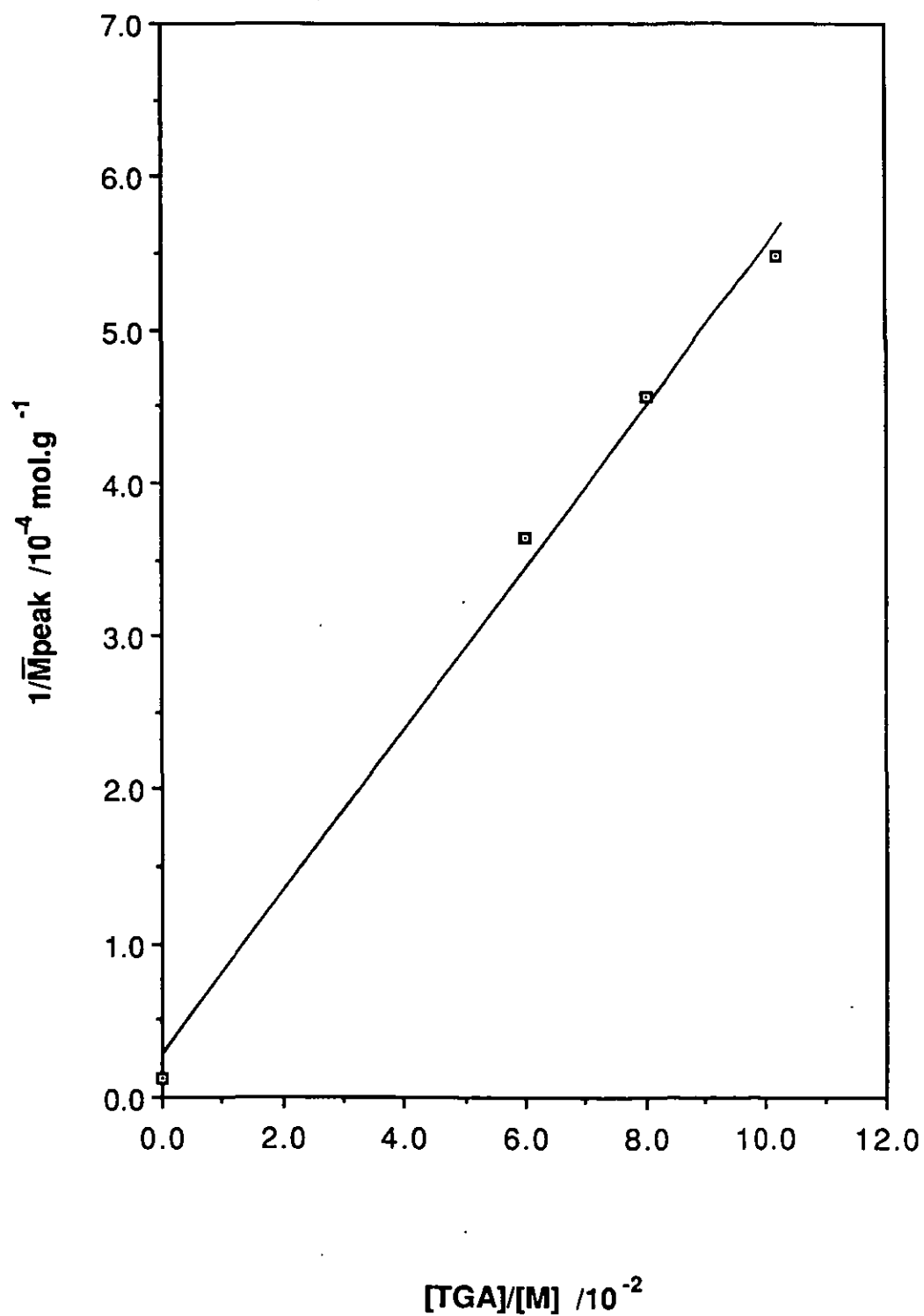
(ii) PEHA-3 and PEHA-6 characterized using mixed gel column, other polymers characterized using column with 500Å pore size.

TABLE 4.7 GPC CHARACTERIZATION SHOWING THE EFFECT OF ISOLATION PROCEDURE ON THE FRACTIONATION OF CARBOXYL-TERMINATED PREPOLYMER PEHA-14

ISOLATION METHOD	$\bar{M}_{Peak}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n
	←—————units $\text{g}\cdot\text{mol}^{-1}$ ————→				
Ethyl acetate evaporated	1.55	1.15	1.80	1.44	1.57
Methanol room temperature	2.82	2.18	2.80	2.47	1.28
Methanol -10°C	2.57	1.97	2.62	2.27	1.33
Methanol near freezing point	1.74	1.33	2.01	1.64	1.51

NB Polymers characterized using column with 500Å pore size.

FIGURE 4.6 THE EFFECT OF CHAIN TRANSFER AGENT CONCENTRATION ON THE MOLAR MASSES OF CARBOXYL-TERMINATED PEHA PREPOLYMERS



obtained by evaporating the solvent can be considered as being unfractionated. It is evident from table 4.7 that after isolation of the polymer in methanol at room temperature, there is a marked shift to a higher molar mass and this is accompanied by the production of a much narrower molar mass distribution. Therefore, there is considerable fractionation and a large quantity of low molar mass polymer is removed. Altering the methanol temperature to -10°C does not prevent this fractionation and the molar masses and the molar mass distribution obtained are similar. However, by cooling the methanol close to its freezing point, serious fractionation and a loss of considerable amounts of polymer are both prevented. The molar masses obtained by this method are only slightly higher than the unfractionated sample and there is less change in the molar mass distribution. This preferred purification procedure was applied repeatedly to PEHA prepolymers before being converted to macromonomers. The GPC chromatograms of the purified prepolymers indicated that the impurities, originally present at the low molar mass tail of the impure PEHA prepolymer molar mass distribution, had been removed. This was monitored using GPC by a similar manner to that illustrated for PMMA prepolymers in figure 4.2, section 4.1.1.1. Table 4.8 shows the GPC characterization of purified prepolymers which were prepared on a larger scale in order to produce sufficient quantities of prepolymer to be converted to macromonomer. PEHA-50C and PEHA-51C are essentially repeat polymerizations of PEHA-45C and PEHA-40C, respectively.

The purified carboxyl-terminated prepolymers listed in table 4.8 were characterized extensively using GPC, IR, ^1H NMR and EGA. Figure 4.7 illustrates the GPC profiles of both PEHA-50C and PEHA-51C. PEHA-50C shows some separation of oligomers but only at the low molar mass tail of the distribution. However, the oligomers for PEHA-51C are extremely well-resolved and the oligomers are labelled in figure 4.7(b) as 2,3,4 ... 8 for the dimer, trimer, tetramer ... octamer. It is apparent that the peak

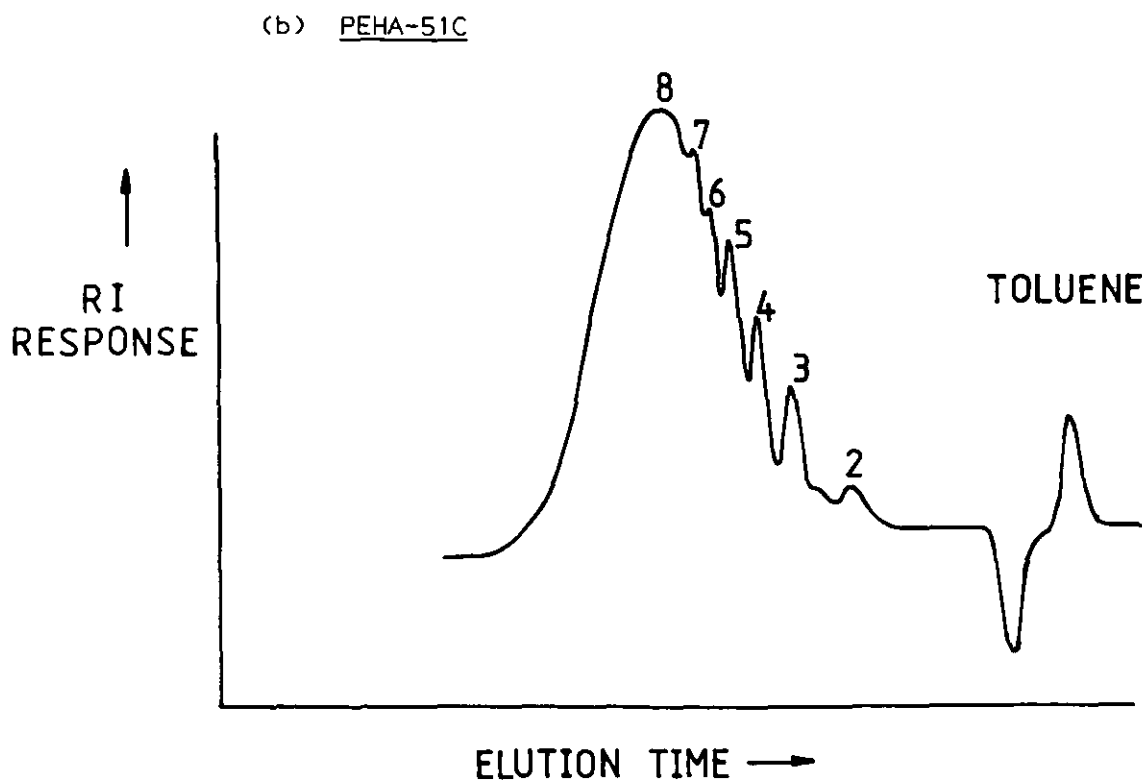
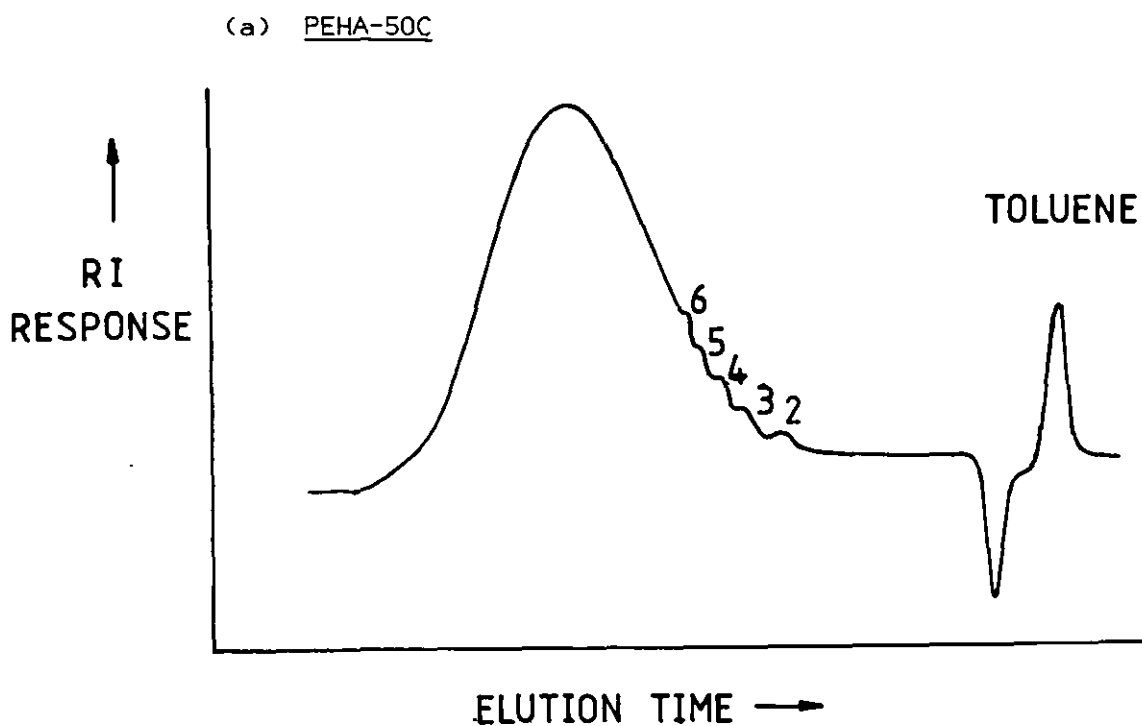
TABLE 4.8 GPC CHARACTERIZATION OF PURIFIED CARBOXYL-
TERMINATED PREPOLYMERS USED TO PREPARE
MACROMONOMERS

SAMPLE	[ACVA]	[TGA]	$\bar{M}_{Peak}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n
	$/10^{-3}\text{mol}\cdot\text{dm}^{-3}$	$/10^{-1}\text{mol}\cdot\text{dm}^{-3}$	←—————units $\text{g}\cdot\text{mol}^{-1}$ ————→				
PEHA-40C	21.0	3.0	1.80	1.38	1.96	1.64	1.42
PEHA-45C	8.0	1.1	3.67	2.96	4.73	3.74	1.58
PEHA-50C	8.0	1.1	3.80	2.87	4.40	3.55	1.53
PEHA-51C	21.0	3.0	1.88	1.30	1.88	1.56	1.45

NB (i) Polymer characterized using column with 500Å pore size.

FIGURE 4.7

GPC CHARACTERIZATION OF PURIFIED CARBOXYL-TERMINATED PEHA PREPOLYMERS



of the chromatogram corresponds to the octamer and it can be inferred that, on average, each chain contains eight PEHA repeating units. This means that the molar mass of PEHA-51C can be calculated from the oligomer analysis (see table 4.10). The molar mass of PEHA-40C is very similar to PEHA-51C and this can also be obtained from oligomer analysis.

Figure 4.8 illustrates the IR spectrum of PEHA-51C. The main structural features which produce absorption above $\sigma=1500\text{cm}^{-1}$ are labelled in figure 4.8. The strongest absorption occurs at 1736cm^{-1} due to the PEHA acrylate ester carbonyl stretch. The presence of a carboxyl group is indicated by the broad O-H stretch centred at 3230cm^{-1} . As for PMMA carboxyl-terminated prepolymers, the strength of this absorption was molar mass dependent. Therefore, although the IR spectra for the prepolymers listed in table 4.8 were qualitatively identical, the size of the carboxyl O-H stretch was relatively smaller for polymers with higher molar masses. This molar mass dependence again suggests that the carboxyl group is at the terminus of the polymer chain.

An example of a ^1H NMR spectrum of carboxyl-terminated PEHA prepolymers is illustrated in figure 4.9 for PEHA-51C. All purified PEHA prepolymers produced ^1H NMR spectra qualitatively identical to this. The chemical structure of the carboxyl-terminated PEHA prepolymer is shown below (X) and the chemical shifts, due to the protons labelled in this structure, are given in table 4.9. Although the ^1H NMR indicates the presence of the TGA residue protons (j) in addition to the PEHA protons constituting the CRU, the carboxyl O-H proton is not detected. As for PMMA prepolymers, spectra were obtained over the range $\delta=0-13\text{ppm}$ but there was no indication of any protons above $\delta=4\text{ppm}$, apart from at $\delta=7.28\text{ppm}$ due to residual protons in the deuterated chloroform. However, the presence of a carboxyl group was confirmed by IR spectroscopy as previously described. By

FIGURE 4.8 THE IR SPECTRUM OF CARBOXYL-TERMINATED PREPOLYMER
PEHA-51C

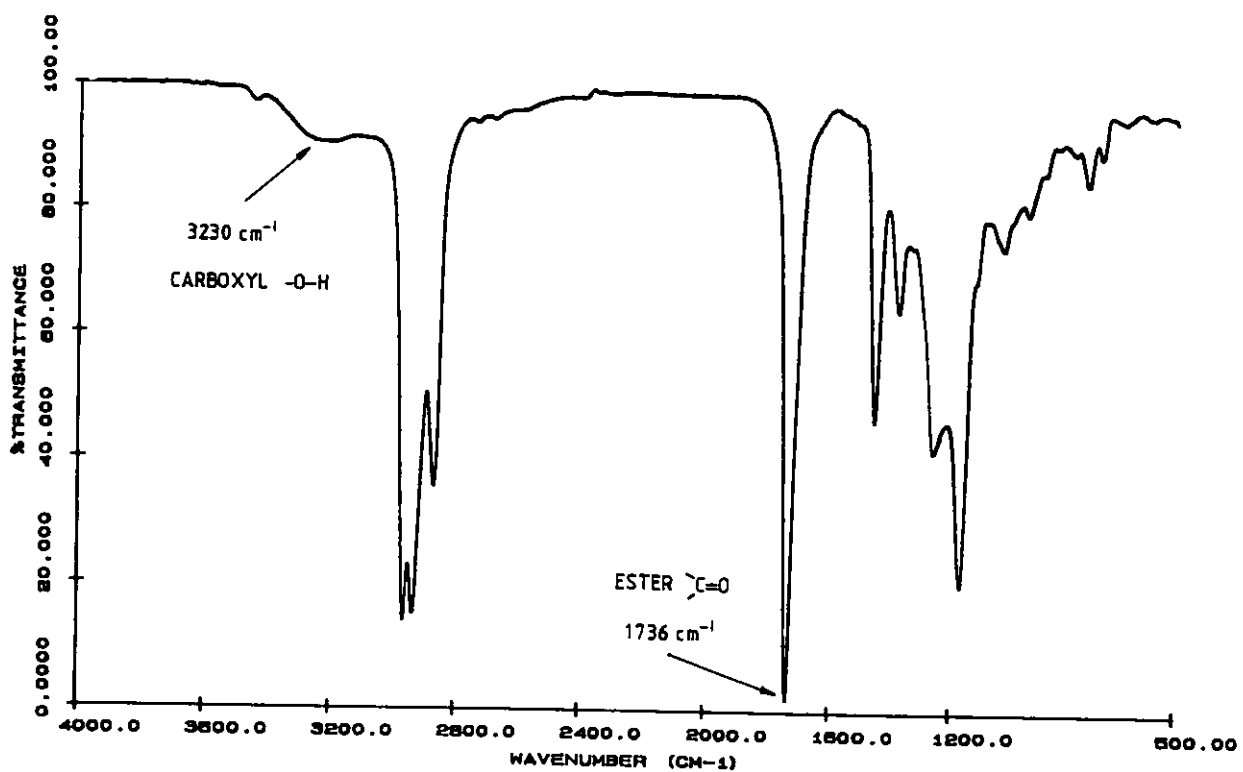


FIGURE 4.9 THE ^1H NMR SPECTRUM OF CARBOXYL-TERMINATED
PREPOLYMER PEHA-51C

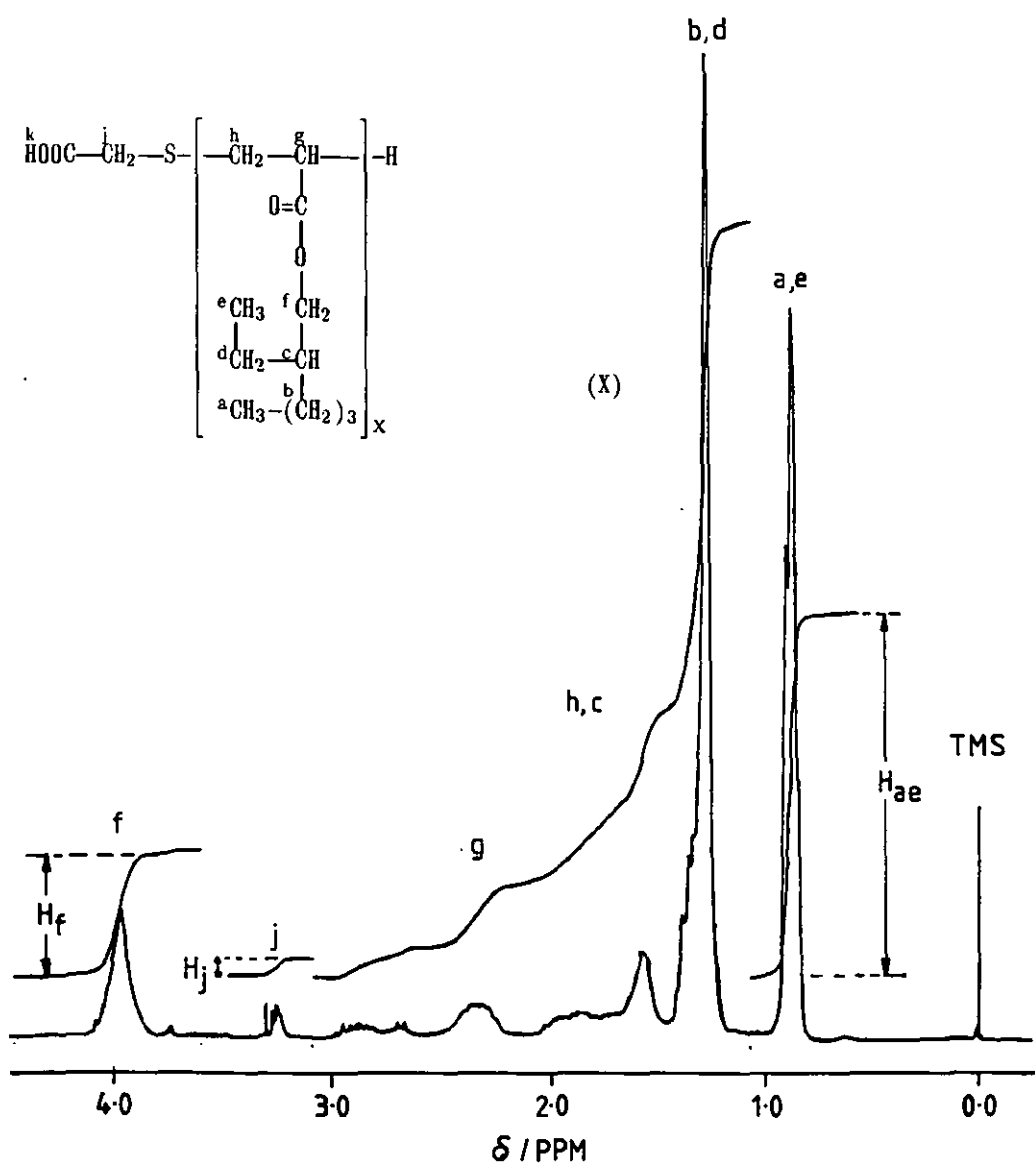
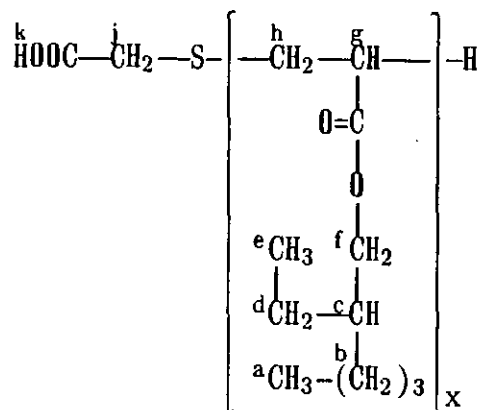


TABLE 4.9 THE ASSIGNMENT OF CHEMICAL SHIFTS IN THE ¹H NMR
SPECTRUM OF CARBOXYL-TERMINATED PREPOLYMER PEHA-
51C

CHEMICAL SHIFT	ASSIGNMENT	LABEL IN STRUCTURE X
δ /ppm		
0.90	-CH ₃	a, e
1.29	-CH ₂ -	b, d
1.50-2.0	-CH ₂ -CH ₂ -COO-	h
	-CH-	c
2.33	-CH ₂ -CH ₂ -COO	g
3.25	HOOC-CH ₂ -S-	j
3.97	-COO-CH ₂ -	f



comparison of the integration H_f of the PEHA ester $-O-CH_2-$ group (f) at $\delta = 3.95\text{ppm}$ or the integration $H_{a,e}$ of the PEHA methyl groups (a and e) at $\delta = 0.9\text{ppm}$ to the integration H_j of the end-group protons (j) at $\delta = 3.25\text{ppm}$, it is possible to obtain the molar ratio of PEHA repeating units to end-groups. These resonances were chosen since they are well-resolved and suffer no interference from the resonances of other protons. In a similar fashion to PMMA prepolymers, this comparison produces the average number of PEHA repeating units per chain (x in structure X) which then allows the number average molar mass to be calculated. Therefore,

$$x = \frac{\text{number of PEHA repeating units}}{\text{number of end-groups}} = \frac{H_f/2}{H_j/2} = \frac{H_{a,e}/6}{H_j/2} \quad (4.3)$$

and values of x were calculated to the nearest integer.

The number average molar masses obtained by ^1H NMR calculated from x, for the various purified carboxyl-terminated PEHA prepolymers, are shown in table 4.10. These values were compared with those from end-group analysis to obtain the functionality f in exactly the same manner as for the PMMA prepolymers. The f values indicate that the PEHA prepolymers are approximately monofunctional. The \bar{M}_n values from oligomer analysis are identical to those calculated from the ^1H NMR analysis.

4.1.1.3 Comparison of carboxyl-terminated prepolymers

IR spectroscopy and End-Group Analysis showed that both the PMMA and PEHA prepolymers were terminated with carboxyl groups. Although ^1H NMR spectroscopy illustrated the presence of the TGA residue, the carboxyl O-H proton was not detected. Classically, when carboxyl groups are hydrogen-bonded, the O-H protons exhibit some of the lowest field resonances recorded ($\delta = 9-13\text{ppm}$) [169]. For example, in thioglycollic acid itself, the carboxyl proton resonates at $\delta = 9.0\text{ppm}$ [170] but no such resonance occurred in the spectra of the carboxyl-terminated prepolymers. Assuming that the chains are monofunctional, there is only one carboxyl O-

TABLE 4.10 THE COMPARISON OF \bar{M}_n VALUES OBTAINED BY VARIOUS METHODS FOR PURIFIED CARBOXYL-TERMINATED PEHA PREPOLYMERS

SAMPLE	\bar{M}_n (¹ H NMR)/10 ³ g.mol ⁻¹	\bar{M}_n (EGA)/10 ³ g.mol ⁻¹	\bar{M}_n GPC (Oligomer analysis) /10 ³ g.mol ⁻¹	f
PEHA-40C	1.56	1.51	1.56	1.03
PEHA-45C	3.04	3.18	-	0.96
PEHA-50C	3.04	2.92	-	1.04
PEHA-51C	1.56	1.42	1.56	1.10

NB (i) EGA performed using non-aqueous titrations.

H proton per chain and its concentration is therefore very low. The first consequence of this is that the O-H proton is unlikely to be involved in hydrogen-bonding, which may also be hindered by the fact that the carboxyl group mobility may depend on the oligomeric chain to which it is attached. Therefore, this proton will resonate at a higher field-strength than if it were hydrogen-bonded [169]. The second consequence of this low concentration is that detection will be difficult since it represents such a small part of the molecule. It therefore appears likely that the carboxyl O-H proton resonance will be masked under the proton resonances of the PMMA or PEHA repeating units in the chain.

As figures 4.1 and 4.6 illustrated, carboxyl-terminated prepolymers of desired molar mass can be readily prepared by controlling the feed ratio of chain transfer agent to monomer. The reduction in the number average degree of polymerization resulting from transfer reactions in free-radical polymerization, is given by the chain transfer equation [89,108].

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + C_M + C_I \frac{[I]}{[M]} + C_S \frac{[S]}{[M]} + C_X \frac{[X]}{[M]} + C_P \frac{[P]}{[M]} \quad (4.4)$$

Where \overline{DP} = number average degree of polymerization due to transfer reactions,

\overline{DP}_0 = number average degree of polymerization in the absence of transfer reactions;

[M], [I], [S], [X] and [P] are the concentrations of monomer, initiator, solvent, chain transfer agent and polymer respectively;

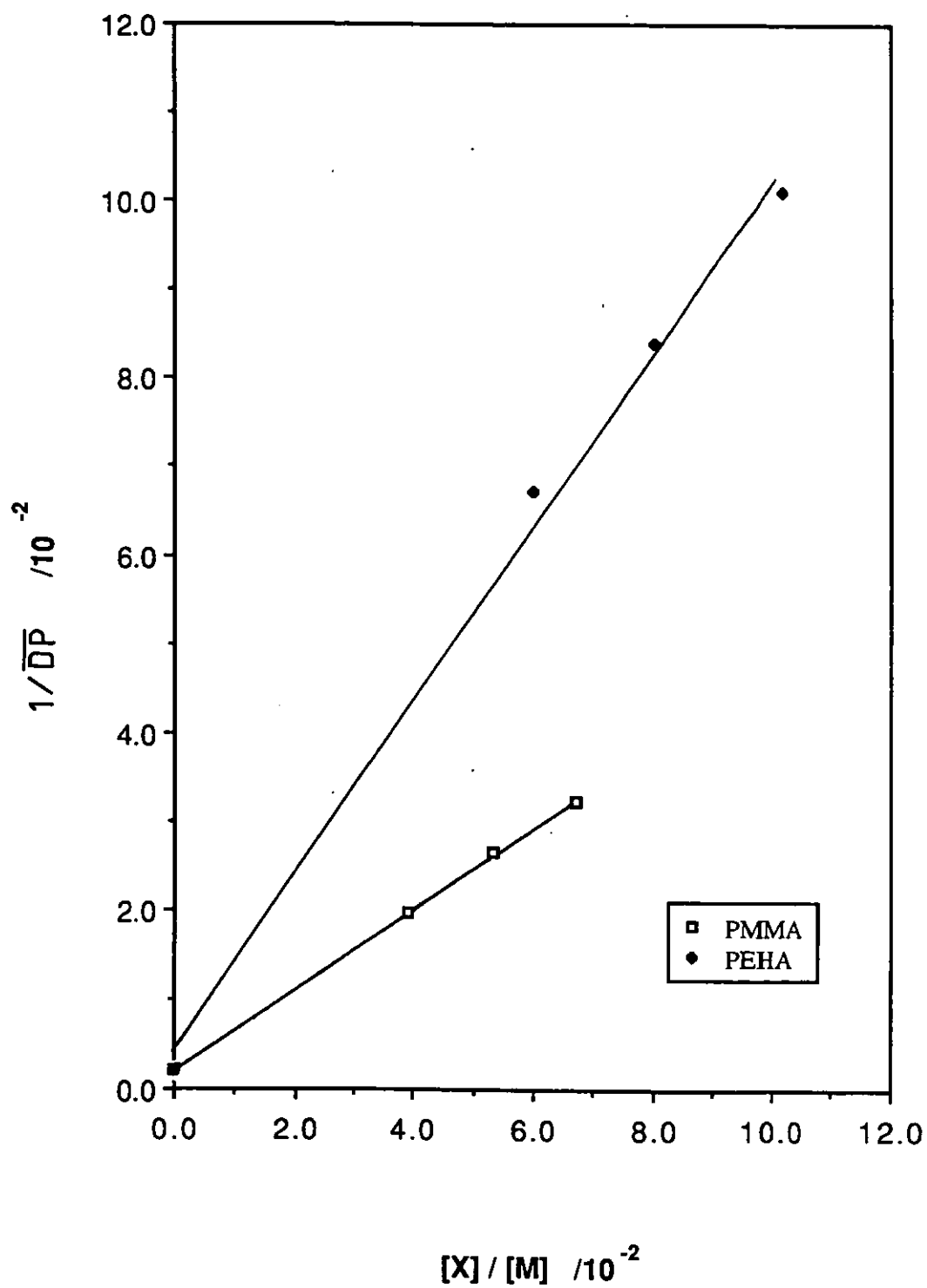
C_M , C_I , C_S , C_X and C_P are the chain transfer constants for monomer, initiator, solvent, chain transfer agent and polymer respectively.

For MMA polymerizations in ethyl acetate at 353 K, C_M , C_I , C_S and C_P values are of the order of 10^{-4} or less [171] and the chain transfer equation can be simplified to [52,108]

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP}_0} + C_x \frac{[X]}{[M]} \quad (4.5)$$

Although there is little kinetic data available in the literature on EHA polymerizations, other acrylates have C_M , C_I , C_S and C_P values of the order of 10^{-4} [171]. Therefore, one can assume that equation 4.5 also applies to EHA polymerizations. The data from figures 4.1 and 4.6 are replotted in figure 4.10 to show the relationship between $\frac{1}{\overline{DP}}$ and $\frac{[X]}{[M]}$ for both MMA and EHA polymerizations in ethyl acetate using TGA as chain transfer agent X. Both graphs are linear and from equation 4.5 it is evident that C_x can be obtained from the slopes of these relationships. These values are only likely to be approximations for two reasons. Firstly, the \overline{DP} values were calculated from the \overline{M}_{peak} values obtained from GPC, due to reasons given in sections 4.1.1.1 and 4.1.1.2. Secondly, the polymerizations were carried out to >50% conversion and equation 4.6 applies to polymerizations performed at low conversion. Nevertheless, the fact that both relationships are linear appears to validate the use of equation 4.5 and the assumptions that C_M , C_S , C_I and C_P are negligible in these polymerizations. From figure 4.10, it was found that $C_x = 0.48$ for TGA in MMA polymerizations and $C_x = 0.98$ for TGA in EHA polymerizations. Data on the C_x values of functionalized chain transfer agents in the literature are limited but $C_x = 0.63$ for the methyl ester of thioglycollic acid at 333 K [108] and $C_x = 0.38$ for 3-mercaptopropionic acid at 343 K [171], both in MMA polymerizations. Roy et al [172] found that for thioglycollic acid in MMA polymerizations at 323 K and 343 K, $C_x = 0.39$ and 0.38 respectively. The value of $C_x = 0.48$ for TGA in MMA polymerizations compares favourably to these literature values. If the chain transfer constant for an added chain transfer agent is equal to unity, then the chain transfer agent is said to behave 'ideally' [108]. This is because when $C_x = 1.0$, the ratio of the rates at which monomer and chain transfer agent are consumed by growing polymer radicals is constant. When $C_x \neq 1.0$, the transfer agent will be consumed at a rate either faster or

FIGURE 4.10 A COMPARISON OF THE EFFECTS OF CHAIN TRANSFER AGENT CONCENTRATION ON THE DEGREES OF POLYMERIZATION OF PMMA AND PEHA CARBOXYL-TERMINATED PREPOLYMERS



slower than the monomer such that the ratio of [X]:[M] will change continuously throughout the polymerization. Therefore, it appears that TGA behaves more ideally in EHA polymerizations than MMA polymerizations. Corner [108] suggests that functionalized transfer agents, used in the production of intermediates from which macromonomers can be synthesized, should possess chain transfer constants in the range 0.1-1.0, preferably between 0.5-2.0. Thioglycollic acid appears to conform to this for both MMA and EHA polymerizations.

The molar masses from GPC were obtained from a polystyrene calibration. The calibration curves of PMMA and PS are almost identical in GPC over a wide range of molar masses [173], so that one would expect the values quoted for PMMA samples to be close to true values. Dawkins [173,174] has shown that the same molar mass calibration curve is obtained for polymers with similar unperturbed dimensions per unit mass. If the unperturbed mean square end-to-end distance $\langle r_0^2 \rangle$ is taken as the universal calibration parameter, the molar mass calibrations at a given volume are given by

$$\log M_x - \log M_{ps} = \log \left[\frac{\langle r_0^2 \rangle}{M} \right]_{ps} \left[\frac{M}{\langle r_0^2 \rangle} \right]_x \quad (4.6)$$

where $\langle r_0^2 \rangle/M$ are the unperturbed dimensions per unit mass, M_x is the molar mass of polymer requiring analysis, M_{ps} is the molar mass of a linear polystyrene standard, X refers to the polymer requiring analysis and PS refers to linear polystyrene standards. The right-hand side is essentially a shift factor which permits the calculation of M_x calibration for the polymer requiring analysis from a M_{ps} calibration established experimentally with linear PS standards. Table 4.11 quotes the values of $\langle r_0^2 \rangle/M^{0.5}$ for various polymers. It can be seen that $\langle r_0^2 \rangle/M^{0.5}$ for PMMA is similar to PS and from this basis, the PMMA molar mass calibration is expected to be similar to PS. Values for PEHA are not readily available but figures for other poly(acrylates) are quoted in table 4.11. From this, it can be expected that the

TABLE 4.11 UNPERTURBED DIMENSIONS PER UNIT MASS FOR VARIOUS
POLYMERS [176]

POLYMER	$\frac{\langle r_g \rangle}{M^{0.5}} / 10^{-4} \text{ nm}$
Polystyrene	670
Poly(methyl methacrylate)	640
Poly(methyl acrylate)	650
Poly(t-butyl acrylate)	607

molar mass calibration for PEHA is also similar to PS. However, it must be stressed that polymers with low molar masses were separated using gels with small pore sizes. Therefore, the relatively high end-group concentration in the prepolymers and the high surface area of gel available may have a pronounced effect on the elution properties of the prepolymers. This is in contrast to high molar mass polymers, where end-group effects can be neglected. Frank et al [175] have found that the slope of the calibration curves of polyethylene samples below a molar mass of $2000\text{g}\cdot\text{mol}^{-1}$ depended upon whether they were alkyl-terminated, monocarboxyl-terminated or dicarboxyl-terminated. Therefore, if the carboxyl end-groups of the PMMA and PEHA prepolymers affected their elution properties, they would be expected to be retained on the column for a longer time period, i.e. the true molar mass would be higher than that obtained from a linear PS calibration.

The functionalities of the carboxyl-terminated prepolymers were obtained by comparing the \bar{M}_n data from ^1H NMR spectroscopy and end-group analysis. $\bar{M}_n(\text{EGA})$ values are likely to be quite accurate with only small error. However, $\bar{M}_n(^1\text{H NMR})$ values are likely to involve a relatively large error, since they were obtained by using the small integration of end-group protons which have a low concentration. Although it is difficult to predict, the error involved is expected to be in the range $\pm 5-10\%$. The functionalities of the PMMA prepolymers generally varied from 0.90 to 1.05, whereas the functionalities of PEHA prepolymers varied from 0.96 to 1.10. These values compare favourably to those quoted by other workers for carboxyl-terminated prepolymers. For example, Tsukahara et al [102] have synthesized carboxyl-terminated polymers from methyl, ethyl, butyl and lauryl methacrylate using TGA as chain transfer agent, with functionalities in the range 0.87-1.19. If only bifunctional chains were produced for PMMA and PEHA prepolymers, functionality values of 2.0 would result, since the end-group analysis would underestimate the molar mass. Considering the errors involved

and the fact that the functionalities were obtained by comparing results from different characterization methods, it is evident that both the PMMA and PEHA prepolymers were approximately monofunctional with respect to carboxyl groups.

As already detailed in section 2.4.3, the use of matched chain transfer polymerization has been used by other workers to produce functionalized prepolymers from various monomers [98,107,108]. However, Corner [108] found difficulty in attempting to polymerize a number of monomers using ACVA in combination with TGA. This prompted him to perform a kinetic analysis of the matched chain transfer polymerization process. This has already been summarized in section 2.4.3. One of his main conclusions was that the degree of polymerization of the polymer prepared should be as low as possible in order to minimize w_t and w_{t_r} , the fraction of chains with unwanted functionality arising from termination and transfer reactions, respectively. This has clearly been achieved for the polymerizations of MMA and EHA. Corner also suggested that polymerizations should be restricted to low conversions. However, conversions of >50% were achieved in the MMA and EHA polymerizations described in this work and monofunctional prepolymers have been obtained despite this. Corner predicted that w_t would be higher for the polymerization of monomers where the mode of termination was combination rather than disproportionation. This is because termination by combination will produce bifunctional polymers whereas termination by disproportionation will produce monofunctional polymers in polymerizations initiated by ACVA. In order to minimize w_t in the polymerizations of MMA and EHA performed in ethyl acetate, the concentration of chain transfer agent was deliberately chosen to be far greater than the initiator concentration, thereby maximizing the number of chains produced by chain transfer. Reconsidering equation 4.5, $\frac{1}{\overline{DP}_0}$ is proportional to the number of chains produced by termination and $C_x \frac{[X]}{[M]}$ is proportional to the number of chains produced by chain

TABLE 4.12 THE PERCENTAGE OF CHAINS PRODUCED BY
TERMINATION (ϵ) CALCULATED FOR VARIOUS
CARBOXYL-TERMINATED PREPOLYMERS

<u>SAMPLE</u>	<u>$\bar{M}_n(\text{EGA})/10^3\text{g}\cdot\text{mol}^{-1}$</u>	<u>$\epsilon/\%$</u>
PMMA-15C	2.80	7.0
PMMA-16C	1.31	4.3
PEHA-50C	2.92	2.9
PEHA-51C	1.42	1.3

transfer. This allows the calculation of the percentage of chains produced by termination (t) shown in table 4.12 for selected prepolymers which were subsequently converted to macromonomers. Combination and disproportionation are important in MMA polymerizations but PMMA radicals prefer to terminate by disproportionation at higher temperatures [108,177], such as 353 K. Therefore, although it is calculated that up to 7% of chains are produced by termination, these will be predominantly monofunctional. However, it is unclear as to whether combination or disproportionation is the dominant mode of termination in polymerizations of EHA or acrylates in general [108,177] and it is probable that both occur simultaneously. In any case, the fraction of chains produced by termination has been minimized. (<3%). Such a small proportion of chains is too small to be determined by ¹H NMR spectroscopy, which showed that PEHA and PMMA chains were terminated exclusively with chain transfer agent residues.

4.1.2 THE CONVERSION OF CARBOXYL END-GROUP TO ACYL CHLORIDE

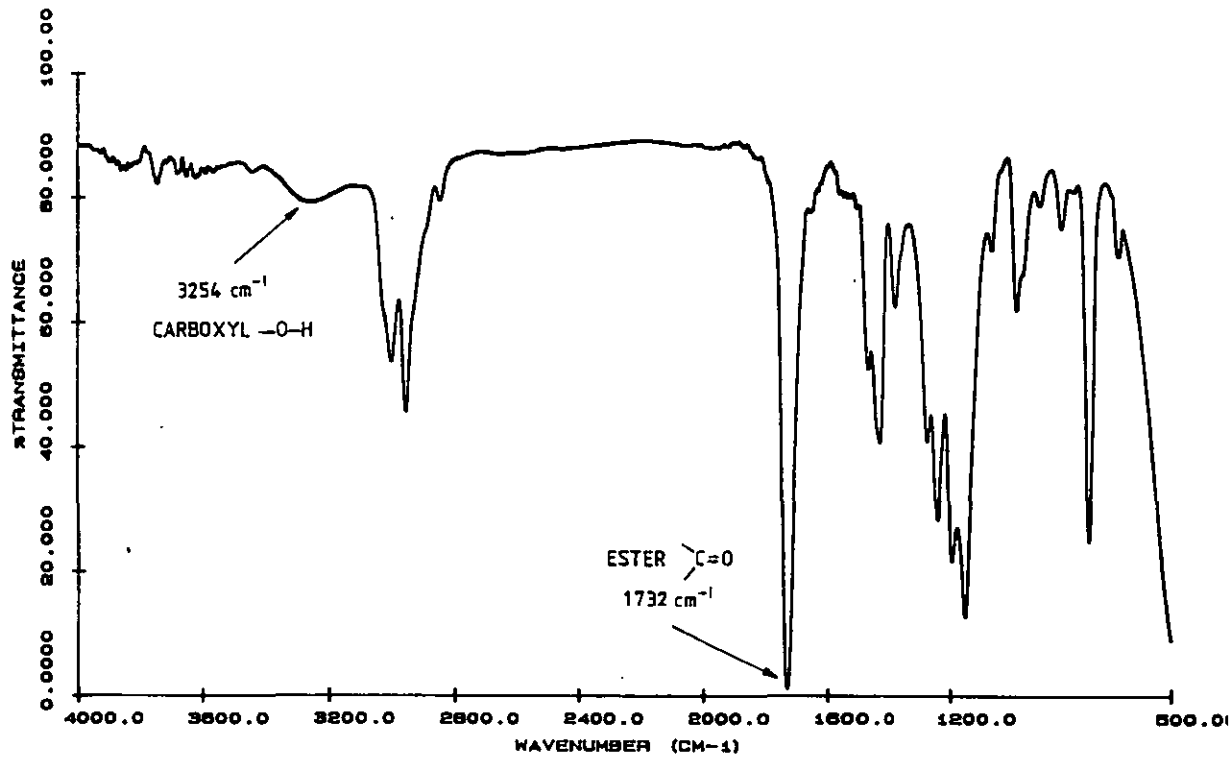
The conversion of carboxyl end-group to acyl chloride was monitored qualitatively by IR spectroscopy for both PMMA and PEHA prepolymers.

4.1.2.1 Poly(methyl methacrylate) polymers

As an example, the IR spectrum of carboxyl-terminated prepolymer PMMA-16C is illustrated in figure 4.11(a) and the corresponding spectrum of the product after reaction with oxalyl chloride, PMMA-16 AC, is illustrated in figure 4.11(b). The strongest absorption occurs at $\sigma = 1732 \text{ cm}^{-1}$ due to the PMMA methyl ester carbonyl stretch and both figures are qualitatively very similar apart from two regions of the spectrum. Figure 4.11(a) shows a broad O-H stretch centred at $\sigma = 3254 \text{ cm}^{-1}$ due to the carboxyl end-group. As figure 4.11(b) illustrates, this absorption

FIGURE 4.11 IR CHARACTERIZATION OF THE CONVERSION OF CARBOXYL
END-GROUP TO ACYL CHLORIDE END-GROUP IN PMMA
PREPOLYMERS

(a) IR SPECTRUM OF PMMA-16C



(b) IR SPECTRUM OF PMMA-16AC

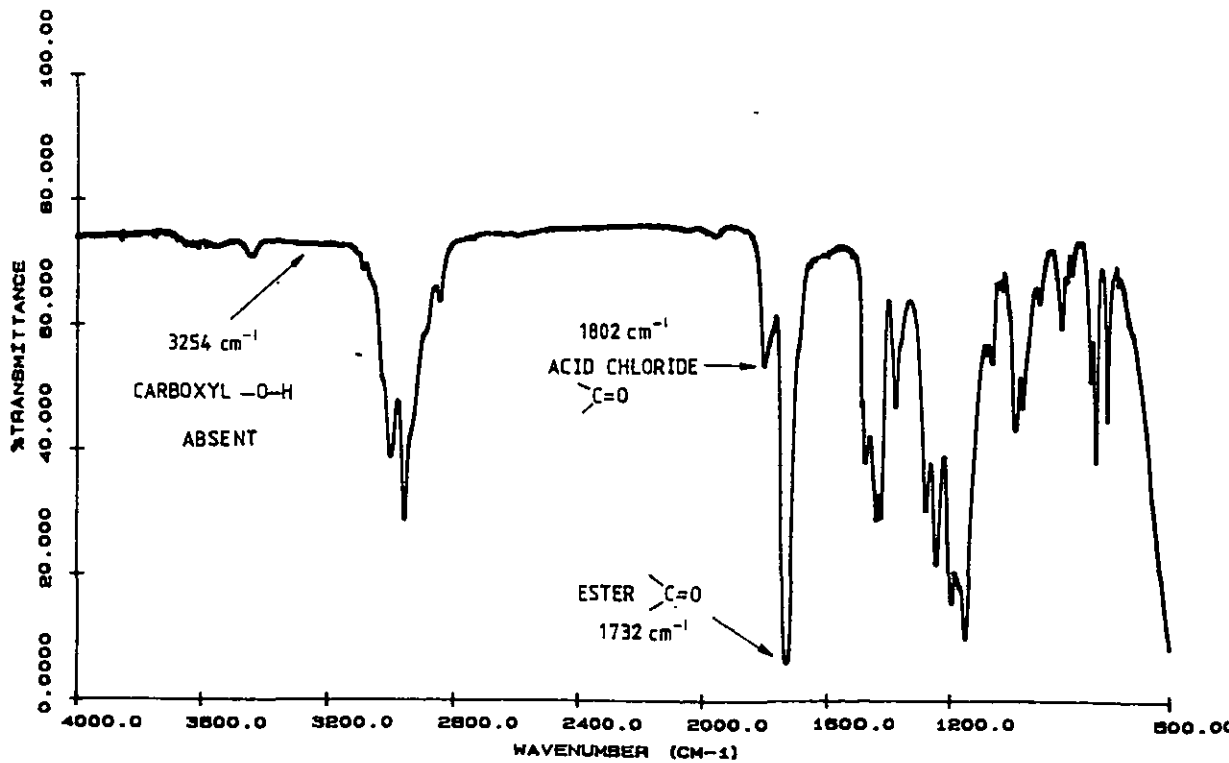
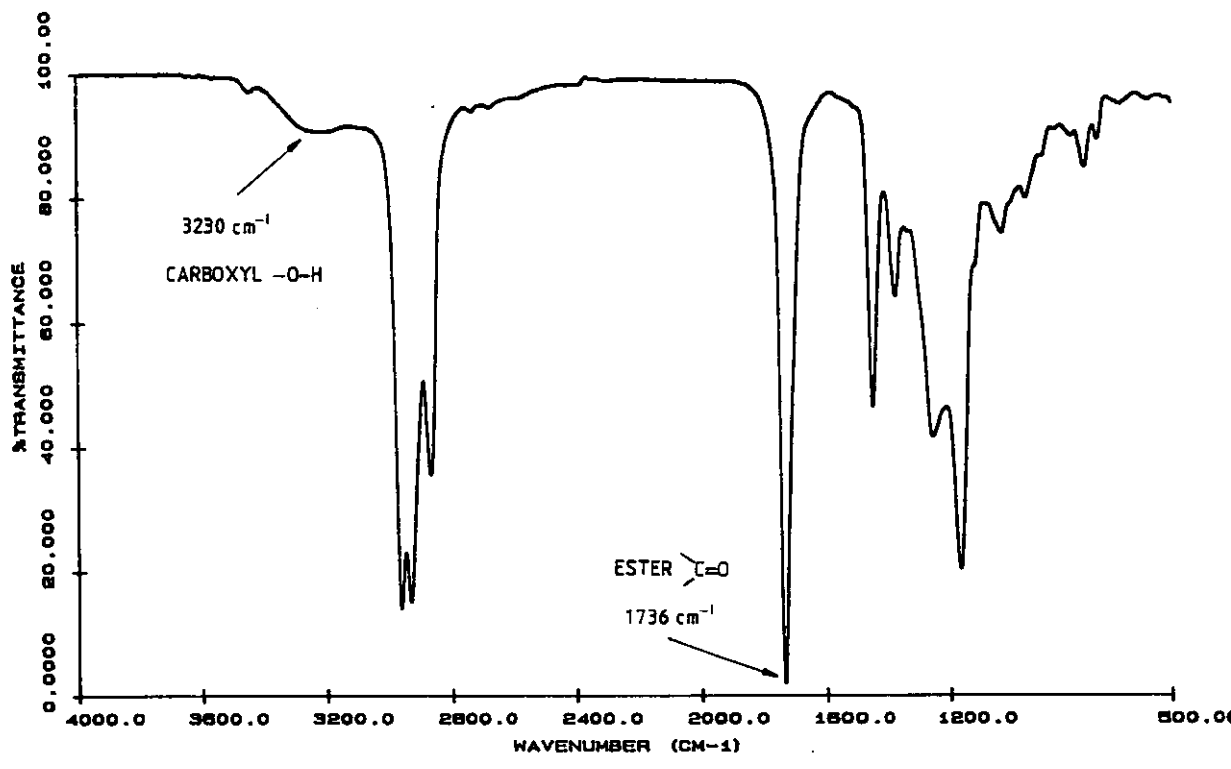
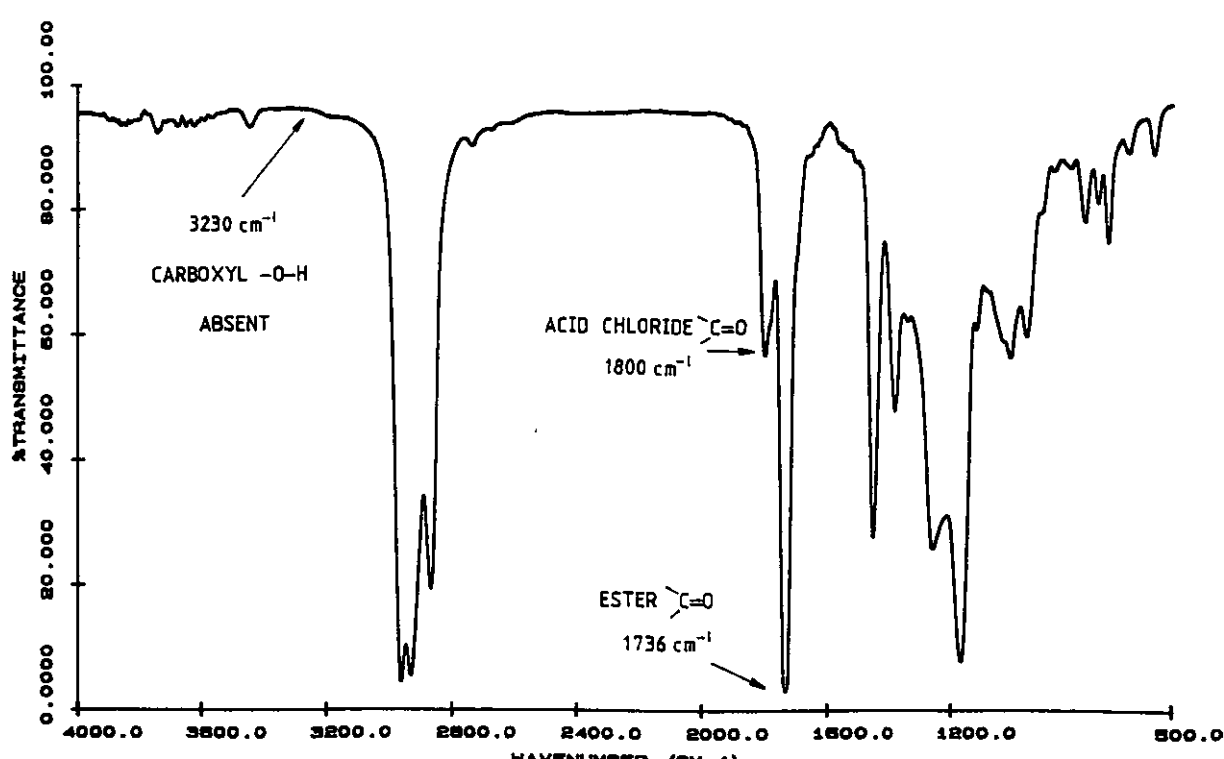


FIGURE 4.12 IR CHARACTERIZATION OF THE CONVERSION OF CARBOXYL END-GROUP TO ACYL CHLORIDE END-GROUP IN PEHA PREPOLYMERS

(a) IR SPECTRUM OF PEHA-51C



(b) IR SPECTRUM OF PEHA-51AC



disappears after reaction and it is accompanied by the appearance of absorption at $\sigma = 1802 \text{ cm}^{-1}$ which is due to the carbonyl stretch of the product acyl chloride.

4.1.2.2 Poly(2-ethyl hexyl acrylate) polymers

As an example, the IR spectrum of carboxyl-terminated prepolymer PEHA-51C is illustrated in figure 4.12(a) and the corresponding spectrum of the product after reaction with oxaly chloride, PEHA-51 AC, is illustrated in figure 4.12(b). The strongest absorption in these cases occurs at $\sigma = 1736 \text{ cm}^{-1}$ due to the PEHA acrylate ester carbonyl stretch and both figures are qualitatively very similar apart from regions of the spectrum where absorption occurs due to the end-groups. After reaction with oxaly chloride (figure 4.12(b)), the O-H stretch centred at $\sigma = 3230 \text{ cm}^{-1}$ due to the original carboxyl group disappears and it is accompanied by the appearance of absorption at 1800 cm^{-1} due to the carbonyl stretch of the resulting acyl chloride.

Therefore, for both PMMA and PEHA prepolymers, IR shows qualitatively that the carboxyl end-groups are converted to acyl chloride. The residual absorption at $\sigma = 3254 \text{ cm}^{-1}$ in figure 4.11(b) and at $\sigma = 3230 \text{ cm}^{-1}$ in figure 4.12(b) due to any remaining carboxyl groups is negligible. This suggests that complete reaction has occurred in both cases. The PMMA and PEHA prepolymers terminated with acyl chloride were characterized immediately after their preparation and they were subsequently subjected to further reaction immediately as a result of their sensitivity to moisture.

4.1.3 THE CONVERSION OF ACYL CHLORIDE END-GROUP TO METHACRYLATE

4.1.3.1 Poly(methyl methacrylate) macromonomers

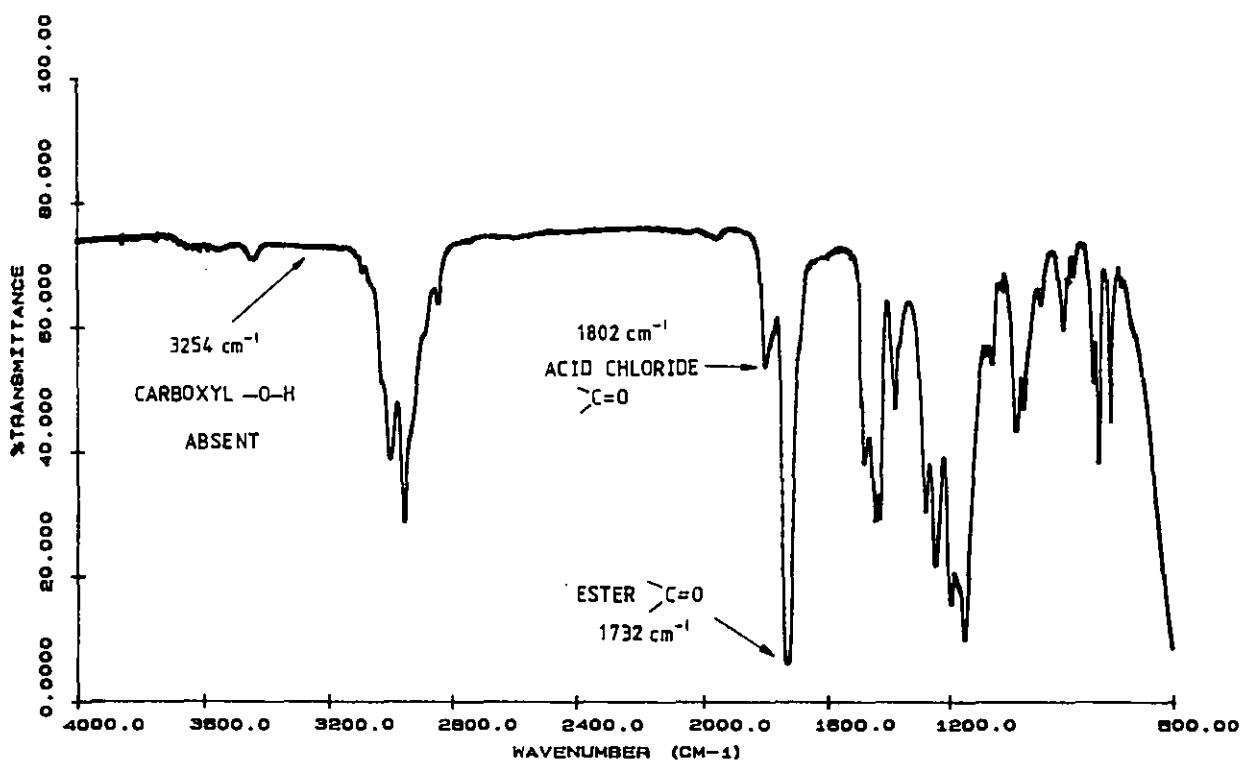
The conversion of acyl chloride end-group to methacrylate end-group was also monitored by IR spectroscopy. For example, the IR

spectrum of acyl chloride terminated PMMA-16AC is shown in figure 4.13(a) and the corresponding spectrum of the product PMMA-16M after reaction with HEMA is illustrated in figure 4.13(b). Both figures are qualitatively similar apart from two regions of the spectrum as a result of the different end-groups involved. In figure 4.13(a), there is absorption at $\sigma = 1802 \text{ cm}^{-1}$ due to the carbonyl stretch of the acyl chloride end-group. However, after reaction with HEMA, this absorption disappears (figure 4.13(b)) and a weak absorption appears at $\sigma = 1637 \text{ cm}^{-1}$ due to the C=C stretch of the resulting terminal unsaturation. There is no residual absorption at 1802 cm^{-1} which suggests that the conversion of acyl chloride to methacrylate is quantitative.

More detailed information on the PMMA macromonomers was obtained from ^1H NMR spectroscopy. For example, figure 4.14 illustrates the ^1H NMR spectrum of unpurified macromonomer PMMA-16M. The assignments of the chemical shifts for the various protons are given in table 4.13. The spectrum shows the characteristics of both methacrylate-terminated PMMA (structure XI) and unreacted HEMA (structure XII). This is not surprising since the HEMA was used in excess. The labelling of protons in these structures corresponds to those in table 4.13. The chemical shifts of the PMMA protons in the CRU labelled a, b, and c are identical to those for the carboxyl-terminated prepolymer PMMA-16C given in table 4.3 (section 4.1.1.1). The spectrum also indicates the presence of the TGA residue d which was also present in the prepolymer. The remaining protons in structure XI, e, f, g and h are due to the adduct formed after reaction of HEMA with the acyl chloride-terminated polymer. Consider the structure of the HEMA which remains unreacted (XII) and the structure for the terminal methacrylate produced by the reaction of HEMA (XI). The olefinic protons t and h resonate at the same point in the spectrum irrespective of whether the hydroxyl group has reacted or not, since their environments are identical. The same situation applies to the α -methyl groups g and s. However, differences can be seen between the reacted and unreacted HEMA due to the

FIGURE 4.13 IR CHARACTERIZATION OF THE CONVERSION OF ACYL CHLORIDE END-GROUP TO METHACRYLATE IN PMMA MACROMONOMER SYNTHESIS

(a) IR SPECTRUM OF PMMA-16AC



(b) IR SPECTRUM OF PMMA-16M

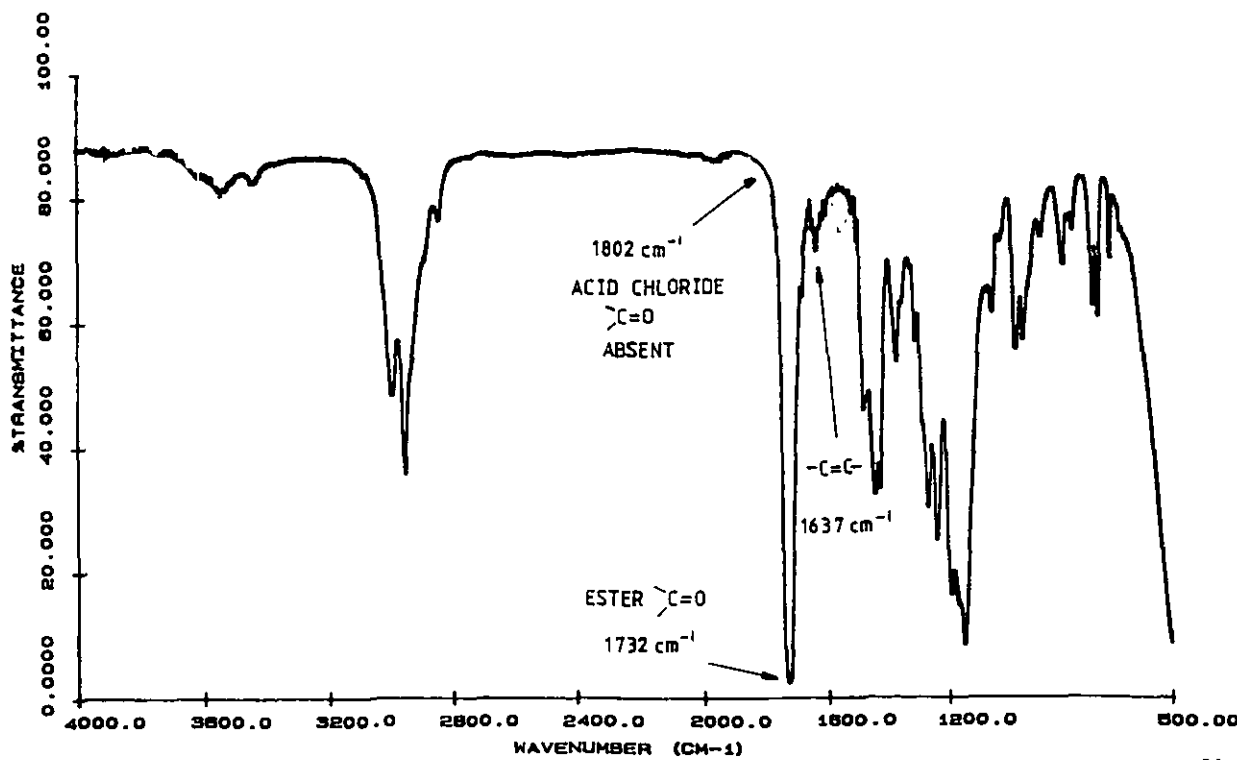


FIGURE 4.14

THE ^1H NMR SPECTRUM OF METHACRYLATE-TERMINATED
MACROMONOMER PMMA-16M

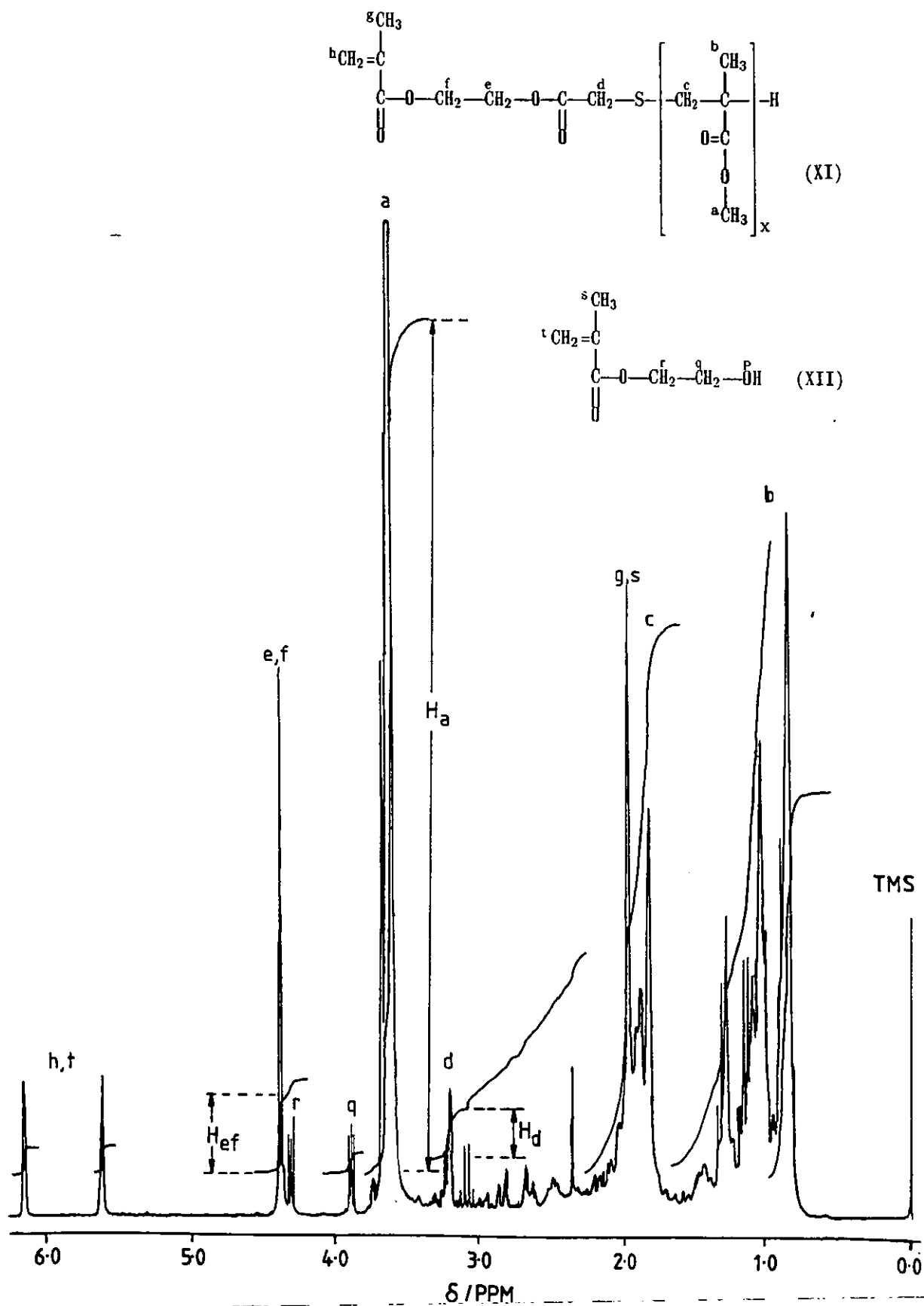
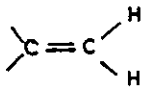
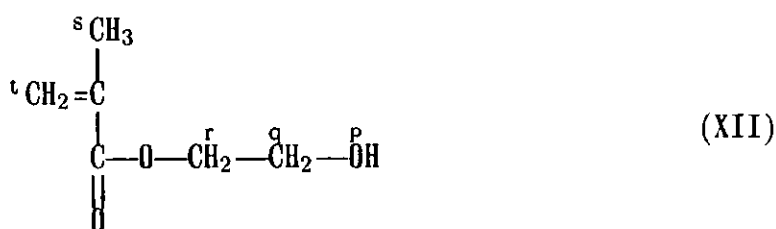
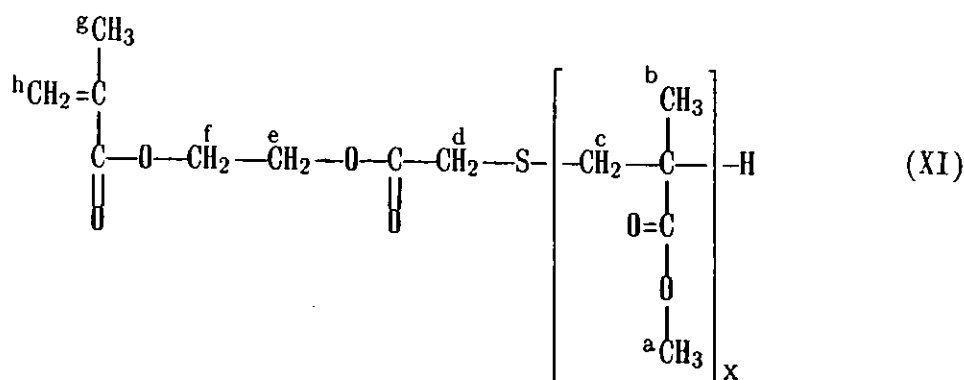


TABLE 4.13 THE ASSIGNMENT OF CHEMICAL SHIFTS IN THE ¹H NMR SPECTRUM OF MACROMONOMER PMMA-16M

CHEMICAL SHIFT δ/PPM	ASSIGNMENT	LABEL IN STRUCTURES XI OR XII
0.82-1.26	PMMA α-methyl -CH ₃	b
1.81-2.0	PMMA -CH ₂ -	c
1.95	Terminal methacrylate α-methyl -CH ₃	g a
3.20	Thioglycollic acid residue -S- <u>CH₂</u> -COO	d
3.60	PMMA ester methyl -COO- <u>CH₃</u>	a
3.88	Unreacted HEMA -COO-CH ₂ - <u>CH₂</u> -OH	q
4.30	Unreacted HEMA -COO- <u>CH₂</u> -CH ₂ -OH	r
4.38	Terminal methacrylate -COO- <u>CH₂</u> - <u>CH₂</u> -COO	e f
5.62 } 6.15 }	Methacrylate olefin protons 	h t



HEMA

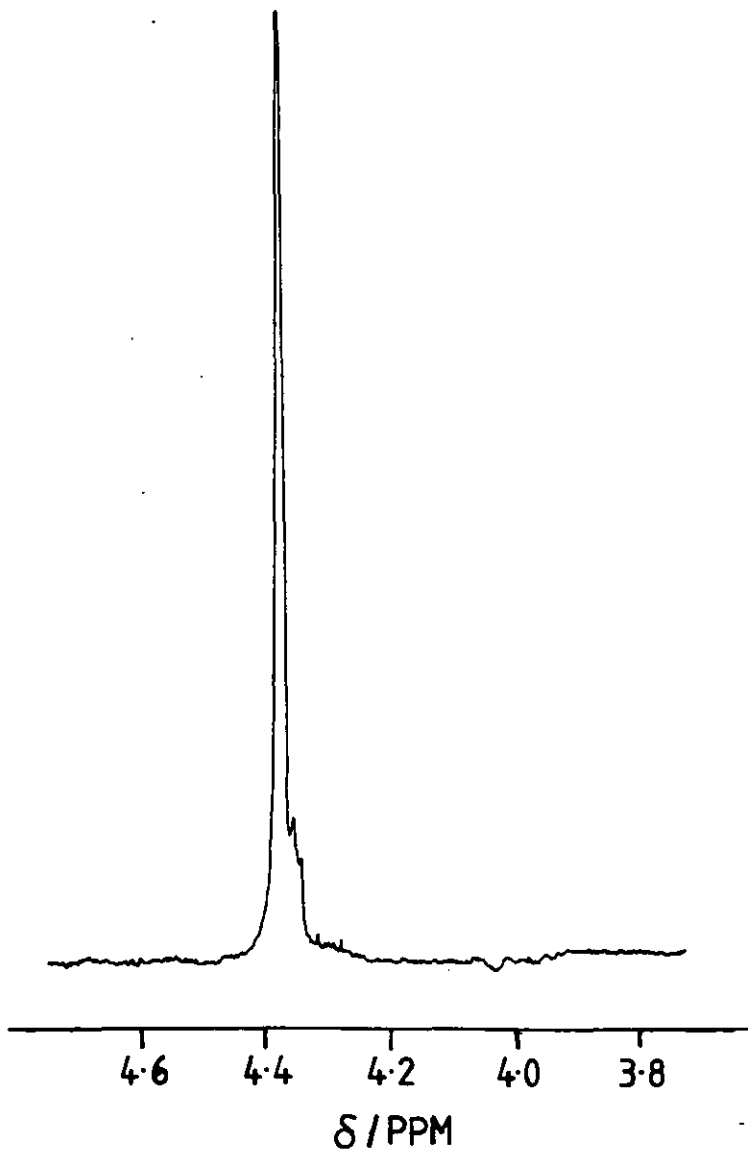
ethyl ester group. In the unreacted HEMA (XII), one $-\text{CH}_2-$ group (r) is flanked by an ester function whereas the other $-\text{CH}_2-$ group (q) is flanked by a hydroxyl group. This causes these methylene protons to resonate in different parts of the spectrum. However, after the HEMA reacts to form the terminal methacrylate function on the PMMA chain, the hydroxyl group is converted to an ester so that each $-\text{CH}_2-$ group (XI, e and f) is now flanked by an ester group. Therefore, both $-\text{CH}_2-$ groups resonate at the same point in the spectrum. This occurs at a lower field strength ($\delta = 4.38$ ppm) than r in unreacted HEMA ($\delta = 4.30$ ppm) as a direct result of the influence of two ester functions rather than one. The discrimination shown by ^1H NMR between the reacted HEMA, forming the macromonomer end-group, and the unreacted HEMA was used for monitoring the purification of macromonomers. This is illustrated in figures 4.15(a) and (b), which show expanded regions of the spectra for unpurified and purified macromonomers respectively.

FIGURE 4.15 THE EXPANDED ^1H NMR SPECTRA OF METHACRYLATE-TERMINATED PMMA MACROMONOMERS

(a) UNPURIFIED MACROMONOMER PMMA-16M



(b) PURIFIED MACROMONOMER PMMA-16MP



After purification, by dissolving in acetone followed by isolation in water (twice), virtually all of the unreacted HEMA is removed, since the resonances at $\delta = 3.88$ and 4.30ppm disappear. Apart from this region, the spectra for purified macromonomers were qualitatively identical to figure 4.14. By the comparison of the integration H_a of the PMMA methyl ester group (a) to the integration $H_{e,f}$ of the ethyl ester group (e,f) associated with the macromonomer methacrylate end-group, the ratio of PMMA repeating units to polymerizable end-groups was obtained (x in structure XI).

Therefore,

$$x = \frac{\text{number of PMMA repeating units}}{\text{number of end-groups}} = \frac{H_a/3}{H_{e,f}/4} \quad (4.7)$$

This then allowed the macromonomer molar mass to be calculated. The ethyl ester protons e and f were used for this determination rather than the olefin protons because

(i) the peaks were larger as a result of the response to a larger number of protons and their integration is more accurate.

(ii) the peak size was independent of sample purity.

The macromonomer functionality, ie. the average number of polymerizable methacrylate groups per molecule was calculated in two ways:

(a) The macromonomer molar mass calculated by ^1H NMR was compared to the corresponding carboxyl-terminated prepolymer molar mass determined by end-group analysis but allowing for the adduct which appears after the reaction of HEMA. If \bar{M}_n^* values are the corrected $\bar{M}_n(\text{EGA})$ values, then

$$f_1 = \frac{\bar{M}_n^*}{\bar{M}_n(1\text{H NMR})} \quad (4.8)$$

(b) The macromonomer functionality was obtained directly from the ^1H NMR spectra of macromonomers by comparing the integration H_{ef} of the ethyl ester protons (e and f) associated with the methacrylate end-group, with the integration H_d of the TGA residue, which was also originally present in the prepolymer. Therefore

$$f_2 = \frac{\text{no. of methacrylate end-groups}}{\text{no. of prepolymer end-groups}} = \frac{H_{ef}/4}{H_d/2} \quad (4.9)$$

Table 4.14 shows the molar masses and functionalities calculated for various PMMA macromonomers. Molar masses of macromonomers PMMA-15MP and PMMA-16MP were also calculated by GPC and these results are shown in table 4.15.

4.1.3.2 Poly(2-ethyl hexyl acrylate) macromonomers

The conversion of acyl chloride-terminated PEHA to methacrylate-terminated PEHA was also shown monitored by IR spectroscopy. For example, the IR spectrum of PEHA-51AC is shown in figure 4.16(a) and the spectrum of the product formed after reaction with HEMA is illustrated in figure 4.16(b). The figures clearly indicate the conversion of the acyl chloride to the methacrylate since the absorption at $\sigma = 1800\text{cm}^{-1}$, due to the carbonyl stretch of the acyl chloride, disappears and it is accompanied by the appearance of a weak absorption at $\sigma = 1638\text{cm}^{-1}$ as a result of the product terminal unsaturation. As for PMMA samples, there is no significant residual absorption at $\sigma = 1800\text{cm}^{-1}$, suggesting that the conversion to the methacrylate end-group is quantitative.

An example of the ^1H NMR spectrum of PEHA macromonomers is illustrated in figure 4.17. The spectrum indicates the characteristics of both the methacrylate-terminated macromonomer (structure XIII) and the unreacted HEMA (structure XII)

The chemical shifts taken from figure 4.17 which arise due to the

TABLE 4.14 PMMA MACROMONOMER MOLAR MASSES AND FUNCTIONALITIES
CALCULATED FROM ¹H NMR

SAMPLE	\bar{M}_n (¹ H NMR)/10 ³ g.mol ⁻¹	$\bar{M}_n^{\#}$ /10 ³ g.mol ⁻¹	f1	f2
PMMA-15MP	3.20	2.94	0.92	0.90
PMMA-16MP	1.60	1.42	0.89	0.93
PMMA-60/5MP	3.60	3.08	0.86	0.88
PMMA-60/6MP	1.90	1.71	0.90	0.93

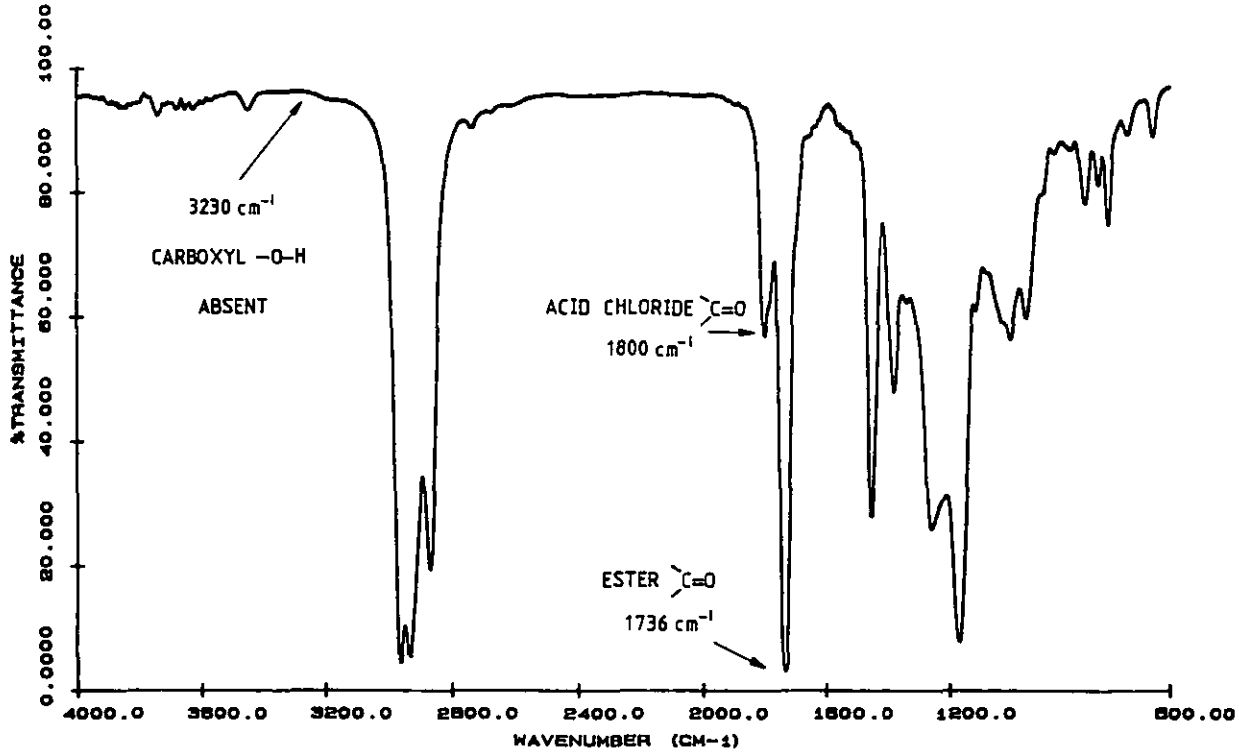
TABLE 4.15 GPC CHARACTERIZATION OF MACROMONOMERS PMMA-15MP
AND PMMA-16MP

SAMPLE	\bar{M}_{peak} /10 ³	\bar{M}_n /10 ³	\bar{M}_w /10 ³	\bar{M}_p /10 ³	\bar{M}_w/\bar{M}_n
	←—————units g.mol ⁻¹ —————→				
PMMA-15MP	3.67	2.70	3.97	3.27	1.47
PMMA-16MP	1.82	1.42	2.04	1.70	1.44

NB Polymers characterized using column with 500Å pore size.

FIGURE 4.16 IR CHARACTERIZATION OF THE CONVERSION OF ACYL CHLORIDE END-GROUP TO METHACRYLATE IN PEHA MACROMONOMER SYNTHESIS

(a) IR SPECTRUM OF PEHA-51AC



(b) IR SPECTRUM OF PEHA-51M

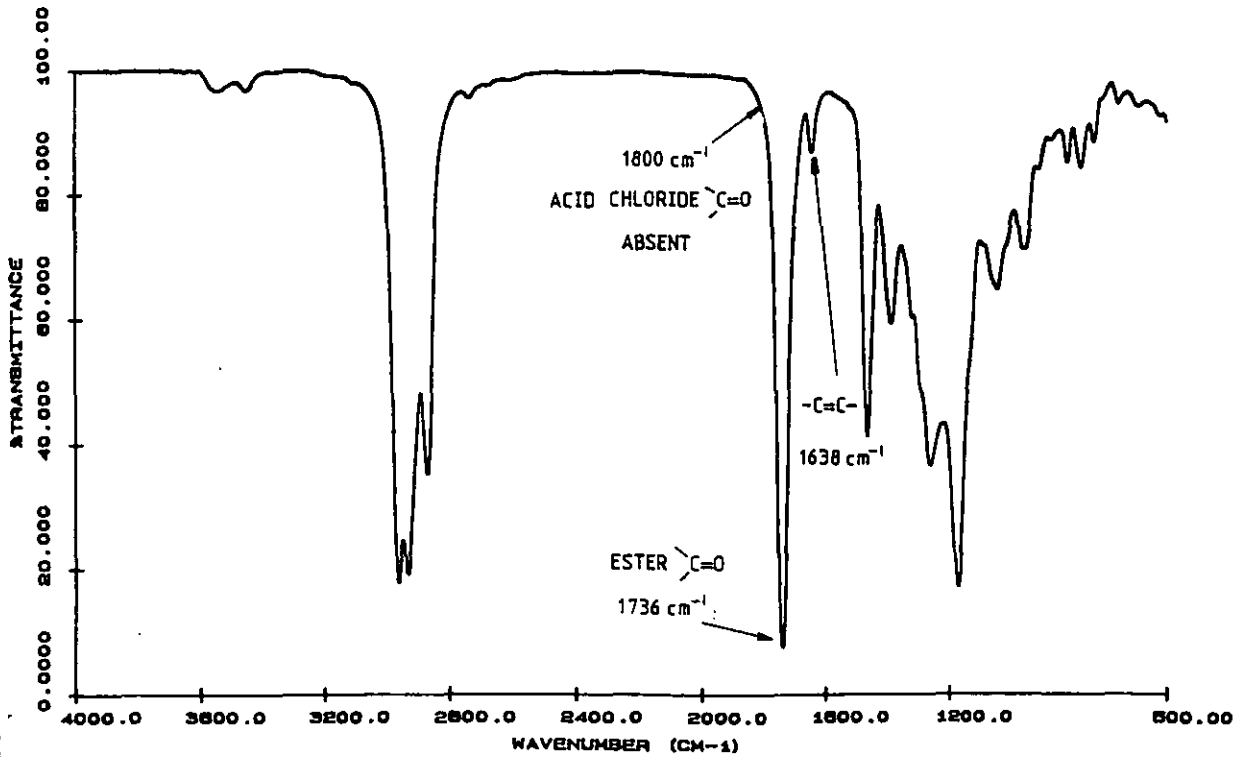


FIGURE 4.17 THE ^1H NMR SPECTRUM OF METHACRYLATE-TERMINATED
MACROMONOMER PEHA-51M

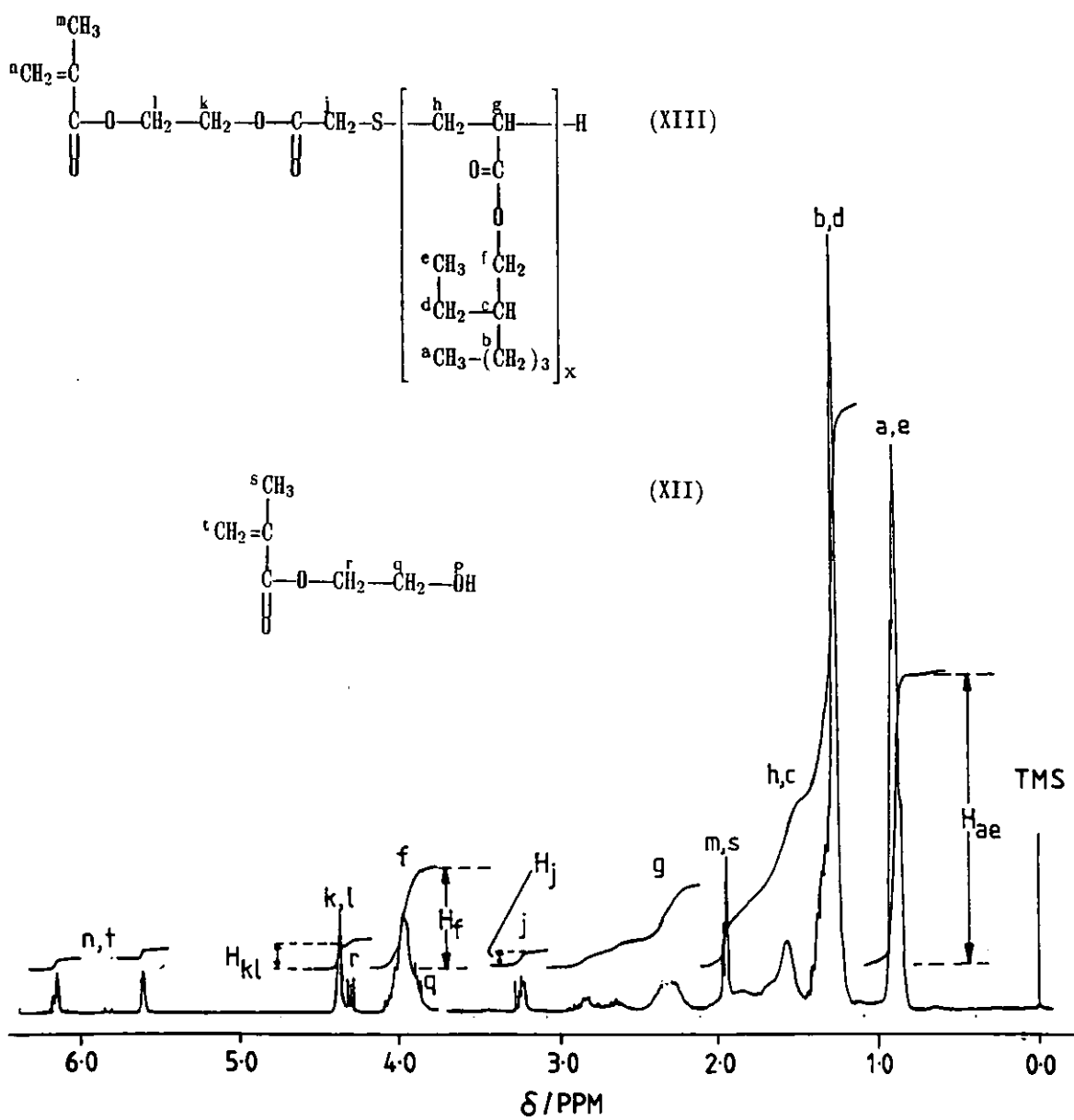
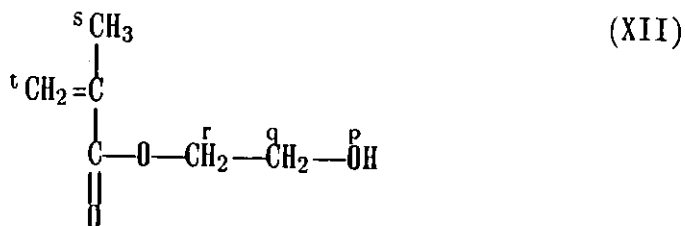
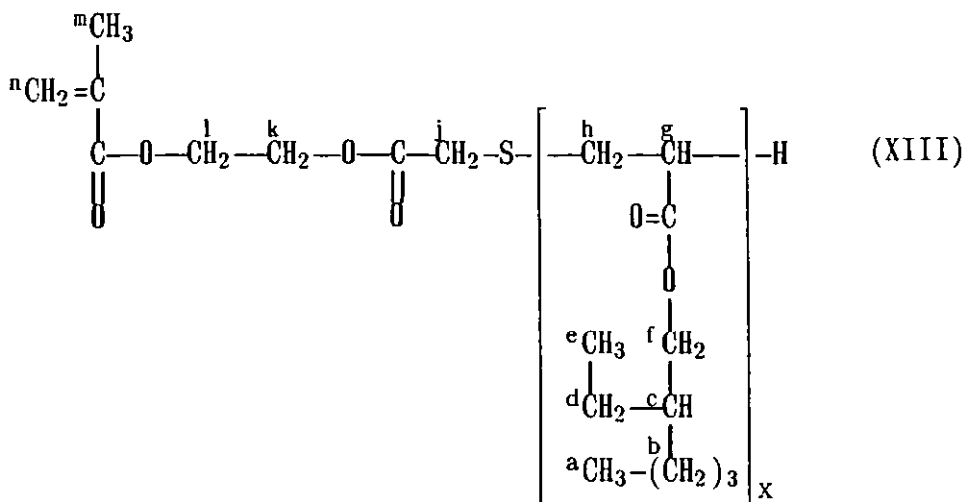


TABLE 4.16

THE ASSIGNMENT OF CHEMICAL SHIFTS IN THE ¹H NMR SPECTRUM OF MACROMONOMER PEHA-51M

CHEMICAL SHIFT δ/PPM	ASSIGNMENT	LABEL IN STRUCTURES XII or XIII
0.90	-CH ₃ PEHA	a e
1.29	-CH ₂ - PEHA	b d
1.5-2.0	$\left\{ \begin{array}{l} \text{-CH}_2\text{-CH-COO-} \end{array} \right\} \text{PEHA}$ $\left\{ \begin{array}{l} \text{-CH-} \end{array} \right\}$	h c
1.95	Terminal methacrylate or-methyl -CH ₃	m e
2.33	-CH ₂ -CH-COO PEHA	g
3.25	Thioglycollic acid residue -S-CH ₂ -COO	j
3.97	-COO-CH ₂ - PEHA	f
3.88	Unreacted HEMA -COO-CH ₂ -CH ₂ -OH	q
4.30	Unreacted HEMA -COO-CH ₂ -CH ₂ -OH	r
4.38	Terminal methacrylate -COO-CH ₂ -CH ₂ -COO-	k l
5.62 } 6.15 }	terminal methacrylate olefin protons CH ₂ = C	n t



HEMA

different environments of the protons labelled in structures XII and XIII are given in table 4.16. The chemical shifts of the PEHA protons in the CRU are identical to those for the carboxyl-terminated prepolymer PEHA-51C given in table 4.9 (section 4.1.1.2). The spectrum also indicates the presence of the TGA residue which was also present in the prepolymer. The remaining protons in structure XIII, k, l, m and n are due to the adduct formed after reaction of HEMA with the acyl chloride-terminated prepolymer. This adduct is precisely the same as that for the PMMA macromonomers in section 4.1.3.1 and the chemical shifts for k, l, m and n are identical to those for e, f, g and h respectively in structure XI. Therefore, the same differences can be seen between the reacted and the unreacted HEMA due to the ethyl ester group and the observations noted in section 4.1.3.1 apply to

the PEHA macromonomers. The discrimination shown by ^1H NMR between the reacted HEMA, forming the macromonomer end-group, and the unreacted HEMA was also used for monitoring the purification of PEHA macromonomers. This is illustrated by figures 4.18(a) and (b) which show expanded regions of the spectra for unpurified macromonomers, respectively. The removal of significant quantities of unreacted HEMA by purification is confirmed by the reduction in size of the resonances at $\delta = 3.88$ and 4.30ppm in comparison to the resonance at $\delta = 4.38\text{ppm}$. Apart from this region of the spectrum, the spectra for purified macromonomers were qualitatively identical to figure 4.17. The ratio of PEHA repeating units to polymerizable end-groups (x in structure XIII) was obtained by comparing the integration H_f of the PEHA- CH_2 - group f to the integration H_{k1} of the ethyl ester $-\text{CH}_2$ - groups associated with the end-group.

Therefore,

$$x = \frac{\text{number of PEHA repeating units}}{\text{number of end-groups}} = \frac{H_f/2}{H_{k1}/4} = \frac{H_{ae}/6}{H_{k1}/4} \quad (4.10)$$

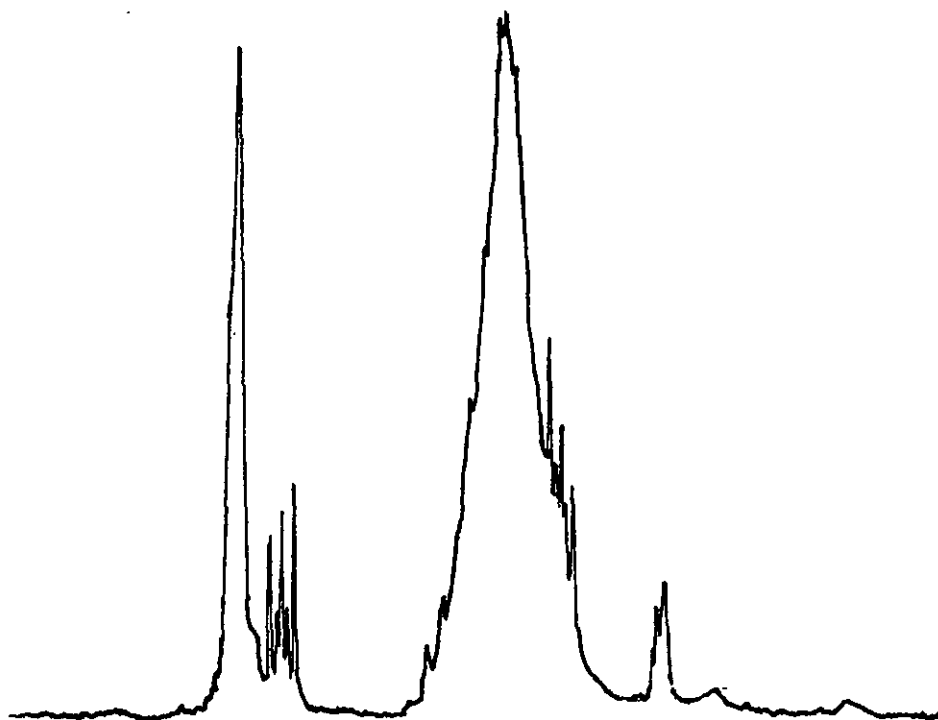
This then allowed the macromonomer molar mass to be calculated. Table 4.17 gives the molar masses and functionalities calculated for various PEHA macromonomers. The values of \bar{M}_n^* , f_1 and f_2 were calculated in a similar manner to the PMMA macromonomers given in the previous section. The GPC characterization of the PEHA macromonomers listed in table 4.17 is given in table 4.18.

4.1.3.3 Comparison of methacrylate-terminated macromonomers

The molar masses obtained from GPC for the macromonomers in tables 4.15 and 4.18 were very similar to those for the corresponding carboxyl-terminated prepolymers in tables 4.4 and 4.8. Therefore, the molar masses of macromonomers are determined

FIGURE 4.18 THE EXPANDED ^1H NMR SPECTRA OF METHACRYLATE-
TERMINATED PEHA MACROMONOMERS

(a) UNPURIFIED MACROMONOMER PEHA-51M



(b) PURIFIED MACROMONOMER PEHA-51MP

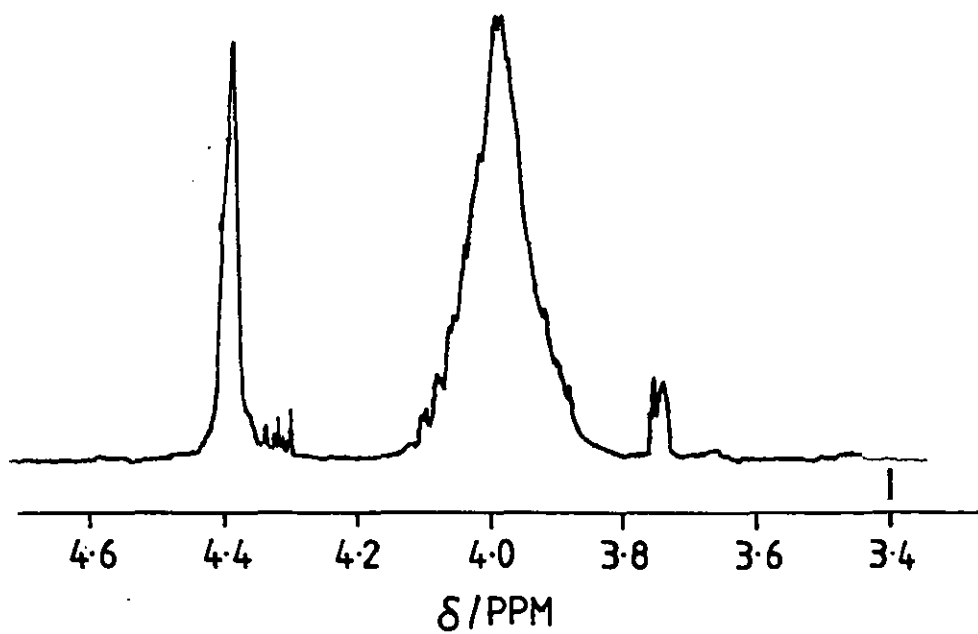


TABLE 4.17 PEHA MACROMONOMER MOLAR MASSES AND FUNCTIONALITIES
CALCULATED FROM ¹H NMR

SAMPLE	$\bar{M}_n(1H\ NMR)/10^3$ g.mol ⁻¹	$\bar{M}_n^*/10^3$ g.mol ⁻¹	f ₁	f ₂
PEHA-40MP	1.77	1.62	0.92	0.94
PEHA-45MP	3.51	3.29	0.94	1.03
PEHA-50MP	3.51	3.03	0.86	0.95
PEHA-51MP	1.68	1.53	0.91	1.01

TABLE 4.18 GPC CHARACTERIZATION OF PEHA MACROMONOMERS

SAMPLE	$\bar{M}_{peak}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n
-----units g.mol ⁻¹ ----->					
PEHA-40MP	1.80	1.40	1.96	1.66	1.40
PEHA-45MP	3.67	2.87	4.48	3.58	1.56
PEHA-50MP	3.80	2.90	4.40	3.55	1.53
PEHA-51MP	1.76	1.27	1.86	1.53	1.46

NB. Polymers characterized using column with 500Å pore size.

by the ratio of chain transfer agent to monomer in the synthesis of prepolymers. The subsequent reactions simply alter the nature of the end-group. The molar masses obtained by GPC are independent of whether the end-group is a carboxyl or methacrylate function. Therefore, it does not appear that the elution properties of the polymer chains are affected by the relatively high concentration of end-groups. It can be assumed that the unperturbed mean square end-to-end distance can be taken as the universal calibration parameter [173,174] and so equation 4.6 can apply to both the carboxyl-terminated prepolymers and the macromonomers prepared from them. Following the discussion centred around this equation and table 4.11 in section 4.1.1.3, it follows that the calibration curves for both PMMA and PEHA are predicted to be similar to linear PS standards. Therefore, the values quoted from GPC analysis for PMMA and PEHA polymers are likely to be close to their real values, irrespective of whether they are terminated with carboxyl or methacrylate groups.

The functionality values f_1 were obtained by comparing the molar mass calculated from ^1H NMR for the macromonomer to the molar mass obtained by EGA for the appropriate prepolymer but allowing for the adduct arising from further reaction. This method is similar to that calculated for the functionality f of carboxyl-terminated prepolymers and it is expected that the f_1 values will contain a similar error. It may be anticipated that f_2 values, which were determined using information from ^1H NMR rather than by the comparison of results from two different methods, will be more accurate than f_1 . However, it must be realized that f_2 values were obtained by comparing the small integrations of different moieties of the end-group. Therefore, it is likely that the functionalities f_1 and f_2 involve the same error, i.e. $\pm 5-10\%$. For PMMA macromonomers, f_1 varied from 0.86-0.92 and f_2 values were similar, 0.88-0.93. For PEHA macromonomers, f_1 ranged from 0.86-0.94 whereas f_2 values were marginally higher, 0.94-1.03. Considering the errors discussed above, it can be concluded that the PMMA and PEHA macromonomers are approximately monofunctional with respect to methacrylate end-groups. The

conversion of carboxyl to methacrylate end-groups is high and the 30% molar excess of HEMA is sufficient to produce a high percentage of chains bearing a terminal unsaturation. In general, higher levels of capping agents have been used to produce macromonomers from prepolymers prepared by free-radical polymerization. For example, in the conversion of various carboxyl-terminated prepolymers to macromonomers, 50% molar excess of glycidyl methacrylate [99,102,103], 50% molar excess of oxarinyl vinyl monomers [107] and 300% molar excess of chloromethylstyrene [104] have been used. The PMMA and PEHA macromonomer functionalities f_1 and f_2 obtained compare favourably with those quoted in the literature for other macromonomers, including those prepared by anionic polymerization. Examples of these are reproduced in table 4.19.

TABLE 4.19 EXAMPLES OF MACROMONOMER FUNCTIONALITIES QUOTED IN
THE LITERATURE

POLYMERIZATION MECHANISM	POLYMER	END-GROUP	FUNCTIONALITY	REFERENCE
F	poly(vinyl pyrrolidone)	styrene	≥0.95	[104]
F	polystyrene	allyl	1.0-1.2	[95]
F	polystyrene	styrene	0.8-1.3	[96]
F	poly(vinyl acetate)	styrene	0.75-1.02	[97]
A	polystyrene	methacrylate	≥0.85	[71]
			≥0.90	[72]
			0.96	[73]
			0.86	[143]
A	polysiloxane	methacrylate	0.96-1.0	[85]
A	polysiloxane	methacrylate/ styrene	0.84-1.07	[86]
A	poly(ethylene oxide)	methacrylate/ styrene	0.85-1.0	[81]
A	poly(butyl methacrylate)	styrene	1.12	[83]
A	poly(2-vinyl pyridine)	styrene	≥0.96	[142]
A	poly(methyl methacrylate)	styrene	0.86-0.92	[84]
C	poly(tetrahydrofuran)	methacrylate/ acrylate	0.8-1.0	[91]
C	poly(tetrahydrofuran)	styrene	0.9-1.1	[92,93]
C	polyisobutylene	styrene	0.9-1.1	[94]
GT	poly(methyl methacrylate)	styrene	0.83	[112]

Where F = free-radical polymerization
C = cationic polymerization

A = anionic polymerization
GT = group-transfer polymerization

4.2 THE PREPARATION OF GRAFT COPOLYMERS

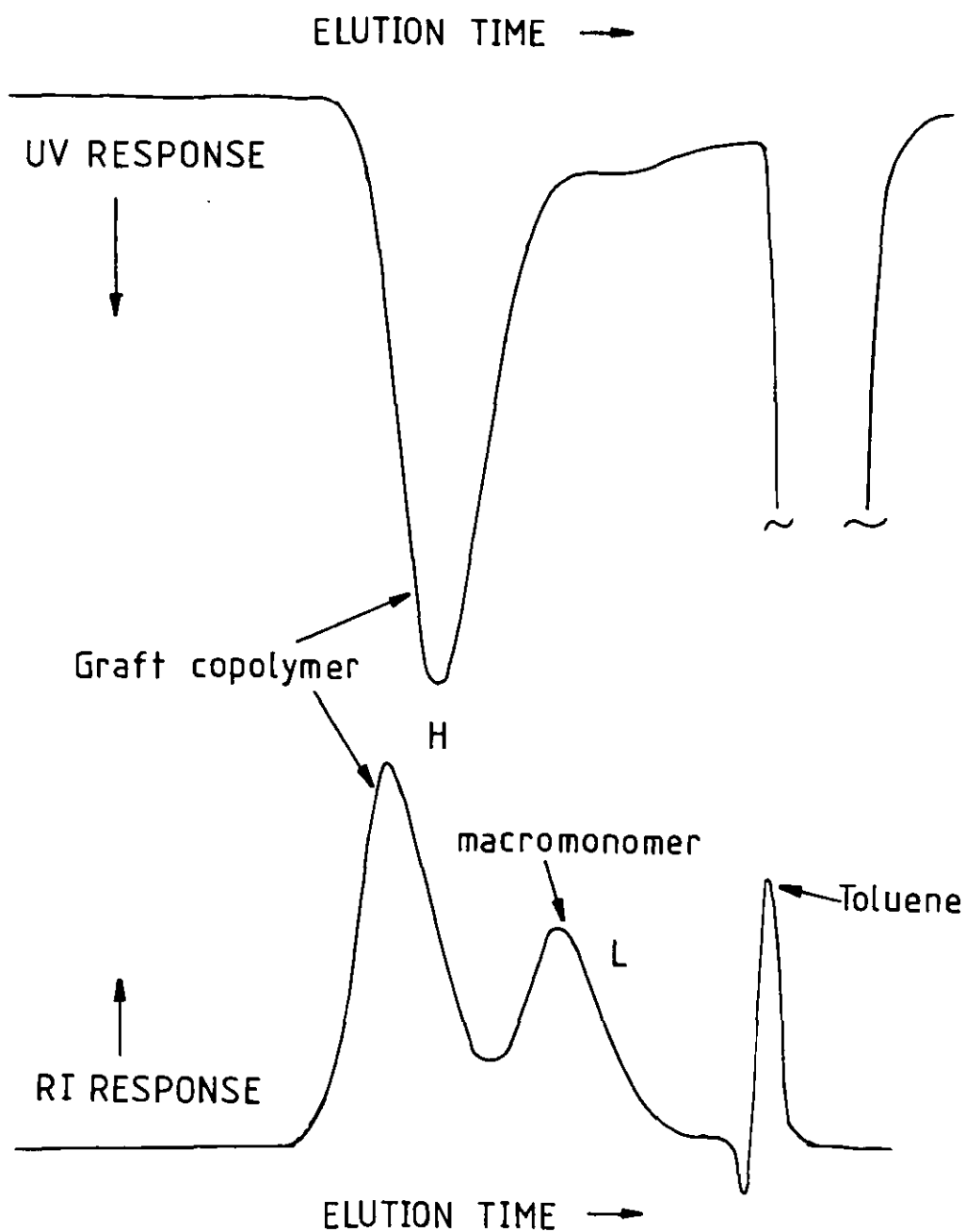
4.2.1 THE CHARACTERIZATION OF UNPURIFIED GRAFT COPOLYMERS

For all PMMA and PEHA macromonomer copolymerizations with styrene at 333 K, the resulting solutions were transparent after copolymerization times of 10 hours and 31 hours. This suggests that there was no phase separation and that the reactions were homogeneous. There was also no indication of gelation, which may have occurred if the macromonomer chains had been bifunctional.

Before purification, all PS-graft-PMMA and PS-graft-PEHA copolymers were characterized by GPC using a combination of RI and UV detectors. The dual detector GPC chromatogram of an unpurified PS-graft-PMMA copolymer SM-13^a is illustrated as a typical example in figure 4.19. The chromatogram shows the presence of two polymeric species. The peak (L) occurs at the same elution time as macromonomer; it has a low UV response at 267 nm and it is due to unreacted macromonomer. The peak (H) at higher molar mass has a relatively high UV response and corresponds to the graft copolymer product which has a significant styrene content. The UV/RI response ratio for the peak H is lower than that obtained for a polystyrene homopolymer PS-1^a. This indicates that the macromonomer has been incorporated to produce graft copolymer. The UV/RI response ratio of peak H was found to decrease for products resulting from comonomer feeds richer in macromonomer, i.e. for copolymers with a lower styrene content. The UV response of the internal standard toluene is very large in comparison to the RI response. This is a result of the unreacted styrene present which elutes at the same time as toluene. In comparison of graft copolymers which were prepared using the same concentrations of reactants but which were copolymerized for different times, it was found that the peak area A(H) of the high molar mass fraction increased while the peak area A(L) of the low molar mass fraction decreased.

NB (a) The reaction conditions for the synthesis of this polymer are illustrated in section 4.2.3.2.

FIGURE 4.19 A TYPICAL CHROMATOGRAM FROM THE GPC
CHARACTERIZATION OF AN UNPURIFIED PS-graft-PMMA
COPOLYMER USING BOTH RI AND UV DETECTORS



The macromonomer conversion was obtained from chromatograms such as that illustrated in figure 4.19 by a similar method to that used by Niwa et al [178]. The area obtained with a refractive index detector for the peak L, $A_{RI}(L)$, is given by

$$A_{RI}(L) = c(K_u(RI) \cdot W_u) \quad (4.11)$$

where $K_u(RI)$ is the instrument constant for the refractive index detector for the macromonomer, W_u is the weight fraction of unreacted macromonomer in the resulting polymer and c is the concentration of sample. The area for the RI detector $A_{RI}(H)$ and the area for the UV detector $A_{UV}(H)$, for the peak H, are given by

$$A_{RI}(H) = c[(K_R(RI) \cdot W_R) + (K_S(RI) \cdot W_S)] \quad (4.12)$$

$$A_{UV}(H) = c[(K_R(UV) \cdot W_R) + (K_S(UV) \cdot W_S)] \quad (4.13)$$

W_R and W_S are the weight fractions of copolymerized macromonomer and styrene respectively, K_R and K_S are the instrument constants for polymacromonomer and polystyrene respectively, and (RI) and (UV) identify the detectors. The mole fraction conversion of macromonomer (X_M) is defined as

$$X_M = \frac{W_R}{(W_R + W_U)} \quad (4.14)$$

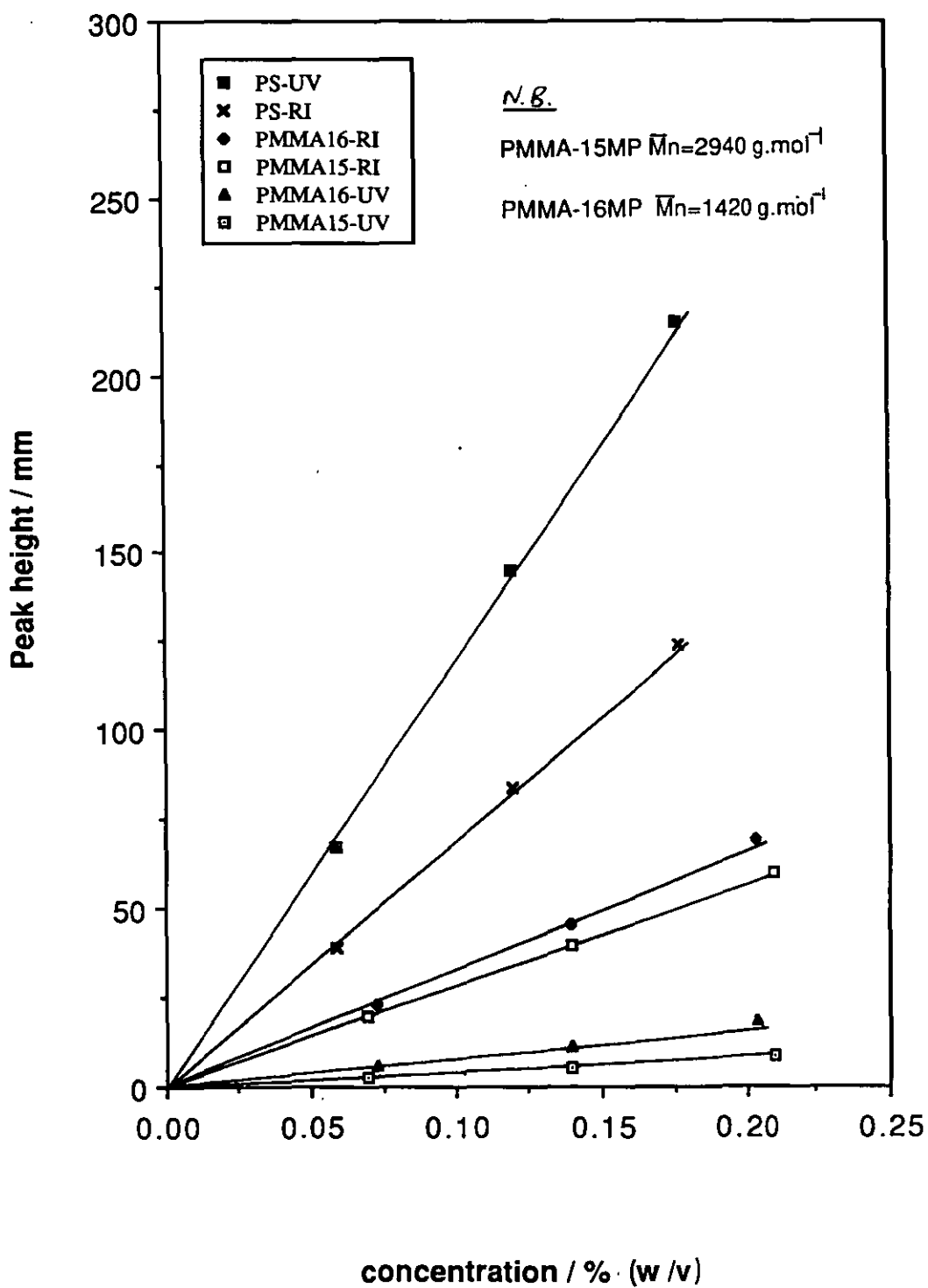
From equations 4.12, 4.13 and 4.14,

$$X_M = \frac{\left\{ \frac{A_{UV}(H)}{K_S(UV)} - \frac{A_{RI}(H)}{K_S(RI)} \right\}}{\left[\frac{A_{UV}(H)}{K_S(UV)} - \frac{A_{RI}(H)}{K_S(RI)} + \left\{ \frac{K_R(UV)}{K_S(UV)} - \frac{K_R(RI)}{K_S(RI)} \right\} \frac{A_{RI}(L)}{K_u(RI)} \right]} \quad (4.15)$$

However, as figure 4.19 illustrates for the copolymerization of styrene with macromonomer PMMA-16MP ($M_n^* = 1.42 \times 10^3 \text{g.mol}^{-1}$), the graft copolymer produced and the unreacted macromonomer are incompletely resolved despite the fact that the \bar{M}_{Peak} value for the graft copolymer peak H is approximately $35.0 \times 10^3 \text{g.mol}^{-1}$ (by a polystyrene calibration). Slightly poorer resolution was

obtained for graft copolymers prepared from macromonomers with $\bar{M}_n \sim 3.0 \times 10^3 \text{g.mol}^{-1}$ under the same reaction conditions, although the peak L was still distinguishable. The graft copolymer molar mass would have to be significantly higher than that obtained to observe baseline resolution, thereby allowing the peak areas to be calculated accurately. This is partly a result of the broad macromonomer molar mass distributions ($\bar{M}_w/\bar{M}_n \sim 1.5$) obtained from their synthesis via free-radical polymerization (see tables 4.15 and 4.18, section 4.1.3). As a result of the incomplete resolution of the two peaks H and L, peak heights rather than areas were used in equation 4.15. The response K_R of polymacromonomer was also assumed to be equal to the response K_U of the particular macromonomer used. The instrument constants were obtained by calibrating the detectors with polystyrene and macromonomer samples. The macromonomer used for this determination was identical to the macromonomer used to produce the sample being analysed. The polystyrene sample used for the calibration was identical for all cases, i.e. PS-1 shown in table 4.20, section 4.2.3.2. In order to illustrate the relative responses of the polymers involved, figure 4.20 shows the relationship between peak height and concentration for PS-1 and PMMA macromonomers, for both RI and UV detectors. The calibration constants of macromonomers, obtained from the slopes of such relationships, varied slightly depending on the molar mass. PEHA macromonomers gave similar respective RI and UV calibrations to PMMA with the same molar mass, although examples are not illustrated. Macromonomer conversions calculated according to equation 4.15 are subsequently presented in sections 4.2.3.2 and 4.2.3.3, together with copolymer composition data. As a result of the various assumptions noted above, the conversions calculated from this GPC analysis are only expected to be approximations. The likely error in this conversion data is likely to be of the order of $\pm 5\%$. There are a number of examples in the literature where the macromonomer conversion has been assessed by GPC using a combination of RI and UV detectors [18,91,95,178]. However, these have generally involved situations where either the

FIGURE 4.20 CALIBRATION OF THE RI AND UV DETECTOR RESPONSES IN GPC DUAL DETECTOR CHARACTERIZATION OF GRAFT COPOLYMERS



macromonomer or the polycomonomer do not absorb in the UV wavelength range, i.e. the UV detector is completely selective for either component. The determination of macromonomer conversion in such cases is simpler than the present one. Although figure 4.20 illustrates that the UV responses of macromonomers are low in comparison to polystyrene, they must be considered in the analysis of macromonomer conversion. A wavelength of 267 nm was chosen since the UV detector response produced the greatest selectivity at this wavelength between polystyrene and poly(meth)acrylate polymers.

In order to establish that the macromonomers copolymerized through the terminal double bond and not by transfer reactions to the PMMA or PEHA segments, styrene was polymerized in toluene solution at 333 K in the presence of either carboxyl-terminated PMMA or PEHA. The conditions used were analogous to the copolymerizations of macromonomers, except that macromonomer was replaced by carboxyl-terminated prepolymer. Products were analysed by GPC using the combination of RI and UV detectors. The appearances of chromatograms obtained from characterization of these reactions were similar to figure 4.19, in that a product (H) at high molar mass and unreacted prepolymer (L) at low molar mass were observed. However, the ratio of the UV/RI responses for the peak H in these cases were almost identical to that for a polystyrene homopolymer prepared under free-radical conditions (i.e. PS-1, table 4.20 in section 4.2.3.2). This is in contrast to the graft copolymers, where the UV/RI response of peak H was substantially lower than that for polystyrene due to the PMMA or PEHA segments present. Therefore, it can be concluded that negligible grafting occurred in these control experiments, and the incorporation of macromonomers into graft copolymers produced by their copolymerization is a result of the reaction of the terminal unsaturation and not due to transfer reactions.

4.2.2 THE PURIFICATION OF GRAFT COPOLYMERS

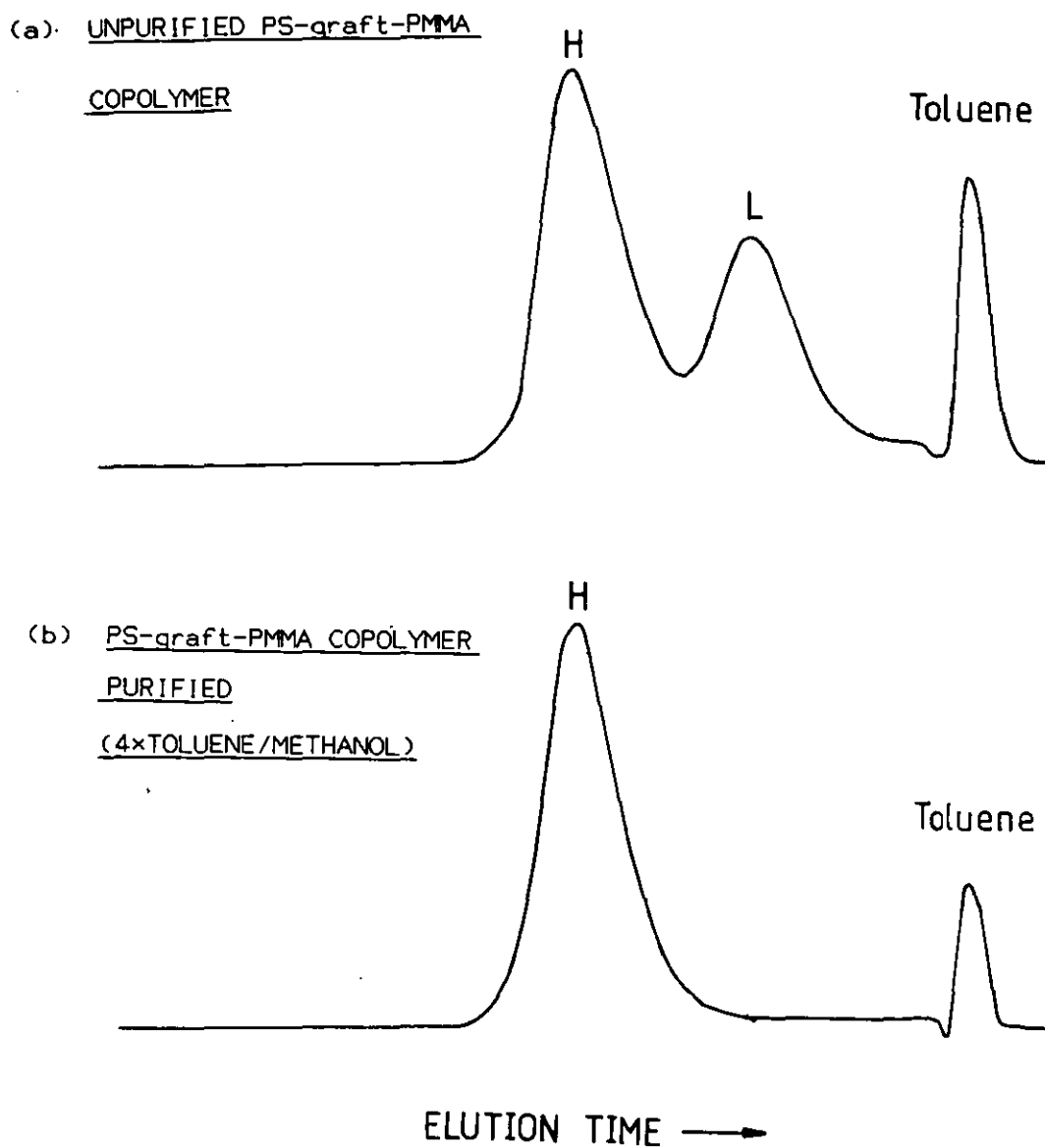
Removal of unreacted macromonomer and comonomer were necessary in order to characterize the graft copolymers produced by spectroscopic methods, since both unreacted monomers and copolymers produced contain the same functional groups. All PS-graft-PMMA and PS-graft-PEHA copolymers were purified repeatedly by dissolving in toluene and precipitating in hot methanol in order to selectively remove unreacted macromonomer and styrene. The extent of purification was monitored by GPC as a result of the discrimination shown by this technique between the graft copolymer product and the unreacted macromonomers. This is illustrated in figure 4.21. The GPC refractive index chromatogram of the impure graft copolymer (a) shows the graft copolymer (H) at high molar mass and the unreacted macromonomer (L) at low molar mass. After 4 purification steps, the GPC refractive index chromatogram of the purified graft copolymer (b) shows that the macromonomer peak L disappears. This illustrates that the purification method selectively precipitated the graft copolymer. The \bar{M}_{Peak} values of the impure and purified graft copolymers were found to be identical. This suggests that fractionation of graft copolymers during purification is not a problem. The number of purification steps required so that unreacted macromonomer (L) disappeared was found to depend upon both the extent of conversion and the weight fraction of macromonomer in the feed, i.e. the amount of unreacted macromonomer present.

4.2.3 THE CHARACTERIZATION OF PURIFIED GRAFT COPOLYMERS

4.2.3.1 Polystyrene homopolymer contamination

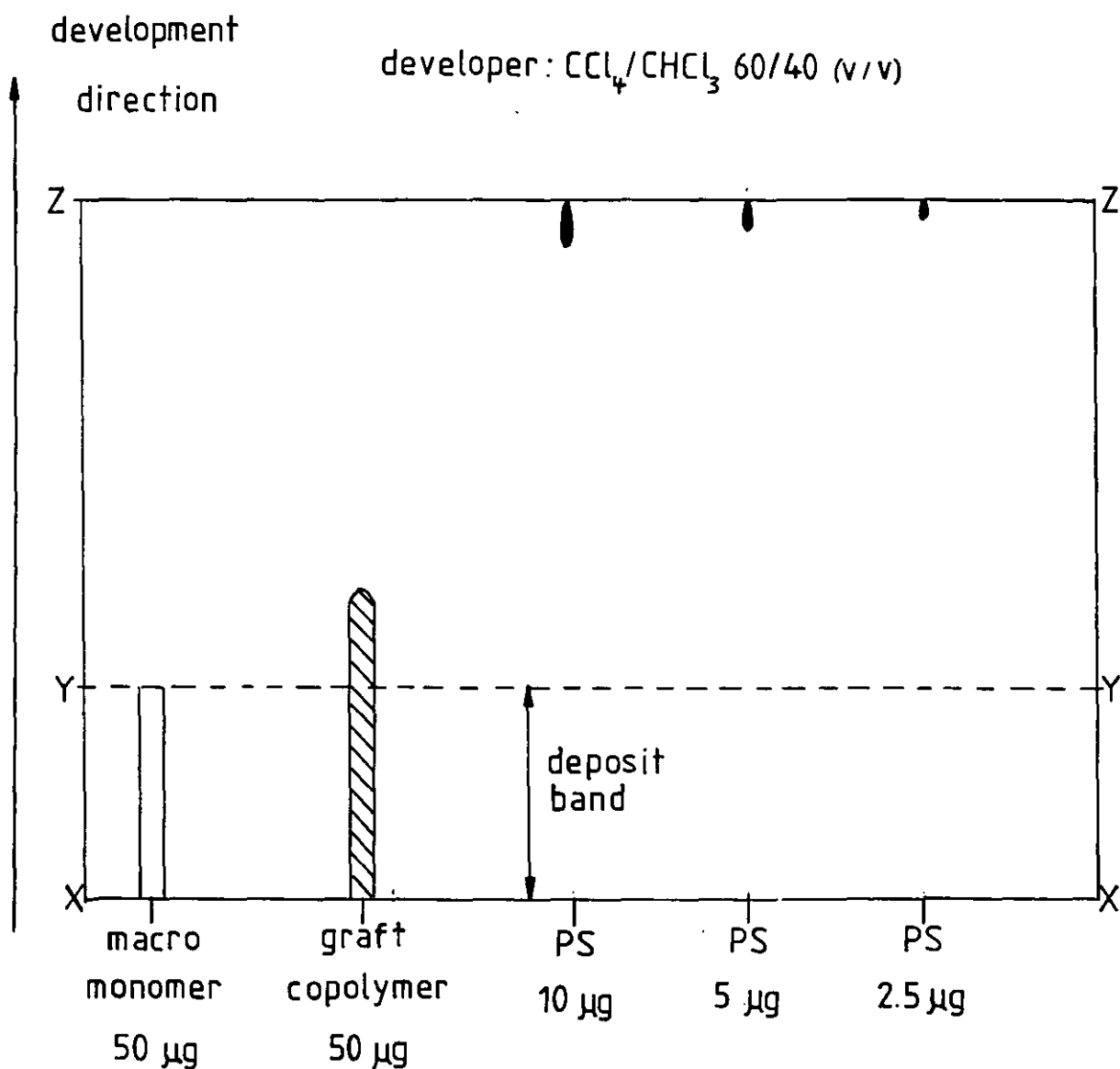
The coproduction of PS homopolymer was assessed using the TLC technique described in section 3.5.5, where it was shown that the choice of developer used to separate PS homopolymer from

FIGURE 4.21 THE USE OF GPC (RI DETECTOR RESPONSE) TO MONITOR THE PURIFICATION OF GRAFT COPOLYMERS



styrene copolymers is crucial to prevent an overestimation of the amount of homopolymer produced. A mixture of 60/40 (v/v) $\text{CCl}_4/\text{CHCl}_3$ was used as a developer since this was found to give optimum selectivity in the development of polystyrene. The representation of a typical TLC plate after the development of various samples is illustrated in figure 4.22. PMMA and PEHA macromonomers do not migrate since they are more polar than the developer used ($R_f=0$), whereas PS migrates with the solvent since it is less polar ($R_f=1$). The PS spot size increases with sample loading and an appropriate assessment of the PS homopolymer contamination in a sample was made by comparing the spot size at the solvent front to the standard PS loadings. Examples of the development of a PS-graft-PMMA or a PS-graft-PEHA copolymer are also illustrated in figure 4.22. This shows that there is no trace of material at the solvent front, i.e. there is zero homopolymer contamination. There is a slight movement of some material vertically and this is likely to be graft copolymer with a high styrene content. This is not surprising since the statistical chemical heterogeneity of graft copolymers produced from the copolymerization of macromonomers is predicted to be quite large [145,146,147]. For all PS-graft-PMMA and PS-graft-PEHA copolymers synthesized at 333 K (see tables 4.20-4.23 in sections 4.2.3.2 and 4.2.3.3), the PS homopolymer produced was found to be negligible in all cases. This compares favourably to the few reports in the literature concerning the production of backbone homopolymer in macromonomer copolymerizations (0-2.5%) [70,72,97]. The determination of backbone homopolymer contamination is an important consideration in the characterization of graft copolymers (see also section 4.2.4.2). Such contamination may affect molar masses obtained from GPC and determinations of copolymer compositions by spectroscopic methods will be affected, producing incorrect values. Removal of homopolymer can also be time-consuming and inefficient. For example, in attempting to precipitate backbone homopolymer selectively, graft copolymer can act as an emulsifier for the homopolymer, thereby preventing its precipitation [179]. It is somewhat surprising, therefore, that

FIGURE 4.22 TLC CHARACTERIZATION OF PS HOMOPOLYMERS, PS-graft-PMMA (OR PS-graft-PEHA) COPOLYMERS AND PMMA (OR PEHA) MACROMONOMERS



Z=solvent front

XY=samples before development

many reports concerning the synthesis of graft copolymers from macromonomers do not include an assessment of homopolymer contamination. It must be emphasized that no assessment was made of the formation of polymacromonomer homopolymer in the present copolymerizations, since its production was thought to be extremely unlikely. This is discussed further in section 4.2.4.2.

4.2.3.2 Polystyrene-graft-poly(methyl methacrylate) copolymers

Both IR and ^1H NMR spectroscopy showed the characteristic peaks of PS and PMMA segments. For example, the IR spectrum of PS-graft-PMMA copolymer SM-5 is shown in figure 4.23. The absorbance at $\sigma = 1729\text{cm}^{-1}$ is assigned to the carbonyl stretch of PMMA segments and absorbances at $\sigma = 3030\text{cm}^{-1}$ (aromatic C-H) and $\sigma = 1603, 1492$ and 1452cm^{-1} (aromatic C-C) are characteristic of PS segments. From such spectra, the copolymer composition was determined by calibration of the ester carbonyl absorption with PMMA macromonomers, as described in section 3.5.2.2. The ^1H NMR spectrum of graft copolymer SM-1 is illustrated in figure 4.24. The peaks at $\delta = 6.55$ and 7.1ppm are assigned to the aromatic protons of the PS segments, whereas the peak at $\delta = 3.6\text{ppm}$ is due to the ester methyl group in the PMMA segments. The copolymer composition was obtained from ^1H NMR for samples with intermediate macromonomer conversion by comparing the integration of PS protons to the integration of PMMA protons, ie

$$\frac{\text{No. of moles of PS repeating units}}{\text{No. of moles of PMMA repeating units}} = \frac{H_{\text{PS}}/5}{H_{\text{PMMA}}/3} \quad (4.16)$$

where H_{PS} and H_{PMMA} are the integrations of PS and PMMA segments as illustrated in figure 4.24. This enabled chemical compositions to be calculated by mass, by taking account of the molar masses of the CRU's.

Tables 4.20 and 4.21 show the information obtained from the

FIGURE 4.23 THE IR SPECTRUM OF PS-graft-PMMA COPOLYMER SM-5

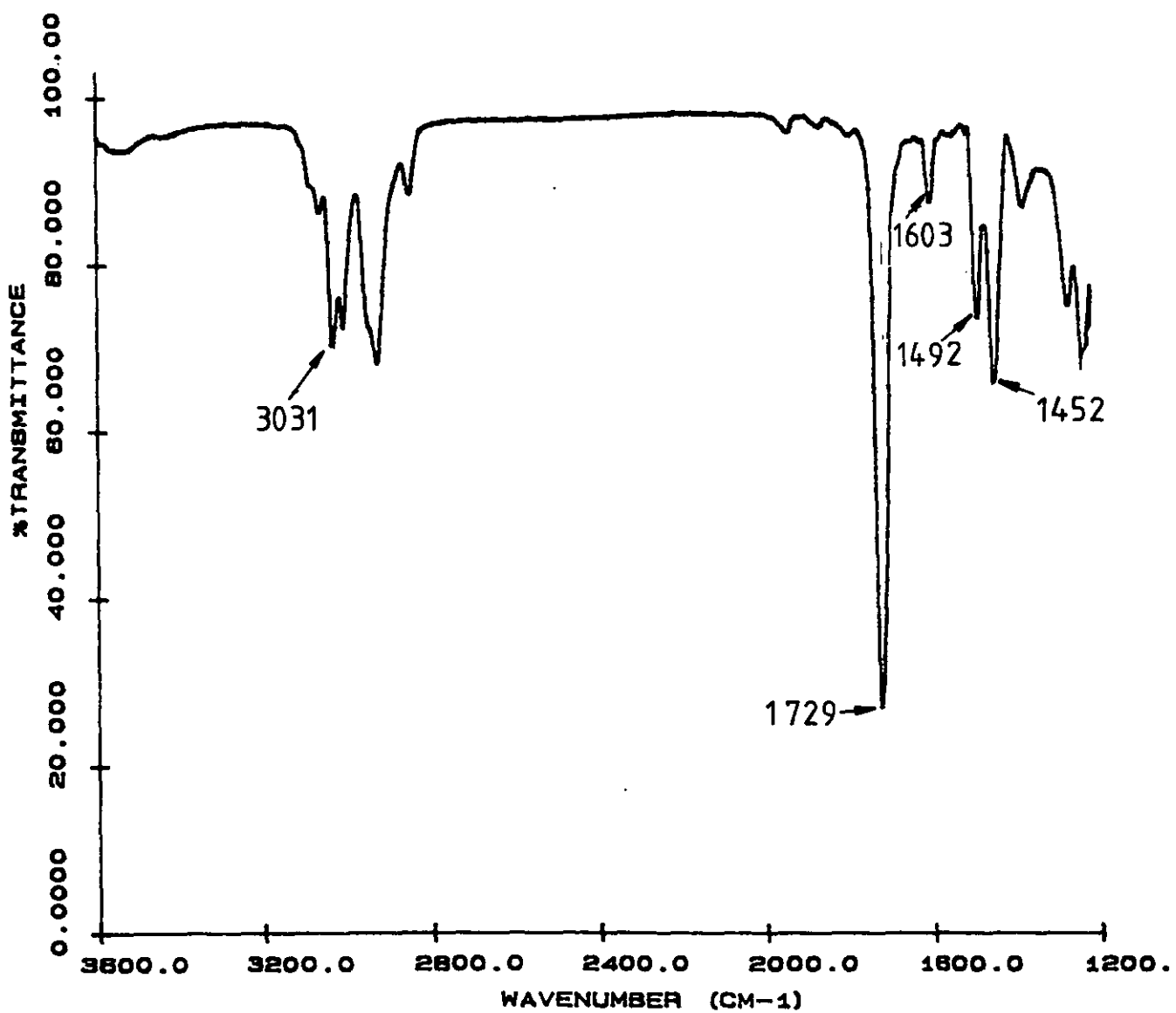


FIGURE 4.24 THE ^1H NMR SPECTRUM OF PS-graft-PMMA COPOLYMER SM-1

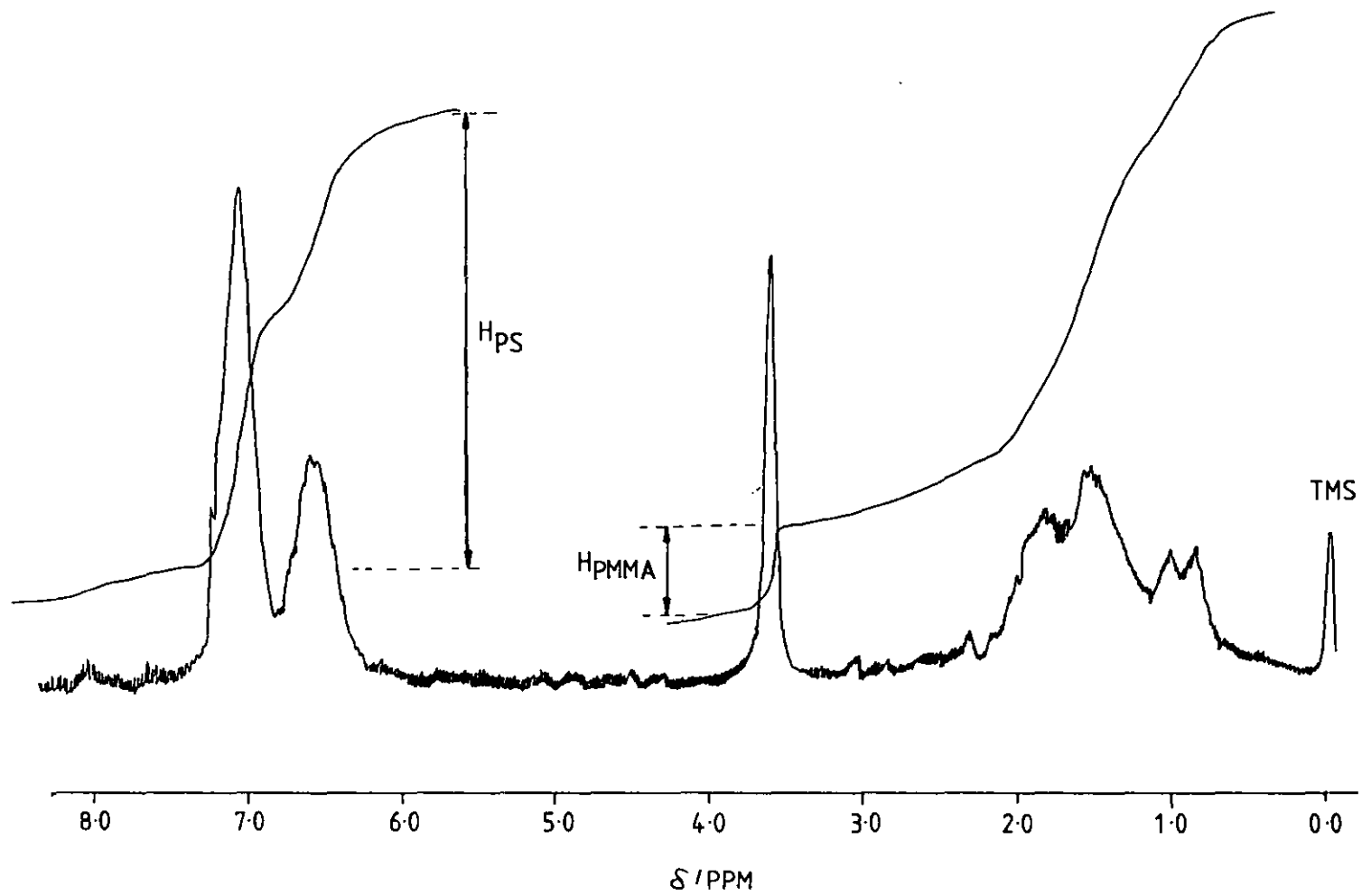


TABLE 4.20 THE SYNTHESIS AND CHARACTERIZATION OF PS-graft-PMMA COPOLYMERS
(a) INTERMEDIATE MACROMONOMER CONVERSION¹

GRAFT COPOLYMER CODE	MACROMONOMER COPOLYMERIZED		MACROMONOMER CONVERSION ² / mole-%	WEIGHT FRACTION OF METHACRYLATE (i.e. macromonomer) FEED ³			COPOLYMER MOLAR MASSES ⁴					\bar{N}_g ⁵
	TYPE	$\bar{M}_n/10^3 \text{g.mol}^{-1}$		(IR)	(¹ H NMR)	$\bar{M}_{\text{Peak}}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n		
SM-1	PMMA-15MP	2.94	35	0.25	0.30	0.29	37.2	20.0	30.9	27.2	1.85	2.0
SM-2	PMMA-15MP	2.94	38	0.37	0.42	0.42	37.2	19.9	38.1	27.5	1.91	2.8
SM-3	PMMA-15MP	2.94	39	0.50	0.59	0.56	35.5	17.4	34.6	24.5	1.99	3.5
SM-4	PMMA-16MP	1.42	41	0.25	0.32	0.30	35.5	18.6	35.9	25.8	1.94	4.2
SM-5	PMMA-16MP	1.42	41	0.37	0.43	0.42	37.1	19.8	39.0	27.8	1.97	6.0
SM-6	PMMA-16MP	1.42	36	0.50	0.55	0.58	38.5	21.9	40.2	29.7	1.84	8.5
6PS-1	-	-	-	-	-	-	33.9	18.8	33.2	25.0	1.77	-

NB 1 Polymerization time of 31 hours at 333 K. Total [M] = 30% (w/v) in toluene. [AIBN] = 0.75% (w/w) on monomer.

2 Determined by GPC.

3 Determined gravimetrically, weight fraction based on total monomer.

4 Determined by GPC.

5 Average number of grafts per molecule, see equation 4.19.

6 PS homopolymer prepared under same conditions specified by note 1.

TABLE 4.21

THE SYNTHESIS AND CHARACTERIZATION OF PS-graft-PMMA COPOLYMERS
(b) LOW MACROMONOMER CONVERSION¹

GRAFT COPOLYMER CODE	MACROMONOMER COPOLYMERIZED		MACROMONOMER CONVERSION ² / mole-%	WEIGHT FRACTION OF METHACRYLATE (i.e. macromonomer) FEED ³ COPOLYMER (IR)		COPOLYMER MOLAR MASSES ⁴					\bar{N}_g ⁵
	TYPE	$\bar{M}_{n,2}/10^3 \text{g.mol}^{-1}$		$\bar{M}_{\text{Peak}}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n	Units g.mol^{-1}		
SM-7	PMMA-15MP	2.94	9	0.12	0.18	34.7	18.2	33.7	24.8	1.85	1.1
SM-8	PMMA-15MP	2.94	11	0.25	0.31	33.1	19.5	36.3	25.6	1.86	2.0
SM-9	PMMA-15MP	2.94	16	0.37	0.46	35.1	18.1	34.1	24.8	1.89	2.9
SM-10	PMMA-15MP	2.94	19	0.50	0.58	37.2	20.3	36.0	27.0	1.88	4.0
SM-11	PMMA-16MP	1.42	9	0.13	0.19	35.5	20.9	34.7	26.9	1.66	2.7
SM-12	PMMA-16MP	1.42	18	0.25	0.33	38.0	21.6	37.9	28.6	1.75	5.0
SM-13	PMMA-16MP	1.42	17	0.37	0.45	36.3	22.2	38.9	29.4	1.75	7.0
SM-14	PMMA-16MP	1.42	20	0.50	0.57	38.9	23.9	41.1	31.3	1.72	9.6
PS-26	-	-	-	-	-	33.9	19.4	32.5	25.1	1.67	-

- NB 1 Polymerization time of 10 hours at 333 K. Total [M] = 30% (w/v) in toluene. [AIBN] = 0.75% (w/w) on monomer.
 2 Determined by GPC.
 3 Determined gravimetrically, weight fraction based on total monomer.
 4 Determined by GPC.
 5 Average number of grafts per molecule, see equation 4.19.
 6 PS homopolymer prepared under same conditions specified by note 1.

characterization of purified PS-graft-PMMA copolymers prepared from the copolymerization of PMMA macromonomers. The characterization of PS homopolymers prepared by the polymerization of styrene using the same total monomer and initiator concentrations are also shown. Table 4.20 summarizes polymerizations where the polymerization time was 31 hours. The macromonomer conversions were approximately constant (approximately 40%) and independent of the molar mass of the PMMA macromonomer used and the comonomer feed compositions. The resulting graft copolymer molar masses were similar ($\bar{M}_n = 17.4-22 \times 10^3 \text{g.mol}^{-1}$) and the polydispersities varied from 1.85 to 1.99. Table 4.21 summarizes polymerizations where the polymerization time was restricted to 10 hours. In this series, the macromonomer conversions were also similar with no obvious dependence upon the comonomer feed composition or the molar mass of the macromonomer copolymerized. The graft copolymer number average molar masses ($\bar{M}_n = 18-24 \times 10^3 \text{g.mol}^{-1}$) were close to those obtained at higher conversions but the polydispersities were generally lower ($\bar{M}_w/\bar{M}_n = 1.66-1.88$). The chemical compositions of the resulting copolymers will be discussed in section 4.2.4.

4.2.3.3. Polystyrene-graft-poly(2-ethyl hexyl acrylate) copolymers

Both IR and ^1H NMR spectroscopy showed the presence of PS and PEHA sequences in the products arising from the copolymerization of PEHA macromonomers with styrene. For example, figure 4.25 illustrates the IR spectrum of graft copolymer SE-5. The absorbance at $\sigma = 1729 \text{cm}^{-1}$ is characteristic of the ester carbonyl in PEHA segments whereas the absorptions at $\sigma = 3030 \text{cm}^{-1}$ (C-H stretch) and $\sigma = 1602, 1493$ and 1455cm^{-1} (C-C stretch) are indicative of polystyrene segments. From such spectra, the copolymer compositions were determined by calibration of the ester carbonyl absorption with PEHA macromonomers as previously

described in section 3.5.2.2. The ^1H NMR spectrum of graft copolymer SE-4 is illustrated in figure 4.26. The peaks at $\delta = 7.1$ and 6.6ppm are assigned to the PS segment protons whereas the peaks at $\delta = 3.95$ and 0.89ppm are due to the ester $-\text{CH}_2-\text{O}-$ and saturated methyl groups respectively in PEHA segments (see ^1H NMR spectrum of PEHA-51M, figure 4.17 section 4.1.3.2). The copolymer compositions from such spectra were obtained by comparing the integration of PS protons to the integration of PEHA protons, i.e.

$$\frac{\text{No. of moles of PS repeating units}}{\text{No. of moles of PEHA repeating units}} = \frac{H_{\text{PS}}/5}{H_{\text{PEHA}}/8} \quad (4.17)$$

where H_{PS} and H_{PEHA} are defined in figure 4.26.

Tables 4.22 and 4.23 show the information obtained from the characterization of PS-graft-PEHA copolymers, synthesized from the copolymerizations of PEHA macromonomers with styrene. Both tables also show the characterization of PS homopolymers prepared from the homopolymerization of styrene using the same total monomer and initiator concentrations as in the copolymerization experiments. The chemical compositions will be discussed in section 4.2.4 but the results are very similar to those given in section 4.2.3.2 for PS-graft-PMMA copolymers. Polymerizations where the polymerization time was 31 hours at 333 K are given in table 4.22. The macromonomer conversion obtained was approximately constant ($\sim 40\%$) and independent of the macromonomer molar mass and comonomer feed composition. The graft copolymer molar masses were similar ($\bar{M}_n = 20\text{--}24 \times 10^3\text{g.mol}^{-1}$) and the polydispersities ranged from $\bar{M}_w/\bar{M}_n = 1.67\text{--}2.02$. Table 4.23 shows the results from copolymerizations where the reaction time was restricted to 10 hours in order to achieve a lower conversion. In this series, the PEHA macromonomer conversion was again approximately constant ($\sim 15\%$). Generally, the graft copolymer molar masses were slightly higher ($\bar{M}_n = 21\text{--}27 \times 10^3\text{g.mol}^{-1}$) than those obtained at higher conversions and the polydispersities were lower ($\bar{M}_w/\bar{M}_n = 1.56\text{--}1.76$).

FIGURE 4.25 THE IR SPECTRUM OF PS-graft-PEHA COPOLYMER SE-5

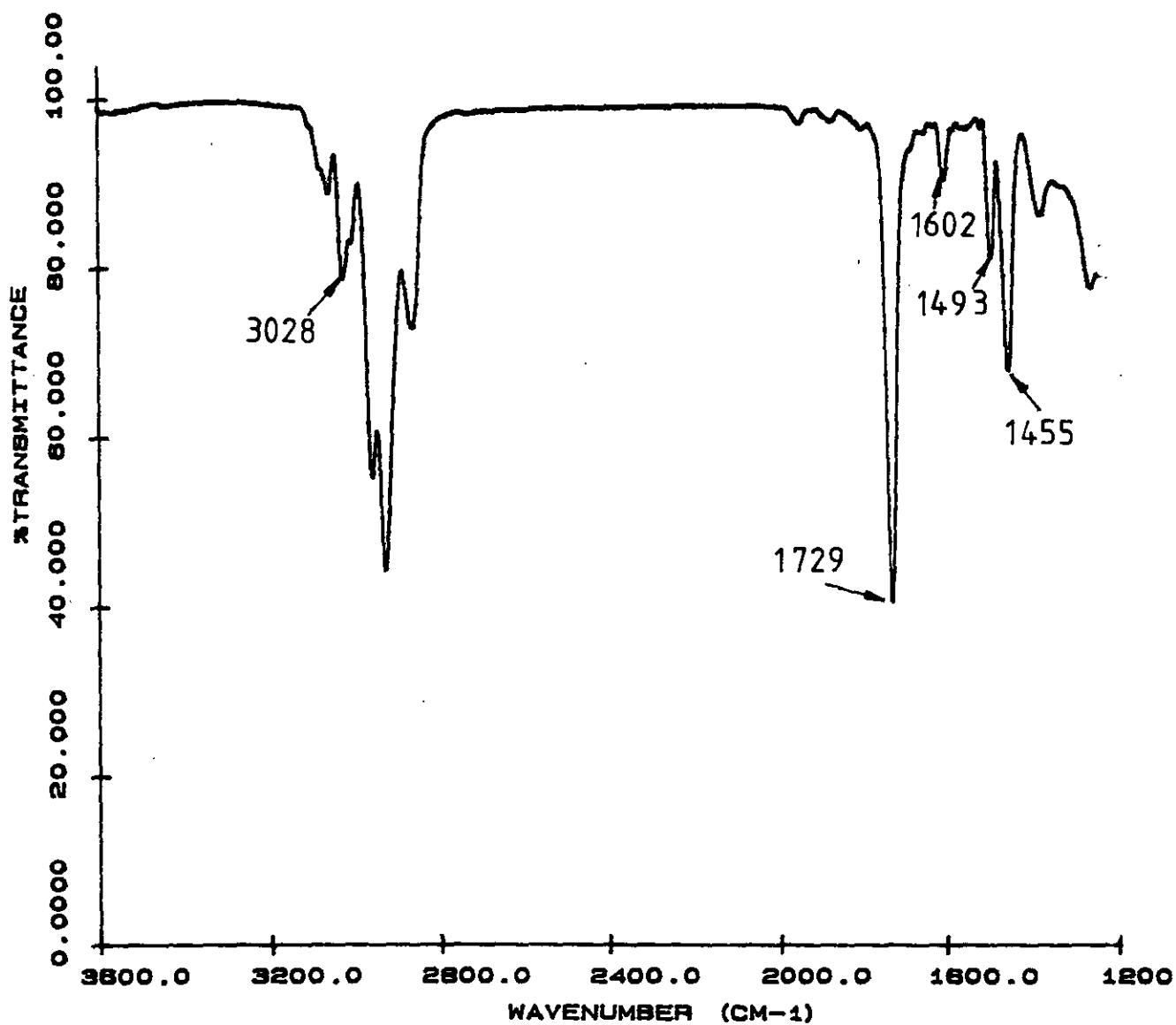


FIGURE 4.26 THE ^1H NMR SPECTRUM OF PS-graft-PEHA COPOLYMER SE-4

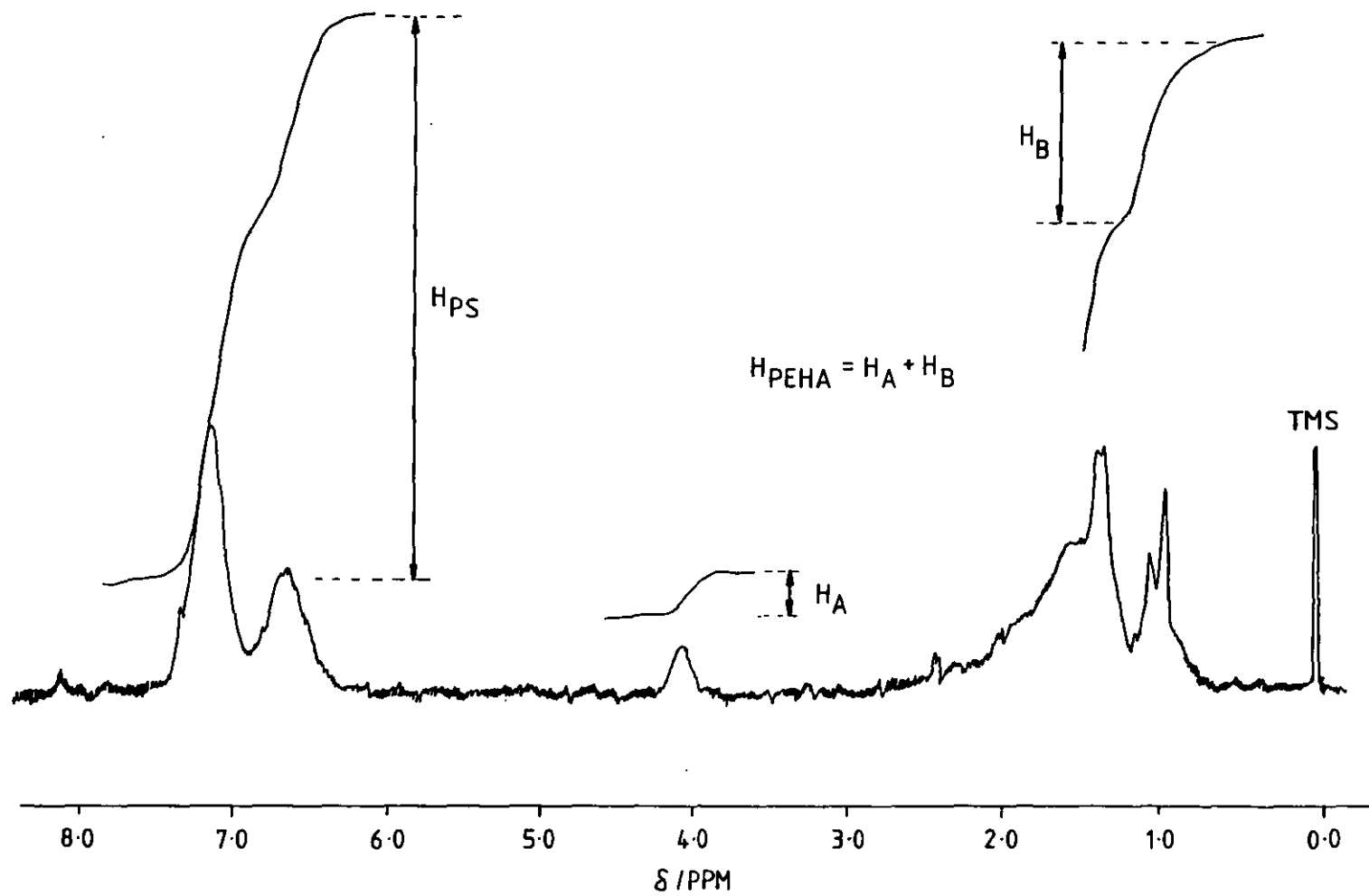


TABLE 4.22 SYNTHESIS AND CHARACTERIZATION OF PS-graft-PEHA COPOLYMERS
(a) INTERMEDIATE MACROMONOMER CONVERSION¹

GRAFT COPOLYMER CODE	MACROMONOMER COPOLYMERIZED		MACROMONOMER CONVERSION ² / mole-%	WEIGHT FRACTION OF ACRYLATE (i.e. macromonomer) FEED ³			COPOLYMER MOLAR MASSES ⁴				\bar{N}_g ⁵	
	TYPE	$\bar{M}_n/10^3 \text{g.mol}^{-1}$		(IR)	(¹ H NMR)	$\bar{M}_{\text{Peak}}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n		
SE-1	PEHA-4OMP	1.62	40	0.25	0.34	0.33	35.5	19.6	35.3	26.3	1.80	4.1
SE-2	PEHA-4OMP	1.62	45	0.37	0.47	0.44	36.3	20.2	36.3	27.0	1.80	5.8
SE-3	PEHA-4OMP	1.62	40	0.50	0.61	0.57	38.9	24.7	41.2	31.9	1.67	9.3
SE-4	PEHA-4SMP	3.29	38	0.25	0.32	0.30	36.3	21.7	37.7	28.6	1.74	2.1
SE-5	PEHA-4SMP	3.29	40	0.38	0.46	0.44	36.3	21.4	38.6	28.8	1.80	3.0
SE-6	PEHA-4SMP	3.29	44	0.51	0.60	0.55	38.0	19.9	40.2	28.3	2.02	3.6
PS-16	-	-	-	-	-	-	33.9	18.8	33.2	25.0	1.77	-

NB 1 Polymerization time of 31 hours at 333 K. Total [M] = 30% (w/v) in toluene. [AIBN] = 0.75% (w/w) on monomer.

2 Determined by GPC.

3 Determined gravimetrically, weight fraction based on total monomer.

4 Determined by GPC.

5 Average number of grafts per molecule, see equation 4.19.

6 Polystyrene homopolymer prepared under same conditions specified by note 1.

TABLE 4.23 THE SYNTHESIS AND CHARACTERIZATION OF PS-graft-PEHA COPOLYMERS
(b) LOW MACROMONOMER CONVERSION¹

GRAFT COPOLYMER CODE	MACROMONOMER COPOLYMERIZED		MACROMONOMER CONVERSION ² / mole-%	WEIGHT FRACTION OF ACRYLATE (i.e. macromonomer) FEED ³ COPOLYMER (IR)		COPOLYMER MOLAR MASSES ⁴				\bar{M}_w/\bar{M}_n	\bar{N}_g ⁵
	TYPE	$\bar{M}_n/10^3 \text{g.mol}^{-1}$		$\bar{M}_{Peak}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	Units g.mol^{-1}			
SE-10	PEHA-40MP	1.62	13	0.13	0.18	39.8	22.9	35.9	28.7	1.57	2.6
SE-7	PEHA-40MP	1.62	17	0.25	0.34	36.3	23.4	36.9	29.4	1.58	4.9
SE-8	PEHA-40MP	1.62	18	0.38	0.44	39.8	26.4	41.1	33.0	1.56	7.1
SE-9	PEHA-40MP	1.62	18	0.50	0.58	39.8	27.0	43.0	34.1	1.59	9.6
SE-14	PEHA-45MP	3.29	15	0.13	0.19	35.6	21.3	36.6	27.9	1.72	1.2
SE-11	PEHA-45MP	3.29	17	0.26	0.37	36.3	21.0	35.7	27.4	1.70	2.4
SE-12	PEHA-45MP	3.29	14	0.38	0.50	36.3	20.6	36.2	27.3	1.76	3.1
SE-13	PEHA-45MP	3.29	18	0.50	0.53	38.0	25.6	41.8	32.7	1.63	4.9
6 PS	-	-	-	-	-	33.9	19.4	32.5	25.1	1.67	-

NB 1 Polymerization time of 10 hours at 333 K. Total [M] = 30%(w/v) in toluene. [AIBN] = 0.75% (w/w) on monomer.

2 Determined by GPC.

3 Determined gravimetrically, weight fraction based on total monomer.

4 Determined by GPC.

5 Average number of grafts per molecule, see equation 4.19.

6 Homopolymer prepared under same conditions specified by note 1.

4.2.3.4 Discussion

The minimum conversion which was obtained in the copolymerization of PMMA or PEHA macromonomers with styrene was approximately 15% due to practical reasons. Polymerizations with macromonomer conversions of <10% were attempted but problems were encountered in removing the increased amount of unreacted macromonomer. As a result of the same problem, the maximum feed concentration of macromonomer used in the copolymerizations was 50% by weight of total monomer. The molar masses and polydispersities for all PS-graft-PMMA and PS-graft-PEHA copolymers were alike at low conversions (generally $\bar{M}_n=20-27 \times 10^3 \text{g.mol}^{-1}$ and $\bar{M}_w/\bar{M}_n=1.60-1.85$). These polydispersities are typical of conventional mechanisms of free-radical polymerization [52,89]. After the same polymerization time used to produce low conversion copolymers, the PS homopolymer molar masses obtained were also similar ($\bar{M}_n=19.4 \times 10^3 \text{g.mol}^{-1}$ and $\bar{M}_w/\bar{M}_n=1.67$). The molar masses of PS-graft-PMMA and PS-graft-PEHA copolymers at intermediate conversion were similar to those at low conversion but polydispersities were generally higher ($\bar{M}_w/\bar{M}_n=1.8-2.0$). For PS homopolymers prepared under similar conditions, the molar masses and polydispersities followed the same trend ($\bar{M}_n=18.8 \times 10^3 \text{g.mol}^{-1}$ and $\bar{M}_w/\bar{M}_n=1.77$). Therefore, although the molar masses of the graft copolymers produced were low, they are comparable to those produced by the homopolymerization of styrene.

The polymerization of styrene in the presence of carboxyl-terminated prepolymers also produced molar masses of the same order. For example, in a polymerization analogous to SE-1, where macromonomer was replaced by carboxyl-terminated prepolymer, the polymer produced had an \bar{M}_{Peak} of $30.2 \times 10^3 \text{g.mol}^{-1}$. As already discussed (section 4.2.1), the polymers produced in these 'blank' experiments were shown to be PS containing no PMMA or PEHA segments. Therefore, the low graft copolymer molar masses obtained are simply due to the concentration of total monomer and not due to chain transfer to the macromonomer chain, as suggested

elsewhere [92,135,139]. Low graft copolymer molar masses have also been explained by low macromonomer mobility and lack of access to the terminal unsaturation [85]. However, in the present case this is unlikely, since the graft copolymer molar masses did not vary with the macromonomer molar mass or the feed composition used.

The graft copolymer molar masses were obtained by GPC calibrated using linear PS standards. It is possible to question the accuracy of these results since the graft copolymers may have different elution properties as a result of

- (i) differences in chemical composition and/or
- (ii) the branched nature of graft copolymers.

With regard to point (i), it is possible for the calibration curves of the PS-graft-PMMA and PS-graft-PEHA copolymers to be different from that of polystyrene since they contain either PMMA or PEHA segments. As already discussed in section 4.1.1.3, Dawkins [173,174] has shown that the same molar mass calibration curve is obtained for polymers with similar unperturbed dimensions per unit mass. . . . It was also demonstrated in section 4.1.1.3 that PMMA and polyacrylates have similar $\langle r_0 \rangle / M^{0.5}$ values to PS. Therefore, one could expect the linear PS calibration to be appropriate for both PS-graft-PMMA and PS-graft-PEHA copolymers provided that the branched nature of the graft copolymers do not affect their elution properties. Since graft copolymers have branched structures, it is predicted that their molar volume is smaller in dilute solution than a linear polymer with the same molar mass [136]. GPC separates on the basis of molecular size and the parameter which is often used to determine chromatographic retention is the hydrodynamic volume of solute molecules [180]. Therefore, the molar masses of graft copolymers obtained from a linear PS calibration may be expected to be lower than true values. However, Drott and Mendelson [181] have determined the calibration curves of several branched polyethylene samples in comparison to linear polyethylene. They

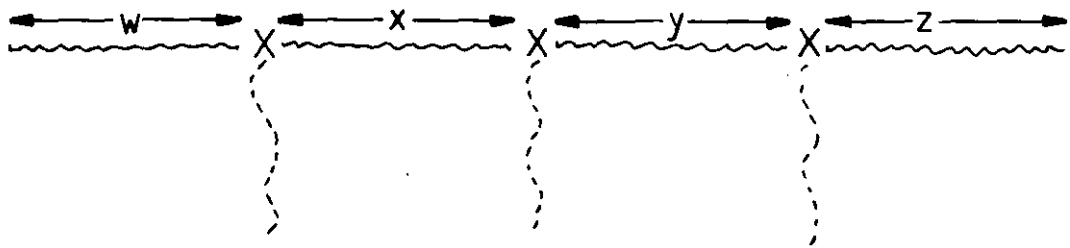
showed that the calibration curves were identical at molar masses of $<10^4 \text{g.mol}^{-1}$ and that the effects of branching only become significant above this molar mass, which is of the same order as the graft copolymer masses prepared here. However, the polyethylene samples contained long-chain branches and the effects of short-chain branches are predicted to be lower [182]. Since the PS-graft-PMMA and PS-graft-PEHA copolymers contain only a small number of relatively short branches, then the effect of branching on calibration is expected to be even smaller. It is reasonable to assume that the effects of branching on the elution properties of the graft copolymers prepared are negligible at $\bar{M}_n \sim 2 \times 10^4 \text{g.mol}^{-1}$. Therefore, it is predicted that the calibration curves of these graft copolymers are similar to polystyrene and that the molar masses obtained from the linear polystyrene calibration are close to true values.

4.2.4 THE CONTROL OF CHEMICAL COMPOSITION AND PHYSICAL ARCHITECTURE

The schematic representation of PS-graft-PMMA or PS-graft-PEHA copolymers is illustrated in figure 4.27. The chemical composition of the backbone is essentially that of the copolymerized comonomer (PS) and the chemical composition of the grafts is that of the copolymerized macromonomer (either PMMA or PEHA). In addition, the chemical composition of the link X at the branching site is known since it originates from the macromonomer end-group, ie. it is a methacrylate. In addition to the chemical compositions, the physical properties of graft copolymers depend upon their architecture. Important characteristics are listed below.

- (i) The ratio of backbone/grafts. This is the chemical composition of the graft copolymer which essentially describes the ASB for the use of graft copolymers as

FIGURE 4.27 A SCHEMATIC REPRESENTATION OF GRAFT COPOLYMER
STRUCTURE



- ~~~~ backbone arising from styrene comonomer
- grafts arising from macromonomer
- X branching sites arising from macromonomer end-group

stabilizers for polymer particles in non-aqueous media.

- (ii) Molar masses. In addition to the overall graft copolymer molar masses, the molar masses of the constituent grafts and the backbone are also important. Since the macromonomers form the grafts, it is assumed that their molar masses are equal. The backbone molar mass can be calculated from the equation

$$\bar{M}_n(\text{backbone}) = \bar{M}_n(\text{copolymer}) \times W_b \quad (4.18)$$

where $\bar{M}_n(\text{backbone})$ and $\bar{M}_n(\text{copolymer})$ are the number average molar masses of the backbone and overall copolymer, respectively and W_b is the weight fraction of backbone.

- (iii) The average number of grafts per molecule (\bar{N}_g). This is defined by the equation

$$\bar{N}_g = \frac{\bar{M}_n(\text{copolymer}) \times W_g}{\bar{M}_n(\text{graft})} \quad (4.19)$$

where W_g is the weight fraction of grafts and $\bar{M}_n(\text{graft})$ is the number average molar mass of each graft.

In calculating $\bar{M}_n(\text{backbone})$, $\bar{M}_n(\text{graft})$ and \bar{N}_g , one elementary assumption has been made. It has been assumed that the branching site X in figure 4.27, which originates from the macromonomer end-group, is part of the graft. This has the following implications:

- (a) the weight fraction of grafts is equal to the weight fraction of macromonomer incorporated into the graft copolymer (ie. $W_m(\text{copol})$, the weight fraction of methacrylate or acrylate determined by IR spectroscopy).

$$\text{ie. } W_g = W_m(\text{copol}) \quad (4.20)$$

(b) the graft molar mass is equal to the macromonomer molar mass,

$$\text{ie. } \bar{M}_n(\text{graft}) = \bar{M}_n(\text{macromonomer}) \quad (4.21)$$

(c) the weight fraction of backbone is equal to the weight fraction of PS segments in the graft copolymer,

$$\text{ie. } W_b = (1 - W_g) = (1 - W_m(\text{copol})) \quad (4.22)$$

Therefore, W_b and $\bar{M}_n(\text{backbone})$ which is calculated from it, ignore the methacrylate branching unit. Section 4.2.4.3 will show that this is not strictly correct. However, the errors arising in the various parameters by assuming that X is not part of the backbone are negligible, since the number of branching sites is small.

4.2.4.1 Backbone/graft ratio

Figures 4.28(a) and 4.28(b) illustrate the relationships between the copolymer compositions and feed compositions for the copolymerizations of macromonomers PMMA-15MP and PMMA-16MP respectively, at both low and intermediate conversions. $W_m(\text{feed})$ and $W_m(\text{copol})$ represent the weight fractions of macromonomer (ie. PMMA or PEHA) in the feed (based on total monomer) and in the resulting copolymer, respectively. In all cases, the methacrylate content in the PS-graft-PMMA copolymers is consistently higher than the macromonomer content in the feed, at all feed compositions. It is evident that the copolymers obtained at higher conversions are lower in methacrylate content than corresponding copolymerizations at low conversions but this difference is small.

Figures 4.29(a) and 4.29(b) illustrate the analogous relationships between the copolymer and feed compositions for the copolymerizations of macromonomers PEHA-40MP and PEHA-45MP,

FIGURE 4.28 THE VARIATION OF PS-graft-PMMA COPOLYMER COMPOSITION WITH COMONOMER FEED COMPOSITION FOR THE COPOLYMERIZATIONS OF PMMA MACROMONOMERS

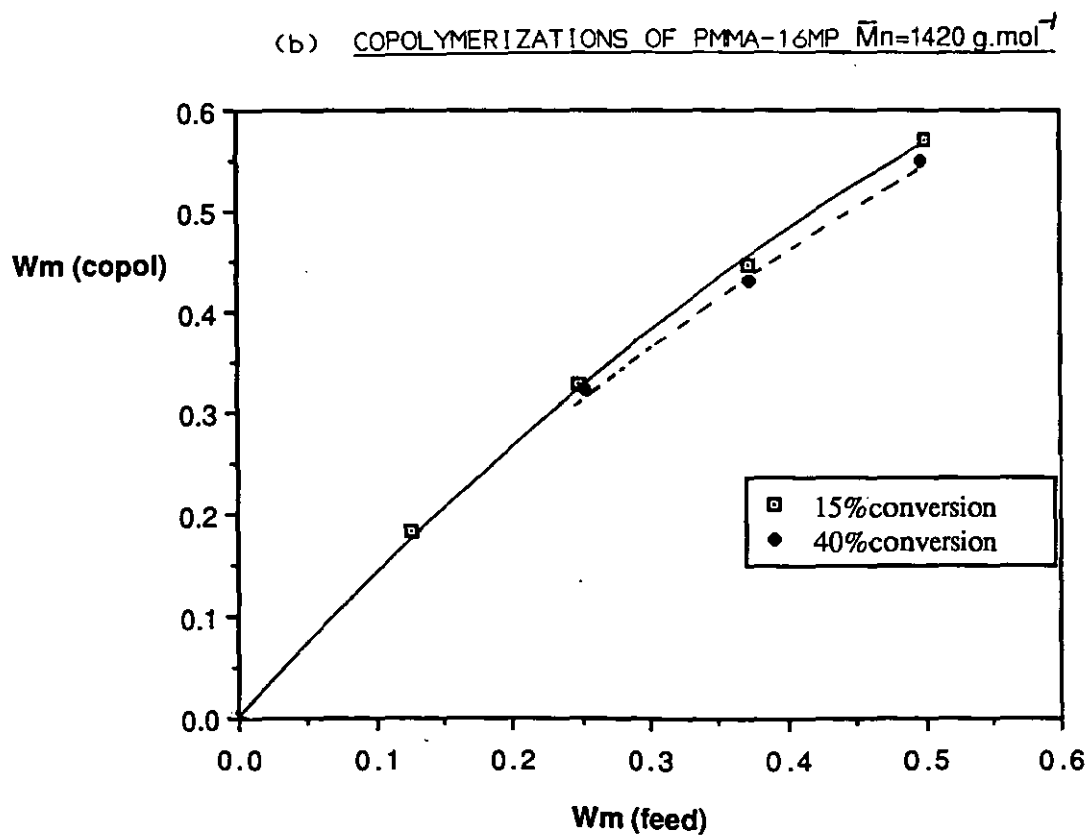
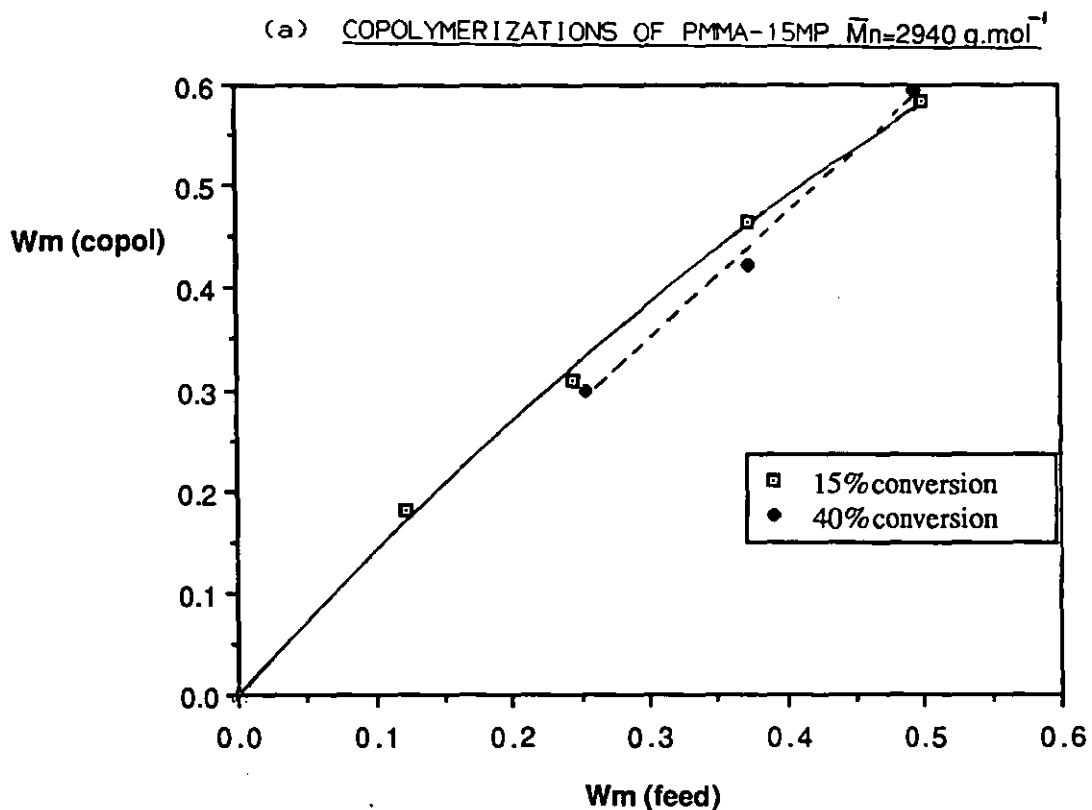
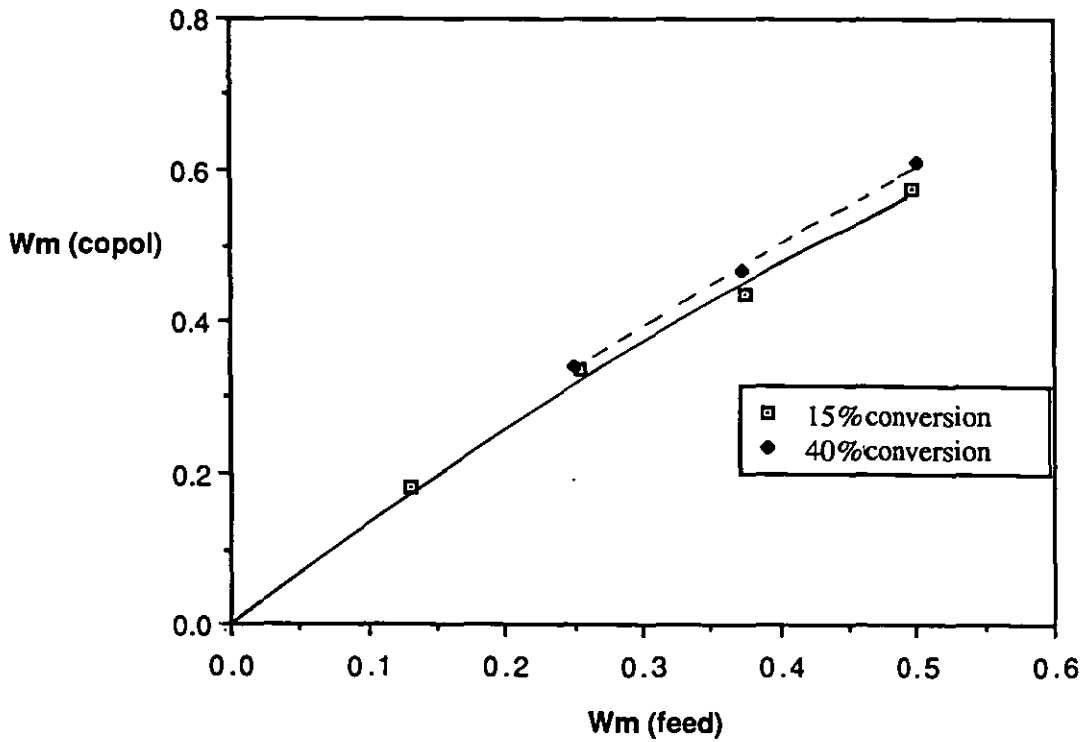
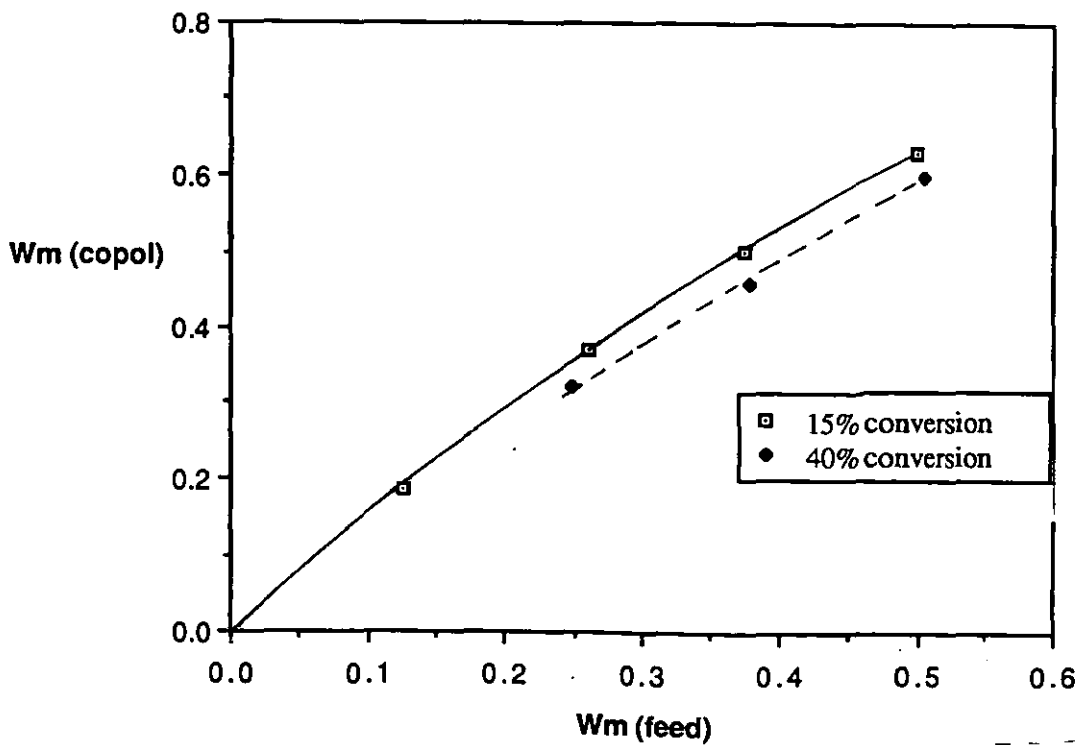


FIGURE 4.29 THE VARIATION OF PS-graft-PEHA COPOLYMER COMPOSITION WITH COMONOMER FEED COMPOSITION FOR THE COPOLYMERIZATIONS OF PEHA MACROMONOMERS

(a) COPOLYMERIZATIONS OF PEHA-40-MP $\bar{M}_n=1620 \text{ g.mol}^{-1}$



(b) COPOLYMERIZATIONS OF PEHA-45MP $\bar{M}_n=3300 \text{ g.mol}^{-1}$



respectively. These relationships are similar to those for the copolymerizations of PMMA macromonomers. Copolymer compositions are consistently richer in macromonomer than the feed compositions and the changes of copolymer composition with conversion are small. In all cases in figures 4.28 and 4.29, the copolymer compositions $W_m(\text{copol})$ are, of course, the average compositions of the copolymers produced. By comparison of figures 4.28(a) and (b) to 4.29(a) and (b), it can be seen that the relationships between copolymer and feed compositions (in terms of weight fractions) are similar. This suggests that the copolymerization behaviour of the different macromonomers is independent of the type of macromonomer copolymerized (see section 4.2.6). The small variation in composition with conversion will be discussed in more depth in section 4.2.4.2.

It must be noted that in all cases, $W_m(\text{feed})$ is the actual amount determined gravimetrically and no correction has been made for end-group functionality. Therefore, it has been assumed that there are no non-functionalized chains and that all macromonomer chains are precisely monofunctional with respect to polymerizable end-groups. Also, $W_m(\text{copol})$ used in figures 4.28 and 4.29 and equations 4.18-4.22 were those obtained from IR spectroscopy rather than ^1H NMR spectroscopy (all data listed in tables 4.20-4.23) since IR characterization was found to be more accurate, despite the need for calibration. A repeat characterization of the same sample by ^1H NMR revealed that differences of composition of 5% were obtained, whereas a repeat characterization by IR produced $\leq 1\%$ differences in composition. From the earlier assumptions, especially equation 4.20, $W_m(\text{copol})$ can be considered as the weight fraction of grafts in the resulting copolymers. Therefore, increasing the macromonomer content in the feed is a convenient method of increasing the graft content of the resulting copolymers. Obviously, this is accompanied by a decrease in the backbone content (ie. equation 4.22, $W_b = (1 - W_g)$), since the total monomer feed concentration was kept constant to produce consistent overall graft copolymer molar masses. Therefore the backbone/graft ratio and hence, the ASB of

graft copolymers in relation to their use as potential stabilizers of polymer particles in non-aqueous media, is readily controlled by altering the feed composition (see also section 4.3.1).

4.2.4.2 The number of grafts per molecule

The variations of \bar{N}_g with the comonomer feed compositions are illustrated in figures 4.30 and 4.31, for PS-graft-PMMA and PS-graft-PEHA copolymers respectively. The average number of grafts per molecule is small (<10) as a result of the low graft copolymer molar masses produced. It is evident that \bar{N}_g for both types of graft copolymer can be readily controlled by the comonomer feed composition, independent of the macromonomer chemical composition and molar mass. For a given graft chain length, the number of grafts is proportional to the weight fraction of macromonomer in the feed. At macromonomer conversions of approximately 15%, \bar{N}_g increases from approximately 1-4 for graft chain lengths of $\bar{M}_n \sim 3000 \text{g.mol}^{-1}$ and \bar{N}_g increases from approximately 3-10 for graft chain lengths with $\bar{M}_n \sim 1500 \text{g.mol}^{-1}$. This is the case for both PS-graft-PMMA and PS-graft-PEHA copolymers. At a constant $W_m(\text{feed})$, an increased number of grafts is obtained by copolymerizing a macromonomer with a lower molar mass. This is a direct result of the higher molar concentration of macromonomer and the increased number of macromonomer chains (with a shorter chain length) available in the copolymerization. Obviously, this increased number of grafts is achieved with a corresponding reduction in the graft chain length. Generally, there is a slight decrease in \bar{N}_g produced at intermediate conversion in comparison to that obtained under identical conditions at low conversion. These changes, which occur for both PS-graft-PMMA and PS-graft-PEHA copolymers, are a direct result of the dependence of \bar{N}_g on copolymer composition and molar mass (equation 4.19), which both drift as copolymerization proceeds as already discussed (sections 4.2.3.4

FIGURE 4.30 THE DEPENDENCE OF THE AVERAGE NUMBER OF GRAFTS PER MOLECULE IN PS-graft-PMMA COPOLYMERS ON COMONOMER FEED COMPOSITION

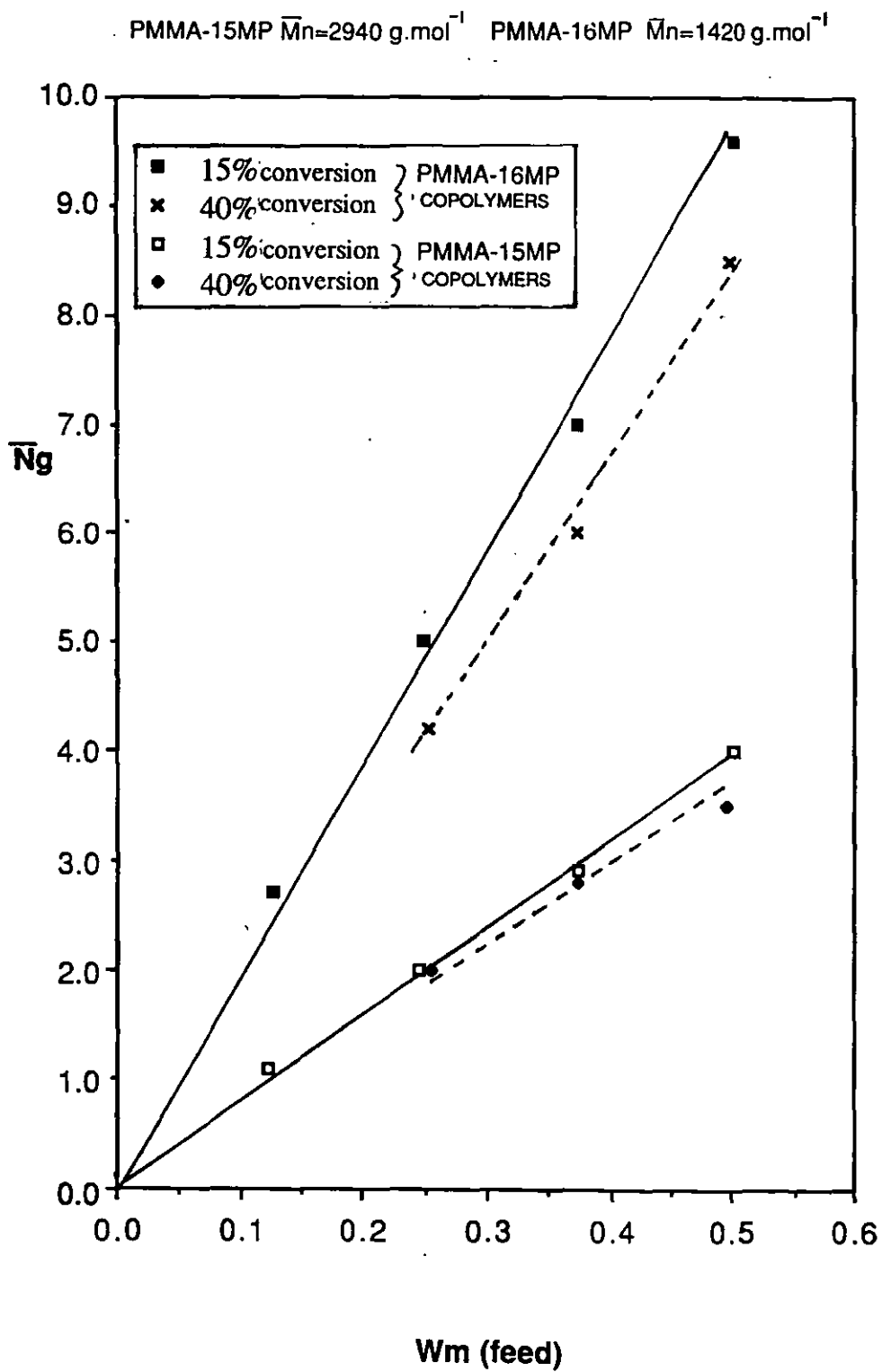
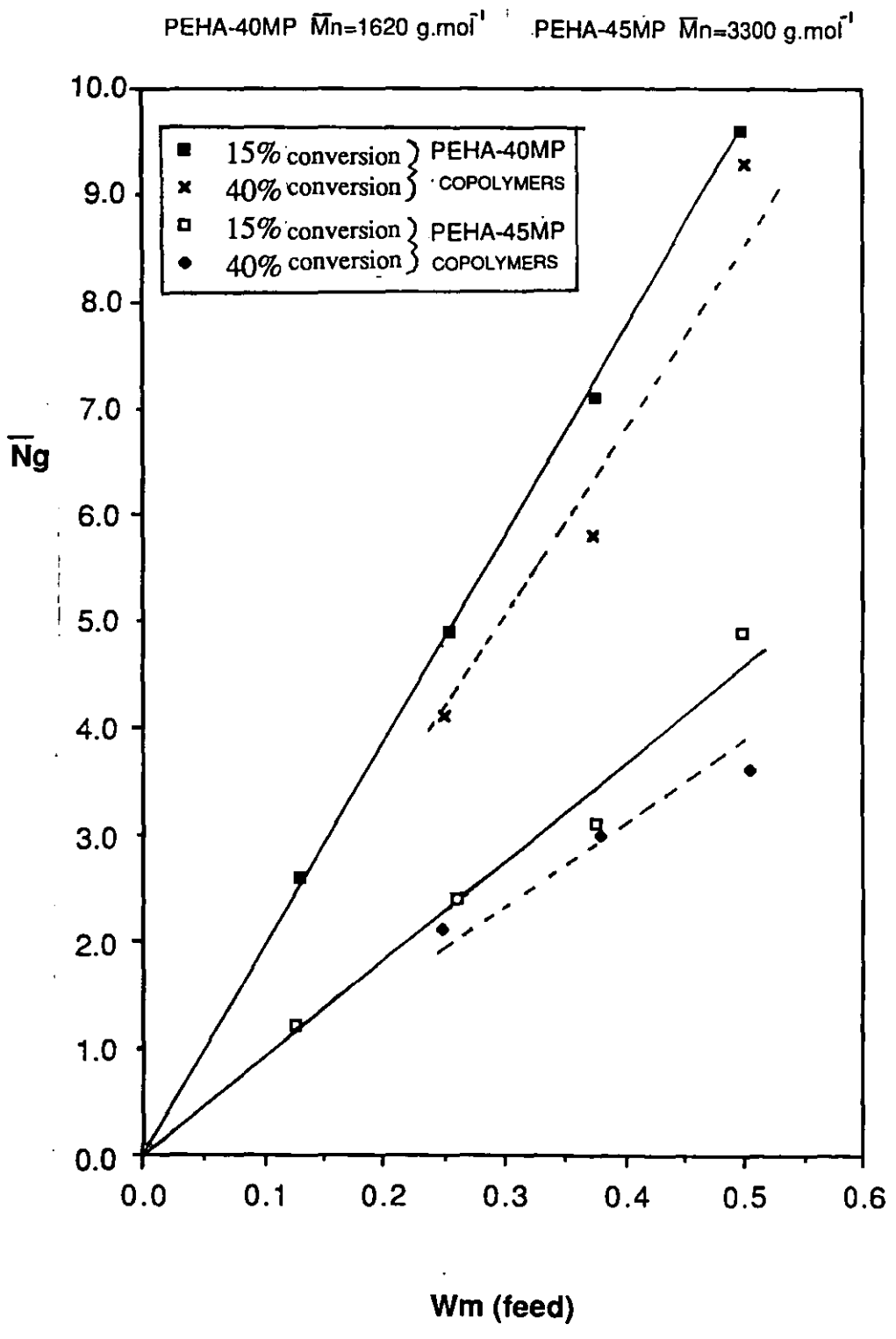


FIGURE 4.31 THE DEPENDENCE OF THE AVERAGE NUMBER OF GRAFTS PER MOLECULE IN PS-graft-PEHA COPOLYMERS ON COMONOMER FEED COMPOSITION



and 4.2.4.2). However, the composition drift is relatively small and consequently, the average number of grafts per molecule does not change significantly up to 40% conversion. These small changes in average composition suggest that the conversion chemical heterogeneity is low in the copolymerizations of all PMMA and PEHA macromonomers. This is in good agreement with theoretical predictions by Stejskal and Kratochvil [148], that the conversion chemical heterogeneity in macromonomer copolymerizations is not affected by the macromonomer molar mass and should not become significant even at higher conversions. Rempp [136] also suggests that the fluctuations in graft copolymer compositions are small up to 50-70% conversion, owing to the low molar concentrations of macromonomers. This is a direct result of the small changes in the relative molar concentrations of macromonomer and comonomer as copolymerization proceeds. Although the changes in copolymer composition with conversion are small, this does not rule out statistical chemical heterogeneity. Stejskal and Kratochvil [146] and more recently, Stejskal, Kratochvil and Jenkins [147] have outlined theories for predicting chemical composition distributions of graft copolymers prepared from macromonomers. It is predicted that the statistical chemical heterogeneity is substantially larger and more asymmetrical than that of conventional statistical copolymers with the same molar mass and average composition. Very few graft copolymers, which have been prepared from the free-radical copolymerization of macromonomers, have been analysed to find chemical composition distributions. Stejskal et al [183] have recently fractionated a poly(methyl methacrylate)-graft-poly(dimethylsiloxane) (PMMA-graft-PDMS) copolymer. Although the average PMMA content in the graft copolymer was 60% (w/w), the content of the fractions varied from 51-75% (w/w). De Simone et al [137] have also fractionated a PMMA-graft-PDMS copolymer. The average composition of the unfractionated copolymer was 80% (w/w) MMA, whereas the compositions of the fractions varied from 60-90% (w/w). Both of these experimental determinations agree with the theoretical predictions of broad chemical composition

distributions. It follows that the PS-graft-PMMA and PS-graft-PEHA copolymers are likely to be significantly heterogeneous. Since \bar{N}_g is small, it is possible to produce PS homopolymer without any grafts as a result of the statistical nature of free-radical copolymerization. This applies particularly to cases where the feed concentrations of macromonomer is very low, resulting in only 1-2 grafts per molecule on average. Therefore, the use of TLC (section 4.2.3.1) which established that the PS homopolymer produced was negligible in all copolymerizations, was extremely important. However, no assessment was made of the formation of polymacromonomer homopolymer. From a statistical basis, this can be neglected as a result of the very low molar concentrations of macromonomer utilized in all copolymerizations (<7 mole-%).

4.2.4.3 The molar masses of grafts, backbone and overall copolymer

The overall graft copolymer molar masses have already been discussed in sections 4.2.3.2-4.2.3.4. The graft molar masses are readily controlled simply by copolymerizing a macromonomer with a different molar mass. This follows from the assumptions at the beginning of section 4.2.4. The relationships between the backbone molar masses and the comonomer feed compositions are illustrated in figures 4.32 and 4.33 for PS-graft-PMMA and PS-graft-PEHA copolymers, respectively. This shows that there is a linear decrease in the backbone molar mass as the concentration of macromonomer in the feed is raised. This arises because the macromonomer content in the feed increases at the expense of styrene comonomer, since the total monomer concentration remains constant. Therefore, the amount of styrene copolymerized decreases, resulting in a lower backbone molar mass. The results given in figures 4.32 and 4.33 are for copolymerizations restricted to macromonomer conversions of ~15%. Similar results were obtained at higher conversions of ~40%, but these are not

FIGURE 4.32 THE VARIATION OF PS-graft-PMMA COPOLYMER BACKBONE MOLAR MASS WITH COMONOMER FEED COMPOSITION

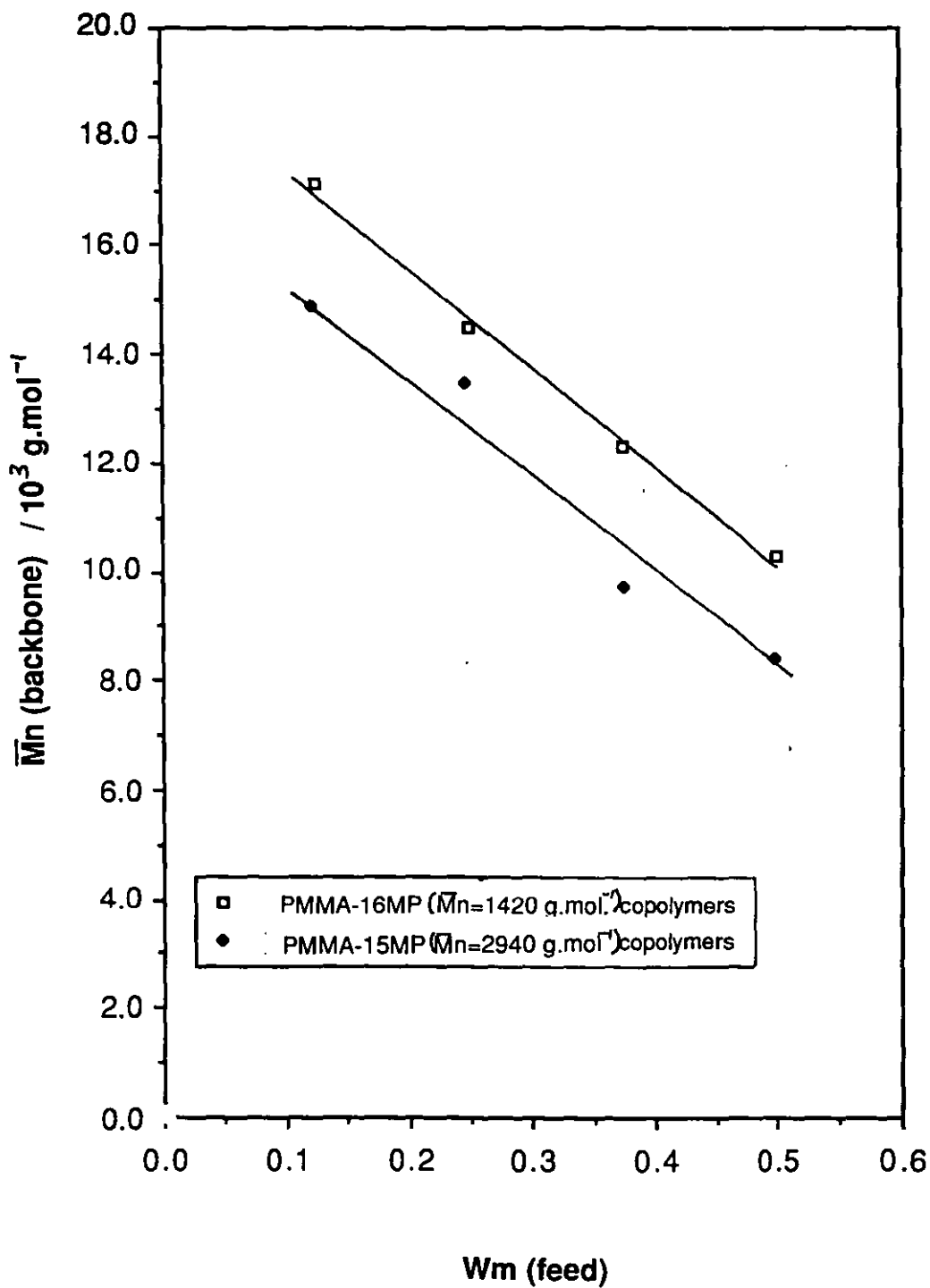
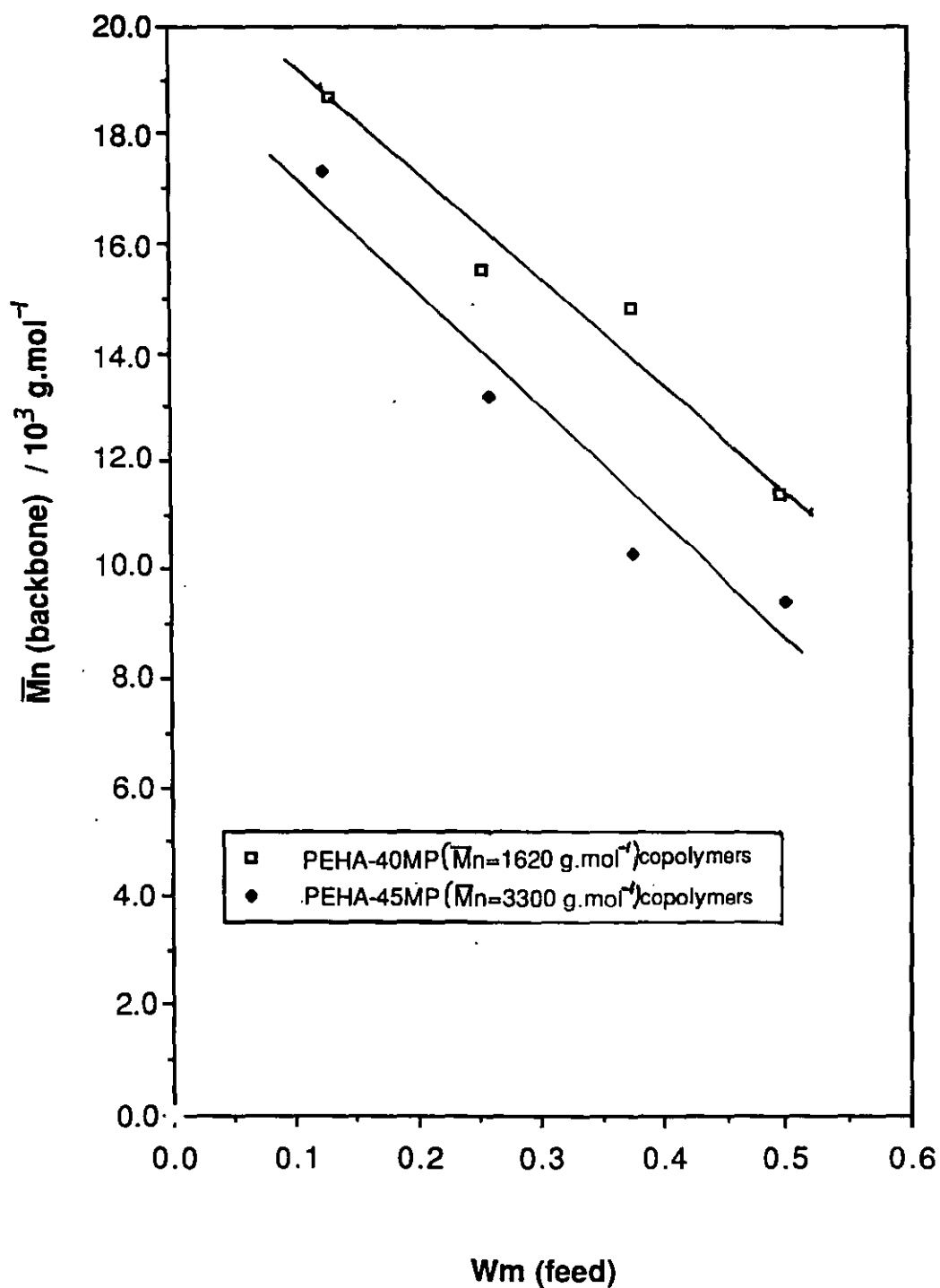


FIGURE 4.33 THE VARIATION OF PS-graft-PEHA COPOLYMER BACKBONE MOLAR MASS WITH COMONOMER FEED COMPOSITION



illustrated since the data was more scattered.

As clearly stated earlier, the chemical link at the branching site (X in figure 4.27) has been treated as part of the graft, which implies that the backbone is pure PS homopolymer. This is strictly not correct, since X can be considered as part of the backbone. Therefore, the backbones in both PS-graft-PMMA and PS-graft-PEHA are strictly poly(styrene-stat-methacrylate) statistical copolymers with very high styrene contents (94-99 mole-%). For example, for sample SM-8 there are 2 grafts per molecule, ie. 2 branching methacrylate sites. It can be calculated that the backbone contains 140 styrene repeating units and 2 methacrylate repeating units on average. Therefore, the backbones are essentially PS segments which are occasionally interrupted with methacrylate segments. In addition to the backbone molar mass, the average PS segment molar mass (ie the average PS molar mass between grafts, $\bar{M}_n(\text{PS segment})$) is also an important parameter which is likely to have an important effect on segmental mobility. $\bar{M}_n(\text{PS segment})$ can be calculated by assuming that the molar mass between grafts is equal to the molar mass between the backbone terminus and the first graft and that the grafts are equally spaced, ie. $w = x = y = z$ in figure 4.27. Therefore,

$$\bar{M}_n(\text{PS segment}) = \frac{\bar{M}_n(\text{backbone})}{(1 + \bar{N}_g)} \quad (4.23)$$

Figures 4.34 and 4.35 illustrate the variation of $\bar{M}_n(\text{PS segment})$ with \bar{N}_g for PS-graft-PMMA and PS-graft-PEHA copolymers, respectively. The figures demonstrate that $\bar{M}_n(\text{PS segment})$ decreases as \bar{N}_g increases. The PS segments are longer for copolymers with a longer graft chain length but the same chemical composition (by weight), since there are less grafts to interrupt the sequences.

Sections 4.2.4.1 to 4.2.4.3 illustrate that the chemical compositions and physical architectures of the PS-graft-PMMA and PS-graft-PEHA copolymers are readily controlled, irrespective of

FIGURE 4.34 THE EFFECT OF THE AVERAGE NUMBER OF GRAFTS PER MOLECULE IN PS-graft-PMMA COPOLYMERS ON THE AVERAGE MOLAR MASS BETWEEN GRAFTS

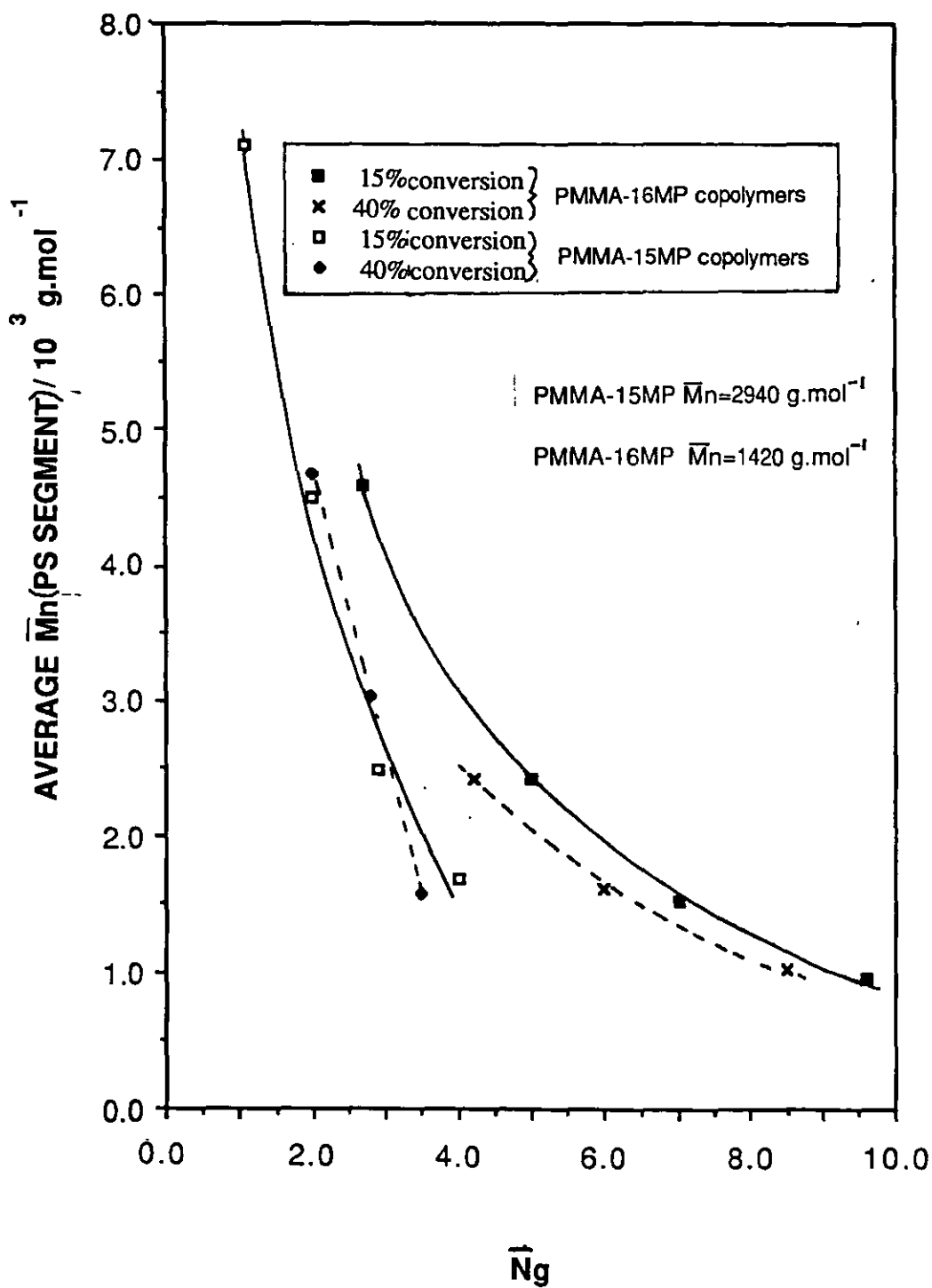
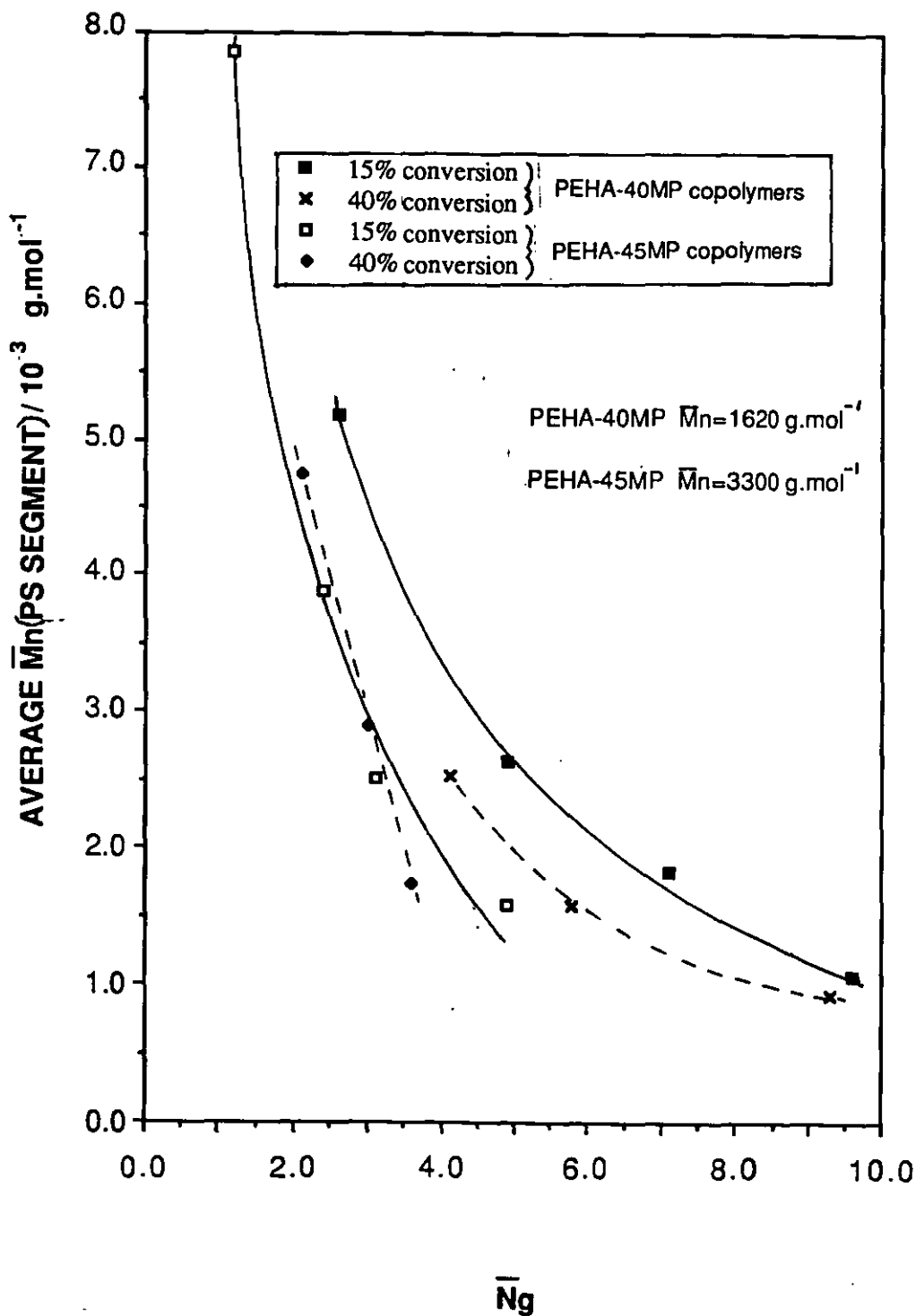


FIGURE 4.35 THE EFFECT OF THE AVERAGE NUMBER OF GRAFTS PER MOLECULE IN PS-graft-PEHA COPOLYMERS ON THE AVERAGE MOLAR MASS BETWEEN GRAFTS



the macromonomer used to synthesize them. Section 4.2.6 will show that this is a result of all macromonomers used behaving like conventional methacrylates. The backbone/graft ratio, the number of grafts and the molar masses of various constituents are important characteristics which can affect the performance of graft copolymers as steric stabilizers for polymer particles in non-aqueous media (see section 4.3.4). It was important to illustrate that the average copolymer composition did not change significantly with conversion, since copolymerizations performed to ~40% conversion were scaled up to produce sufficient quantities of graft copolymers for use as steric stabilizers. This is discussed further in section 4.3.1. All PS backbone molar masses lie in the range $\bar{M}_n = 8-19 \times 10^3 \text{g.mol}^{-1}$ and the PEHA or PMMA graft molar masses are $\bar{M}_n \sim 1500-3000 \text{g.mol}^{-1}$, which respectively represent potentially suitable anchor and soluble components for graft copolymers to behave as steric stabilizers in aliphatic hydrocarbons, as discussed in section 1.

4.2.5 ESTIMATION OF REACTIVITY RATIOS

4.2.5.1 The Jaacks method

The copolymerization of styrene (M_1) with methacrylate-terminated PMMA or PEHA macromonomers (M_2) represents a situation where the propagation of radicals with a terminal M_2 unit may be neglected on a statistical basis, as originally described by Jaacks [144] (see section 2.6.2, equation 2.50). This arises since the molar concentration of styrene is far greater than the macromonomers, despite their concentrations being similar by weight. Equation 2.50 is derived from the copolymerization equation and strictly only applies to low conversions. Therefore, tables 4.24 and 4.25 illustrate r_1 values calculated from this equation generally for copolymerizations where the macromonomer conversion was restricted to approximately 15%. For each series of macromonomer copolymerizations (ie. constant macromonomer molar mass and

chemical composition), r_1 does not vary significantly (within experimental error) and there is no trend as the copolymer compositions vary. Jaacks [144] originally proposed that the molar ratio $d[M_1]/d[M_2]$ in the copolymer should be $>20/1$ for his simplification to apply, in order to restrict the error in r_1 . However, this condition is not fulfilled by all of the data listed in tables 4.24 and 4.25. For certain copolymers, $d[M_1]/d[M_2]$ is <20 and these are labelled with an asterisk. For each group of macromonomer copolymerizations, the average reactivity ratio \bar{r}_1 is calculated but this does not account for those copolymerizations where the conditions stipulated by Jaacks are not fulfilled. Cameron and Chisholm [86] have discussed the validity of the use of the Jaacks simplification and proposed that the determined r_1 value is an apparent one ($r_{1(\text{app})}$) which relates to the real r_1 value ($r_{1(\text{real})}$) by the relationship,

$$r_{1(\text{app})} = r_{1(\text{real})} + \frac{[M_2]}{[M_1]} \quad (4.24)$$

where $r_{1(\text{app})} = r_1$ in equation 2.50. Values for $r_{1(\text{real})}$ calculated from equation 4.24 are also shown in tables 4.24 and 4.25. These reactivity ratios account for the errors produced in $r_{1(\text{app})}$ from differences in copolymer composition. This allows a direct comparison of all $r_{1(\text{real})}$ values, including those where the conditions stipulated by Jaacks are not fulfilled. The average reactivity ratio $\bar{r}_{1(\text{real})}$ for each series of copolymerization is calculated from all of the data. It is evident that $\bar{r}_{1(\text{real})}$ is close to $\bar{r}_1 = (\bar{r}_{1(\text{app})})$ for each set of data. Comparing these values, the styrene reactivity ratios vary from 0.59-0.68. Within experimental error, and accounting for the assumption inherent in the analysis that the propagation of radicals with a terminal macromonomer unit can be neglected, the r_1 values are independent of the molar masses and chemical compositions of the macromonomers used.

Equation 2.50 strictly only applies to low conversions. It is also possible for reactivity ratios to be obtained by the Jaacks

TABLE 4.24 REACTIVITY RATIOS OBTAINED FROM THE JAACKS METHOD
FOR COPOLYMERIZATION OF PMMA MACROMONOMERS (M₂)
WITH STYRENE (M₁)

SAMPLE	MACROMONOMER		$\frac{2d[M_1]}{d[M_2]}$	r ₁	F ₁	r ₁ (real)	F ₁ (real)
	$\bar{M}_n \times 10^3$ g.mol ⁻¹	CONVERSION ¹ /mole -%					
SM-7	2.94	9	127	0.62	0.67	0.62	0.67
SM-8	"	11	63	0.72		0.71	
SM-9	"	16	33	0.68		0.66	
SM-10	"	19	20	0.71		0.67	
SM-11	1.42	9	60	0.64	0.66	0.63	0.67
SM-12	"	18	28	0.67		0.65	
SM-13	"	17	17	0.74		0.70	
SM-14	"	20	10	0.75		0.68	
SM-1	2.94	35	66.3	0.79			
SM-4	1.42	41	29	0.71			

NB 1 Determined by GPC
 2 Determined by IR spectroscopy
 * d[M₁]/d[M₂] <20

TABLE 4.25 REACTIVITY RATIOS OBTAINED FROM THE JAACKS METHOD
FOR COPOLYMERIZATION OF PEHA MACROMONOMERS (M₂)
WITH STYRENE (M₁)

SAMPLE	MACROMONOMER		2 d[M ₁] d[M ₂]	r ₁	F ₁	r ₁ (real)	F ₁ (real)
	M _n × 10 ³ g.mol ⁻¹	CONVERSION ¹ /mole -%					
SE-10	1.62	13	70	0.67	0.67	0.66	0.68
SE-7	"	17	31	0.67		0.65	
SE-8	"	18	20	0.77		0.73	
SE-9	"	18	11	0.73		0.67	
SE-14	3.29	15	138	0.63	0.61	0.63	0.59
SE-11	"	17	53	0.59		0.58	
SE-12	"	14	31	0.60		0.58	
SE-13	"	18	18	0.58		0.55	
SE-1	1.62	40	30	0.65			
SE-4	3.29	38	66	0.69			

NB 1 Determined by GPC
 2 Determined by IR spectroscopy
 # d[M₁]/d[M₂] <20

method at higher conversions by the use of an integrated form of this equation, provided that the excess of M_1 over M_2 remains large throughout the copolymerization. Therefore, in principle, one single copolymerization experiment is sufficient in order to determine r_1 . However, Jaacks [144] recommended that it would be safer either to perform several copolymerizations with different feed compositions (ie. the present case) or to run one copolymerization at various conversions. The latter recommendation has been confirmed by Mühlbach and Percec [18]. They proved that in the copolymerization of poly(ethylene oxide) macromonomers with methacrylate comonomers, the reactivity ratios obtained using a single-point Jaacks experiment were conversion dependent. This was thought to be a result of different induction periods shown by the macromonomer and comonomer. It is possible for such a difference in induction periods to be present in the copolymerizations of styrene with PMMA or PEHA macromonomers. However, tables 4.24 and 4.25 also show r_1 values for several copolymerizations carried out to approximately 40% conversion, where the styrene contents in the copolymers are greatest. Generally, these values are not significantly different to \bar{r}_1 or $\bar{r}_1(\text{real})$ values calculated at low conversion, ie. it appears that there is no conversion dependence on r_1 (ie. there is no difference in the induction periods of PMMA/PEHA macromonomers and styrene). This data at higher conversions was also generated using the differential equation 2.50, rather than an integrated form. The use of this equation is justified since copolymers SM-1, SM-4, SE-1 and SE-4 contain >98% styrene (mole-%) and so changes in composition with conversion are small (as already shown in section 4.2.4). Corrections according to equation 4.24 have a negligible effect on this data, since $[M_2]/[M_1]$ is so small for these cases.

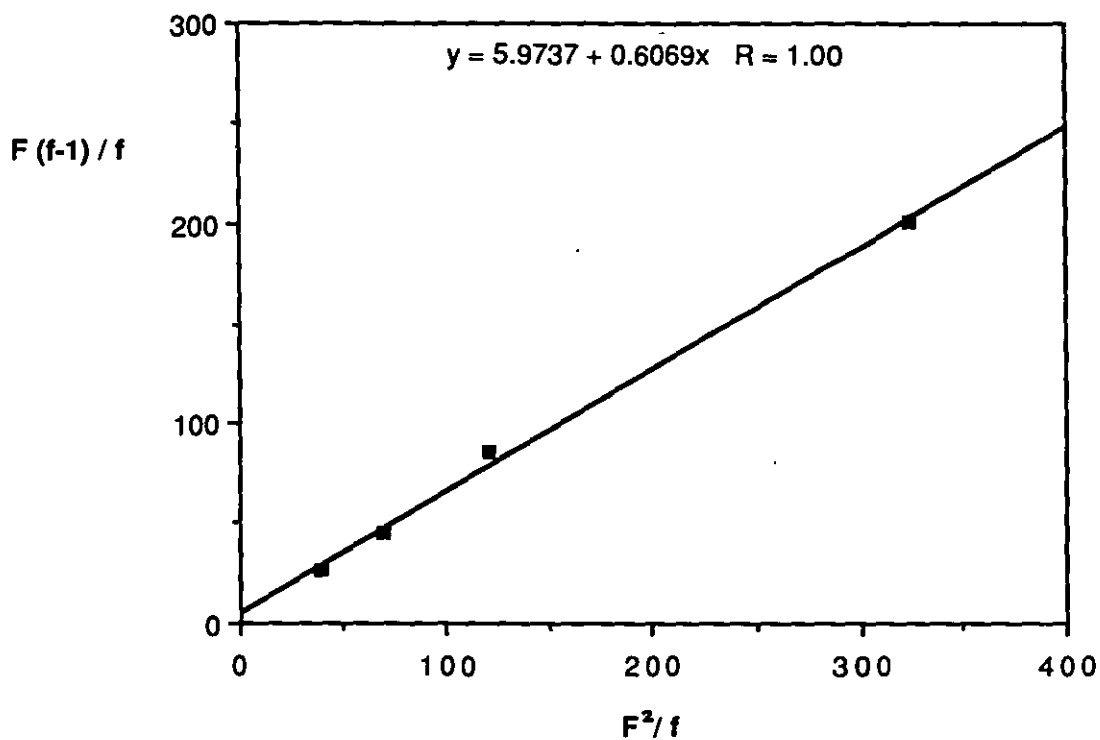
4.2.5.2 Linear least-squares methods

The Finemann-Ross [117] and Kelen-Tüdös [118] methods were used to determine reactivity ratios for copolymerizations where the

macromonomer conversion was restricted to approximately 15%. As already described in section 2.5.4.1, both methods involve the transformation of the copolymerization equation (equation 2.39) into forms which are linear with respect to reactivity ratios r_1 and r_2 (equation 2.44 and 2.46). Figures 4.36-4.39 illustrate the Finemann-Ross and Kelen-Tüdös relationships for the copolymerizations of styrene (M_1) with the various macromonomers (M_2). The reactivity ratio r_1 was obtained from the slope and the r_1 data are shown in table 4.26. The values predicted by the Finemann-Ross and Kelen-Tüdös methods are similar for the same set of data. It is also evident that all r_1 values are similar and that there is no significant dependence of r_1 on the molar mass or chemical composition of the macromonomer copolymerized. The corresponding data determined by the Jaacks method are also given in table 4.26 and it is evident that the reactivity ratios determined by linear least squares are similar to those obtained by the Jaacks method. This appears to justify the use of the Jaacks analysis and the assumption that r_2 can be neglected in the macromonomer copolymerizations. In some cases, determinations of r_2 from the intercept in figures 4.36 to 4.39 resulted in negative values, which is a physical impossibility. Values of r_2 are not quoted because they are meaningless as a result of the huge error involved in their determination. Any slight change in the slope of the Finemann-Ross or Kelen-Tüdös relationships will produce a large difference in r_2 determined from the intercept. The source of this error is the big difference between the styrene and macromonomer mole fractions in both the feed and the copolymer. Meaningful values of r_2 cannot be determined in macromonomer (M_2) copolymerizations by the Finemann-Ross or Kelen-Tüdös methods, except when the macromonomer molar masses are very low and/or when the mole fraction of macromonomer in the feed and the copolymer are much higher. However, it is thought that r_1 can be determined from the slope with some degree of confidence [86].

FIGURE 4.36 REACTIVITY RATIO DETERMINATION FOR THE COPOLYMERIZATIONS OF MACROMONOMER PMMA-15MP WITH STYRENE

(a) FINNEMANN-ROSS PLOT



(b) KELEN-TUDOS PLOT

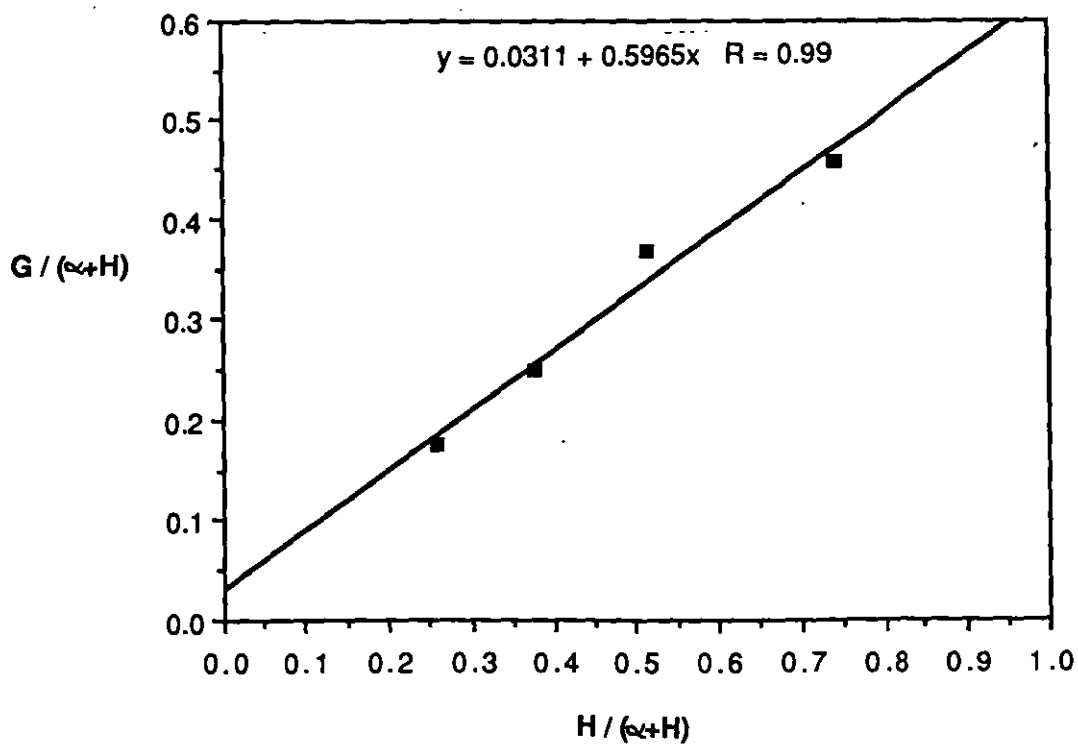
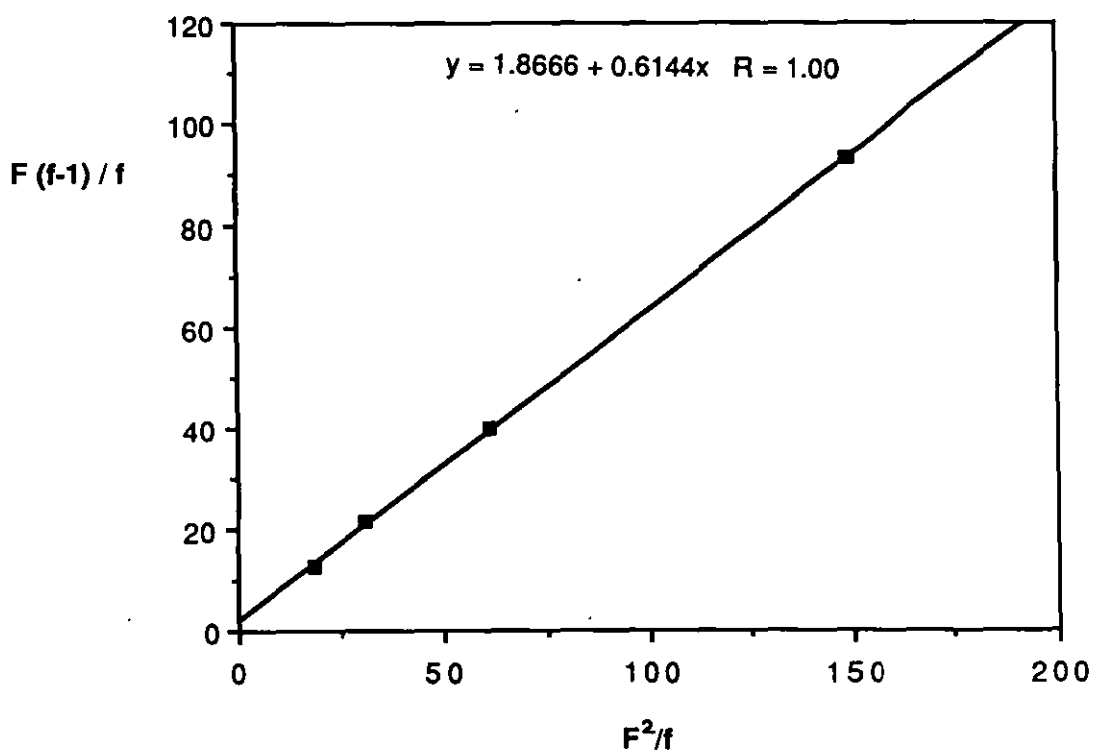


FIGURE 4.37 REACTIVITY RATIO DETERMINATION FOR THE COPOLYMERIZATIONS OF MACROMONOMER PMMA-16MP WITH STYRENE

(a) FINNEMANN-ROSS PLOT



(b) KELEN-TÜDOS PLOT

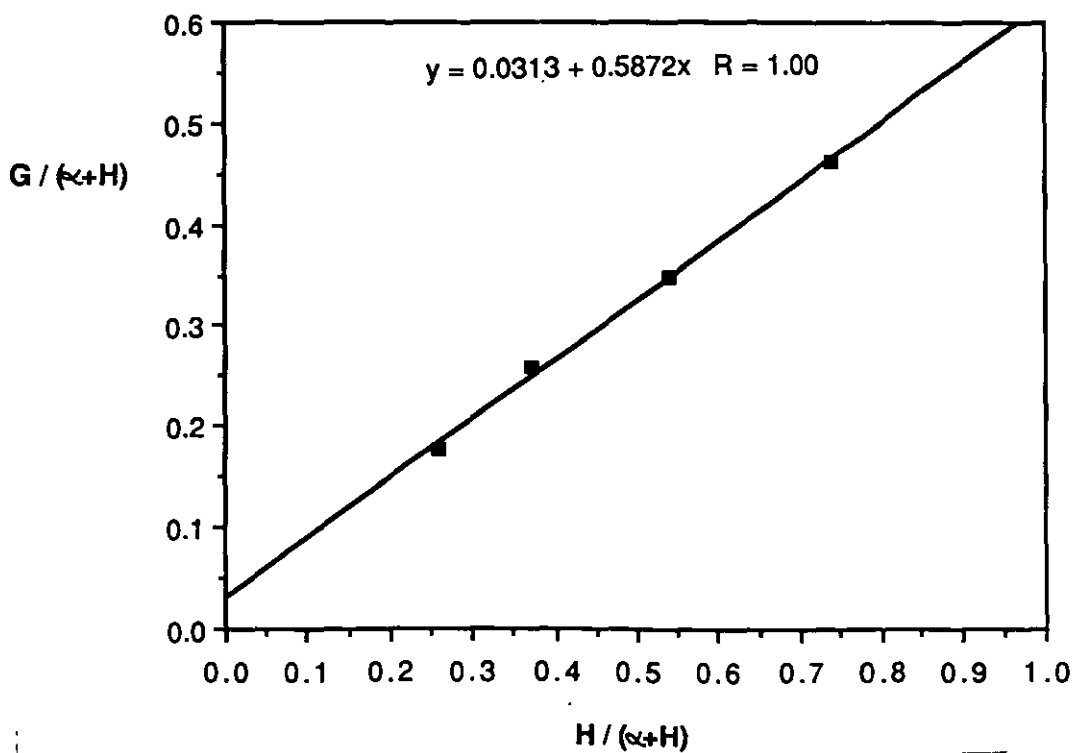
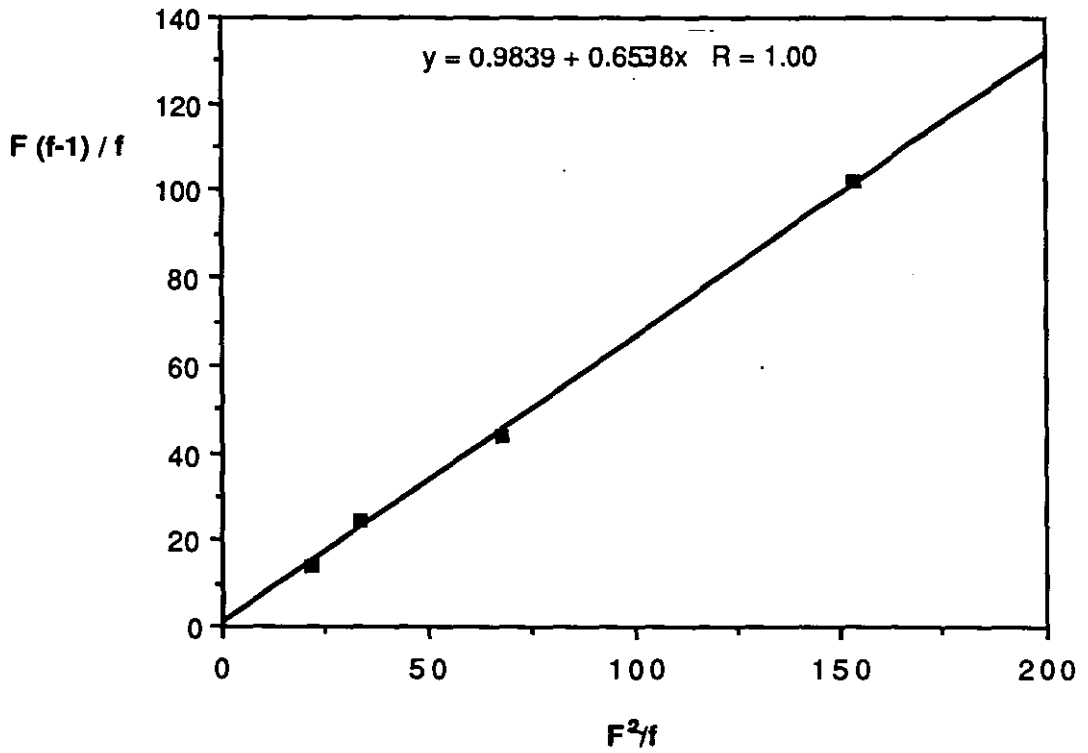


FIGURE 4.38 REACTIVITY RATIO DETERMINATION FOR THE COPOLYMERIZATIONS OF MACROMONOMER PEHA-40MP WITH STYRENE

(a) FINNEMANN-ROSS PLOT



(b) KELEN-TÜDOS PLOT

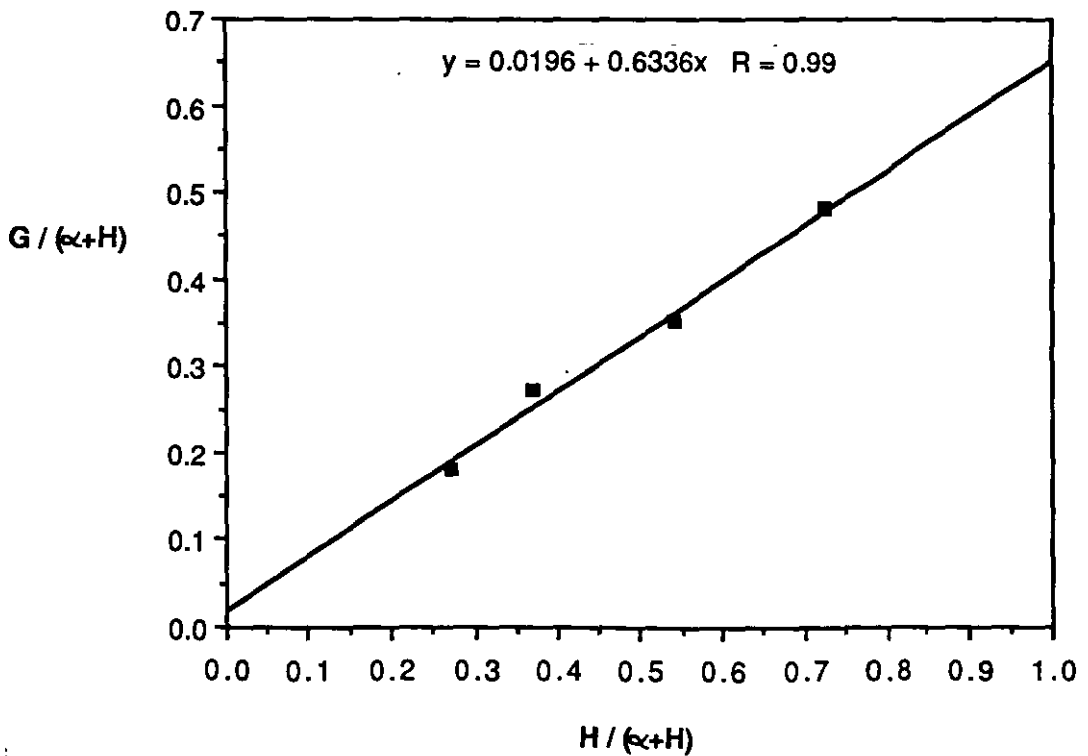
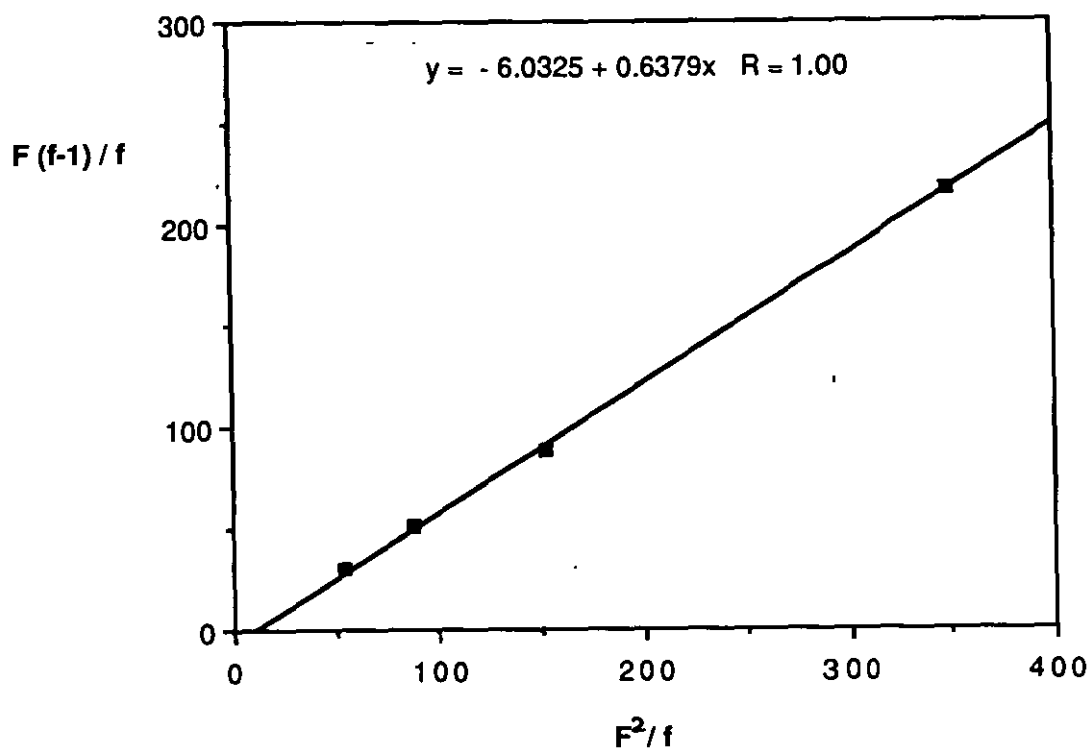


FIGURE 4.39 REACTIVITY RATIO DETERMINATION FOR THE COPOLYMERIZATIONS OF MACROMONOMER PEHA-45MP WITH STYRENE

(a) FINNEMANN-ROSS PLOT



(b) KELEN-TÜDOS PLOT

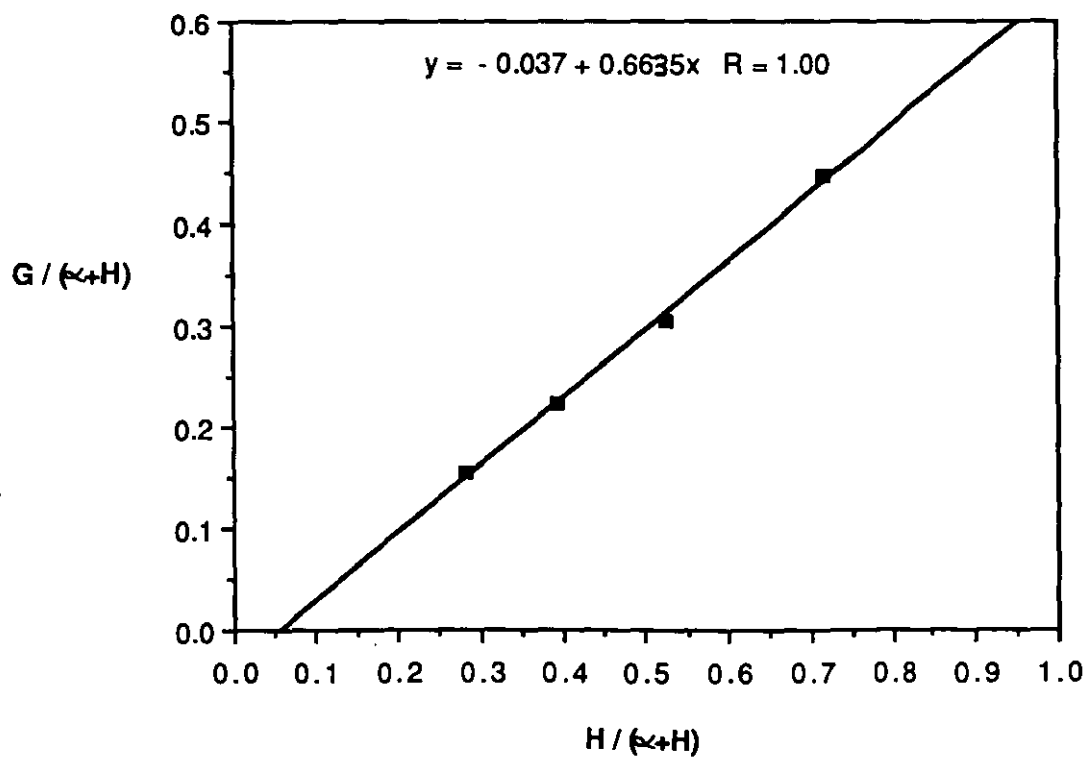


TABLE 4.26 REACTIVITY RATIOS (r_1) OBTAINED BY VARIOUS METHODS
FOR THE COPOLYMERIZATIONS OF STYRENE (M_1) WITH
MACROMONOMERS (M_2)

TYPE	MACROMONOMER M_2	r_1	r_1	$r_1(\text{real})$
	$\bar{M}_n \times 10^{-3}$ g.mol ⁻¹	FINNEMANN-ROSS	KELEN-TUDOS	JAAKS
PMMA-15MP	2.94	0.61	0.60	0.67
PMMA-16MP	1.42	0.61	0.59	0.67
PEHA-45MP	3.29	0.64	0.66	0.68
PEHA-40MP	1.62	0.65	0.63	0.59

4.2.5.3 Errors in the estimation of reactivity ratios

Errors in the estimation of reactivity ratios [119] can arise from the choice of mathematical model, the estimation procedure used or experimental practices and procedures. These will all be considered in turn.

(i) The choice of mathematical model.

The mathematical model used must be correct, otherwise parameters obtained are meaningless. The Finemann-Ross, Kelen-Tüdös and Jaacks methods for determining reactivity ratios are all based on the copolymerization equation (equation 2.39). This is a differential equation and, as such, represents the instantaneous behaviour of a copolymerization. This equation can be used provided that the copolymerizations are performed to a sufficiently low level of conversion that the monomer composition is essentially unchanged. In the copolymerization of conventional monomers, the conversion is typically 5% or less [122]. As a result of experimental problems in removing unreacted macromonomer so that copolymer compositions could be analysed, the minimum macromonomer conversion was significantly higher than this, approximately 15%. However, the use of the instantaneous differential copolymerization equation is vindicated in macromonomer copolymerizations at this conversion level as a consequence of the very small molar concentrations of macromonomer involved. This results in a small composition drift with conversion (even up to 40% conversion, as shown in section 4.2.4). The copolymerization equation is also based on the terminal model, where the basic assumption is that the reactivity of a propagating radical depends only upon the monomer unit in the copolymer chain on which the radical is located. Therefore, it has been implicitly assumed that the terminal model applies. This begs the question of how suitable the terminal model is for representing the copolymerizations of styrene with methacrylate-terminated PMMA or PEHA macromonomers. In simplified terms, these copolymerizations are essentially between styrene and a

methacrylate with an exceptionally long alkyl group. If the effect of this chain on the methacrylate reactivity is negligible, then the reaction of styrene with methyl methacrylate can be taken as a model copolymerization. Since Mayo and Lewis [114] originally proposed the terminal model and the copolymerization equation to describe their experimental work on the copolymerization of styrene and methyl methacrylate, their use in describing the copolymerization of styrene with methacrylate-terminated macromonomers appears justified. Indeed, the copolymerization of styrene and methyl methacrylate is the most measured system and a large amount of experimental work has been performed on it based on the terminal model [184]. The main problem in using the terminal model for the macromonomer copolymerizations under study is that the graft copolymer molar masses produced were quite low. In the derivation of the copolymerization equation, it is assumed that polymer molar masses are high resulting in the negligible consumption of monomer in initiation and termination reactions in comparison to propagation. Therefore, these reactions are likely to have some effect on the reactivity ratios determined for the macromonomer copolymerizations, as a result of the low molar masses produced. It is also recognized that compositional data alone is often inadequate for discriminating between models such as the terminal and penultimate models. It has been predicted and shown that comonomer sequence distributions are much more sensitive to the chain growth process [124,185]. Even for the copolymerization of styrene and methyl methacrylate which has been shown to conform to the terminal model by composition measurements, Fukuda et al [186] have calculated absolute propagation and termination rate constants which are inconsistent with the predictions of the terminal model and have postulated a penultimate unit effect.

(ii) The choice of estimation procedure.

It has been suggested that linear least squares techniques for determining reactivity ratios are statistically invalid

[113,122]. The problem lies in the transformation of the copolymerization equation into a linear form in terms of r_1 and r_2 . Considering the Finemann-Ross equation, both the independent variable F^2/f and the dependent variable $F(f-1)/f$ are fairly complicated functions of the feed and copolymer compositions. Since it is reasonable to expect that there will be a small error in the feed composition and a larger error in the copolymer composition, the linearization has the following consequences [119]. Firstly, the assumptions made using linear least squares, that there are no errors in the independent variable and that the dependent variable has constant variance with normally distributed and statistically independent random errors, are unlikely. Secondly, the linear forms are asymmetrical with respect to the definition of which monomer is M_1 and which is M_2 . Therefore, the re-indexing of monomers can lead to different values of r_1 and r_2 [122]. However, such re-indexing for the copolymerizations of styrene with PMMA/PEHA macromonomers was found to have a negligible effect on the magnitude of the styrene reactivity ratios quoted in table 4.26. The Kelen-Tüdös equation has a further deficiency in that both the independent and dependent variables can be expected to be correlated because of the common denominator $(\alpha+H)$. As a result of these problems, the r_i reactivity ratios quoted in table 4.26 from these methods can only be expected to be rough estimates. O'Driscoll and Reilly [122] claim that linear least squares cannot be expected to give good estimates of reactivity ratios from data containing significant errors. Tidwell and Mortimer [119,20] also predicted that linear least squares techniques can only give approximate estimates. They also state that these techniques are inadequate for obtaining accurate reactivity ratios since it is difficult to obtain valid expressions for the precision and errors in the results. This is because both the independent and dependent variables both contain polymer composition. Tidwell and Mortimer [119] suggested that non-linear least squares analysis is a better technique because it weights the data properly and gives some idea of precision. They

pointed out that the error associated with the point estimates of r_1 and r_2 was a joint error best expressed as a joint confidence region. Hill and O'Donnell [187] also claim that non-linear least squares analysis allows the best values of reactivity ratios to be obtained. Leicht and Fuhrmann [184] have calculated reactivity ratios by non-linear and linear least squares methods for existing data for the copolymerizations of styrene and methyl methacrylate. They showed that r_1 and r_2 depended on the calculation method. By choosing the size of the area of confidence limits as the criterion for the quality of results, they showed that non-linear least squares was the most precise technique, with the Kelen-Tüdös method being more precise than the Finnemann-Ross method.

Tidwell and Mortimer [119,120] also suggested that improved precision in the determination of reactivity ratios could be obtained by proper experimental design. They suggested that, instead of performing a set of experiments where the monomer feed ratios are varied over a range (the empirical design scheme), a repeated number of experiments should be performed from a statistical basis and the two optimum experimental regions are defined by molar feed compositions already given in section 2.5.4.2 by equations 2.47 and 2.48. Tidwell and Mortimer used the Finnemann-Ross technique to obtain the initial estimates of r_1 and r_2 and then performed non-linear least squares analysis on data defined by equations 2.47 and 2.48. McFarlane et al [188] have compared linear and non-linear least squares procedures. They concluded that linear least squares methods can give reactivity ratios which are precisely as good as those obtained by non-linear least squares methods, providing that the experiments are designed according to equations 2.47 and 2.48. However, if an empirical design scheme is followed, then non-linear least squares always gives the more precise analysis.

The conditions required by equations 2.47 and 2.48 are extremely difficult to meet in macromonomer copolymerizations. If one

takes the reactivity ratios of styrene (M_1 , $r_1 = 0.54$) and methyl methacrylate (M_2 , $r_2 = 0.46$) as model values for the copolymerization of styrene with methacrylate-terminated macromonomers, then $F_a = 0.79$ and $F_b = 0.16$. For a macromonomer with a molar mass of $3000 \text{ g} \cdot \text{mol}^{-1}$, F_a corresponds to 96.3% macromonomer by weight in the feed and F_b corresponds to 99.4% macromonomer by weight. It has already been shown that copolymers resulting from >50% by weight of macromonomer in the feed cannot be characterized correctly, since it is very difficult to remove unreacted macromonomer in these cases. If such copolymers could be synthesized, there is also the problem of accurately measuring the small amount (by weight) of styrene comonomer in both the feed and the resulting copolymer. Such problems apply to many of the macromonomer copolymerizations reported in the literature. This is reflected by the fact that the number of systems where both r_1 and r_2 are reported is very limited. The assessment of extremely low contents of comonomer units in graft copolymers have been achieved in a few cases by using a characterization technique which is specific to comonomer units. For example, Asami et al [91] have used UV spectroscopy to measure compositions of poly(2-vinylnaphthalene)-graft-poly(tetrahydrofuran) copolymers. Such methods still require the separation of unreacted macromonomers, which can be very difficult when the feed compositions are rich in macromonomer. However, this problem can be overcome by determining monomer conversions in order to obtain copolymer compositions, rather than isolating copolymers to measure their compositions directly. Such a method has been used by Nabeshima and Tsuruta [110], who measured comonomer and macromonomer conversions using gas chromatography and UV spectroscopy, respectively. However, there are few such examples and only values of the comonomer reactivity ratio r_1 have been extensively reported in the literature. Most of these determinations have been performed using either the Jaacks simplification or linear least squares analysis, despite their shortcomings.

(iii) Experimental practices.

Imprecise polymer characterization will result in less precise values of the reactivity ratios since errors in the polymer composition will be higher. For the production of graft copolymers, the presence of unreacted macromonomers/comonomers or the presence of homopolymers will produce incorrect compositions from spectroscopic techniques because they contain functional groups which are present in the graft copolymers. However, GPC has shown that unreacted macromonomers are removed and TLC has shown that PS homopolymer is not present and so these effects can be neglected. The effects of bias in polymer analysis on reactivity ratios by using different characterization techniques is well-known. For example, Grüber and Elias [189] analysed several different poly[styrene-co-(methyl methacrylate)] copolymers using five different analytical methods, namely IR, UV and ^1H NMR spectroscopies, elemental analysis and refractive index. They found that bias in the different procedures produced different r_1 and r_2 values. More recently, Leicht and Fuhrmann [184] have re-calculated reactivity ratios from the data of Grüber and Elias using non-linear least squares and have calculated confidence intervals. The confidence intervals reported suggested that IR spectroscopy was more precise than ^1H NMR. This was confirmed in the present study in section 4.2.4.1, where it was shown that IR characterization was used in preference to ^1H NMR for the calculation of various parameters, including reactivity ratios, because it was thought that the errors involved were smaller.

It is also possible for bias in the determination of feed compositions to produce imprecise reactivity ratios. The feed compositions used in the determination of reactivity ratios were those measured gravimetrically using a balance accurate to four decimal places and therefore the errors involved in this determination are likely to be negligible. However, this analysis was performed at room temperature. Since the comonomer

(styrene) and the copolymerization solvent (toluene) have a larger vapour pressure than the macromonomers, then the actual composition of the feed at the copolymerization temperature of 333 K may be different to that determined gravimetrically at room temperature. This has not been investigated but it may produce errors in the feed compositions quoted. It must be noted that the use of least squares techniques (both linear and non-linear) assumes that there are no errors in the independent variables (ie. feed composition). Therefore, there is a distinct possibility that this assumption is violated and a more accurate procedure for determining reactivity ratios would be the EVM method [121] (see section 2.5.4.3).

As a result of the various possible sources of error which have been discussed in sections (i), (ii) and (iii), the reactivity ratios r_1 determined previously from the Jaacks method or linear least squares methods can only be expected to be approximate estimates and are in no way intended to convey precise values.

4.2.6 MACROMONOMER REACTIVITY

For the copolymerizations of styrene (M_1) with macromonomers (M_2), r_1 is the styrene reactivity ratio defined by

$$r_1 = \frac{k_{11}}{k_{12}} \quad (4.25)$$

The relative macromonomer reactivities can be estimated by

$$\frac{1}{r_1} = \frac{k_{12}}{k_{11}} \quad (4.26)$$

This gives information about the rate constant for a propagating styrene radical adding macromonomer in comparison to the rate constant for the same radical adding styrene. Reciprocal r_1 values determined by the Jaacks, Finemann-Ross and Kelen-Tüdös methods for the copolymerization of styrene with methacrylate-

terminated PMMA and PEHA macromonomers are shown in table 4.27. The data determined for each method are in good agreement considering the possible errors discussed in the previous section. From these $1/r_1$ values it can be seen that the accessibility of the macromonomer end-group is not affected by the chain to which it is attached, i.e. the macromonomer reactivities are independent of their chain lengths and whether the macromonomer chains are PMMA or PEHA. Since all macromonomers copolymerized contain a terminal methacrylate, the copolymerizations can be considered as being between methacrylates containing exceptionally long ester groups with styrene. Therefore, copolymerizations of styrene (M_1) with conventional methacrylates (M_2) can be considered as model copolymerizations and $1/r_1$ values for such systems are reproduced in table 4.28. All data was taken from Greenley's work [190], where existing literature data was re-calculated according to the Kelen-Tüdös method. For some comonomer pairs in table 4.28, a range of data is given, reflecting differences in values that Greenley obtained from various sources. These values compare favourably to the data in table 4.27 for the macromonomer reactivities. Therefore, it appears that the reactivities of methacrylate-terminated macromonomers PMMA-15MP, PMMA-16MP, PEHA-40MP and PEHA-45MP towards growing polymer radicals with terminal styrene units are similar to the reactivities of conventional methacrylates towards the same radicals. Therefore, in these cases, the macromonomer reactivities are governed by the resonance, steric and polar effects associated with the chemical structure of the end-group. Any effect of the macromonomer chain lengths on their reactivities due to excluded volume, compatibility or solvent effects (section 2.6.4.2) is not apparent. This agrees with many reports where macromonomer reactivity has been shown to be similar to conventional monomers (see section 2.6.4.1). It is the ability of the PMMA or PEHA macromonomers to behave like conventional methacrylates in their copolymerizations, which enables facile control of graft copolymer composition as described in section 4.2.4. The determination of macromonomer

TABLE 4.27 1/r₁ VALUES CALCULATED BY VARIOUS METHODS FOR THE COPOLYMERIZATIONS OF STYRENE (M₁) WITH MACROMONOMERS (M₂)

MACROMONOMER M ₂ TYPE	$\bar{M}_n \cdot 10^{-3}$ g.mol ⁻¹	1/r ₁	1/r ₁	1/r ₁
		FINNEMANN-ROSS	KELEN-TÜDOS	JACOBS
PMMA-15MP	2.94	1.64	1.67	1.49
PMMA-16MP	1.42	1.64	1.69	1.49
PEHA-45MP	3.29	1.56	1.52	1.67
PEHA-40 MP	1.62	1.54	1.59	1.49

TABLE 4.28 REACTIVITY RATIOS FOR THE COPOLYMERIZATIONS OF STYRENE (M₁) WITH CONVENTIONAL METHACRYLATES (M₂)
[190]

MONOMER M ₂	r ₁	1/r ₁
methyl methacrylate	0.41-0.62	1.61-2.44
ethyl methacrylate	0.55-0.67	1.49-1.82
propyl methacrylate	0.57	1.75
isopropyl methacrylate	0.47-0.5	2.0-2.13
butyl methacrylate	0.52-0.74	1.35-1.92
t-butyl methacrylate	0.55	1.82
hexyl methacrylate	0.58	1.72
cyclohexyl methacrylate	0.59	1.69
octyl methacrylate	0.56-0.65	1.54-1.79
dodecyl methacrylate	0.53	1.89

reactivities by the use of equation 4.26 is typical of many studies in the literature where only r_1 has been determined.

There are several reports in the literature concerning the reactivity of polymethacrylate macromonomers. Ito et al [103] have copolymerized methacrylate-terminated poly(stearyl methacrylate) macromonomers ($\bar{M}_n=2.5-4.5 \times 10^3 \text{g.mol}^{-1}$) with methacrylates in benzene and Tsukahara et al [102] have copolymerized various methacrylate-terminated polymethacrylate macromonomers (methyl, ethyl, butyl, and lauryl derivatives with $\bar{M}_n=2.5-7.0 \times 10^3 \text{g.mol}^{-1}$) with methyl methacrylate and methacrylic acid in tetrahydrofuran. In both cases, by plotting the copolymer compositions versus comonomer feed compositions, it was found that these copolymerizations were azeotropic over a wide range of compositions with $r_1 \sim r_2 \sim 1.0$. Therefore, these polymethacrylate macromonomers were found to behave like conventional methacrylates and this is in agreement with the present study. However, these copolymerizations differ from the present study in that both the grafts and the backbones have similar chemical compositions. Therefore, although these examples also confirm the absence of excluded volume effects, any possible thermodynamic repulsive interactions are much weaker than in the copolymerization of PMMA or PEHA macromonomers with styrene. It is well-known that PS and PMMA are incompatible in the bulk state or in concentrated solutions [191] and, therefore, it is possible for thermodynamic repulsive interactions to affect macromonomer reactivity. There are a number of reports in the literature where methacrylate-terminated PS macromonomers have been copolymerized with methacrylates. These result in polymethacrylate-graft-polystyrene copolymers and the chemical natures of the backbone and grafts are reversed in comparison to the PS-graft-PMMA copolymers prepared in this work. However, the copolymerizations are similar in that they involve similar possible thermodynamic repulsive interactions. Ito et al [70] copolymerized a methacrylate-terminated PS macromonomer (M_2 , $\bar{M}_n = 3.2 \times 10^3 \text{g.mol}^{-1}$) with HEMA (M_1) in dimethylformamide as solvent.

Only r_1 was determined using the Finemann-Ross and Kelen-Tüdös methods and from this it was found that the macromonomer showed a lower reactivity than methyl methacrylate. However, this conflicts with the work of Schulz and Milkovich [152], who used the Jaacks method to find that the reactivity of a methacrylate-terminated PS macromonomer ($\bar{M}_n=11.0 \times 10^3 \text{g.mol}^{-1}$) in a solution copolymerization with MMA, was similar to conventional methacrylates. This was confirmed by Tsukahara et al [156] who copolymerized a methacrylate-terminated PS macromonomer (M_2 , $\bar{M}_n=12.4 \times 10^3 \text{g.mol}^{-1}$) with styrene or MMA (M_1) using benzene as a solvent. Using both the Jaacks simplification and the Finemann-Ross method to determine r_1 , it was shown that the macromonomer reactivity was similar to conventional methacrylates. It was also predicted that partial segments of PS and PMMA would be compatible at a concentration of 33.3% (w/v) in benzene, providing that the degree of polymerization was less than 110 (equivalent to PMMA $\bar{M}_n=11.0 \times 10^3 \text{g.mol}^{-1}$ and PS $\bar{M}_n=11.4 \times 10^3 \text{g.mol}^{-1}$). In the present work, the total monomer concentration was similar, approximately 30%(w/v) in toluene. As previously shown in section 4.2.4, the maximum PMMA graft length was $\bar{M}_n=3.29 \times 10^3 \text{g.mol}^{-1}$ and the maximum average PS segment length was $\bar{M}_n=7.0 \times 10^3 \text{g.mol}^{-1}$, which are significantly lower than the limits predicted by Tsukahara et al [156] for the interacting segments to remain compatible. Therefore, from these predictions, the PMMA macromonomer and propagating PS segments should extensively interpenetrate within the time scale of the homogeneous solution copolymerization and the absence of any incompatibility effect can be predicted. The copolymerization of PEHA macromonomers with styrene represents a novel study. However, since PEHA has a significantly lower glass transition temperature (T_g) than PMMA, the absence of any incompatibility effect for this system can also be expected. For high molar mass polymers, $T_g(\text{PMMA}) = 378 \text{ K}$ and $T_g(\text{PEHA}) = 223 \text{ K}$ [192] but the actual T_g for the macromonomers is likely to be substantially lower as a result of their low molar masses.

Toluene is a good solvent for PS, PMMA and PEHA and so any effects on the PMMA or PEHA macromonomer reactivity due to preferential solvency of the backbone or graft segments is not apparent. The nature of the solvent is extremely important. This has been illustrated by Tsukahara et al [157] for the copolymerization of methacrylate-terminated PS macromonomers ($\bar{M}_n=12.4 \times 10^3 \text{g.mol}^{-1}$) with MMA in cyclohexane, a good solvent for PS (at the polymerization temperature) but a poor solvent for PMMA. The macromonomer reactivity was appreciably reduced in comparison to its reactivity in benzene, a common good solvent for both components. This was explained by the decrease in interpenetration of the PS and PMMA segments due to the asymmetric nature of the cyclohexane for the different polymeric components.

The comonomer reactivity ratio r_1 has mostly been the parameter used to determine the reactivities of PS macromonomers in their copolymerizations with methacrylates reported in the literature and previously discussed. However, there is one example where both r_1 and r_2 have been determined in such systems. Takaki et al [193] copolymerized styryl-terminated PS macromonomers (M_2 , $\bar{M}_n=3.0-6.2 \times 10^3 \text{g.mol}^{-1}$) with MMA (M_1) in benzene. Copolymer compositions were determined from the extent of conversion of both macromonomer and comonomer by GPC and IR, respectively. The determination of both r_1 and r_2 (by the Fineman-Ross method) was possible since small amounts of comonomer could be determined accurately because the IR characterization was specific to comonomer. For the macromonomer with $\bar{M}_n=3.0 \times 10^3 \text{g.mol}^{-1}$, r_1 was comparable to conventional model copolymerizations whereas r_2 was lower. However, for the macromonomer with $\bar{M}_n=6.0 \times 10^3 \text{g.mol}^{-1}$, both r_1 and r_2 were lower than model copolymerizations. These results were similar to those achieved by Asami et al [91], another example of where both r_1 and r_2 have been determined. For the copolymerization of poly(tetrahydrofuran) macromonomers (M_2) with 2-vinylnaphthalene (M_1), r_1 was found to be similar to conventional copolymerizations whereas r_2 was significantly lower. This was explained as follows. Since $r_1 = k_{11}/k_{12}$ and r_2

= k_{22}/k_{21} , the copolymerization of macromonomer M_2 with a 'small' conventional comonomer M_1 depends upon the following reactions:

k_{11} (branched or linear) polymer radical + small comonomer

k_{12} (branched or linear) polymer radical + macromonomer

k_{22} ω -branched polymer radical + macromonomer

k_{21} ω -branched polymer radical + small comonomer

The reactions concerned with k_{11} and k_{21} are between growing polymer radicals and small comonomers and the concept of equal reactivity of growing radicals seems valid in these cases. However, k_{12} and k_{22} may be expected to be much lower than those in model copolymerizations because reactions take place between polymer chains. The results suggest that the hindering effect on k_{22} is higher than that on k_{12} because k_{22} involves a ω -branched polymer radical reacting with a macromonomer. Effectively, this causes the position of the growing radical to be in the middle of the polymer chain. Therefore, although it has been calculated earlier in this section that the methacrylate-terminated PMMA or PEHA macromonomer reactivities are similar to conventional methacrylates, this is only in consideration of the reactivity of the macromonomers towards a growing radical with a terminal styrene unit. It is possible that macromonomer reactivities are lower towards propagating chains with terminal macromonomer units (ie. ω -branched radicals) and this would result in r_2 being lower than in the copolymerization of conventional monomers. However, this has not been proven because determination of r_2 was found to be difficult, as discussed in section 4.2.5.

4.3 THE PREPARATION OF NON-AQUEOUS DISPERSIONS

4.3.1 GRAFT COPOLYMERS USED AS STABILIZERS

Having shown that graft copolymer chemical compositions and physical architectures could be readily altered, PS-graft-PEHA copolymer syntheses were performed on a larger scale in order to produce sufficient quantities for use as steric stabilizers in the dispersion polymerization of MMA. Therefore, the syntheses of macromonomers PEHA-40MP and PEHA-45MP were repeated producing macromonomers PEHA-51MP and PEHA-50MP respectively (see sections 4.1.1.2 and 4.1.3.2). The characterization of PS-graft-PEHA copolymers SE-21 to SE-26 resulting from the copolymerization of these macromonomers with styrene is shown in table 4.29. These represent essentially repeat copolymerizations of SE-1 to SE-6 respectively, shown in table 4.22, section 4.2.3.3. The reaction conditions used were exactly the same producing approximately 40% macromonomer conversion, with the only difference that the total weight of reagent and solvent was 40g, compared to 15g previously. The same thorough characterization of these copolymers was performed as for previous samples and discussed in sections 4.2.1-4.2.3. PS homopolymer contamination was found to be negligible in all cases using TLC and copolymers were characterized by IR and GPC. The ASB given in table 4.29 is the ratio of backbone/grafts and the parameters $\bar{M}_n(\text{backbone})$, \bar{N}_g and $\bar{M}_n(\text{PS segment})$ are equivalent to those defined previously in section 4.2.4. These were controlled in an identical manner to that described in section 4.2.4.

4.3.2 POLY(METHYL METHACRYLATE) PARTICLES OBTAINED FROM DISPERSION POLYMERIZATION

The dispersion polymerization of MMA was performed using the PS-graft-PEHA copolymers summarized in table 4.29. Various polymerization procedures were used, including a one-stage and several

TABLE 4.29 PS-graft-PEHA COPOLYMERS FOR USE AS STERIC STABILIZERS IN THE DISPERSION POLYMERIZATION OF MMA

CODE	MACROMONOMER ¹ TYPE	$\bar{M}_n^2/$ 10^3 g.mol^{-1}	WEIGHT FRACTION OF MACROMONOMER (i.e. PEHA)		COPOLYMER ASB	COPOLYMER MOLAR MASSES ⁴					$\bar{M}_n(\text{backbone})$ $/10^3 \text{ g.mol}^{-1}$	\bar{N}_g	$\bar{M}_n(\text{PS segment})$ $/10^3 \text{ g.mol}^{-1}$
			FEED ²	COPOLYMER ³		$\bar{M}_{\text{Peak}}/10^3$	$\bar{M}_n/10^3$	$\bar{M}_w/10^3$	$\bar{M}_p/10^3$	\bar{M}_w/\bar{M}_n			
SE-21	PEHA-S1MP	1.53	0.26	0.32	2.1/1	34.7	17.2	35.0	24.6	2.04	11.7	3.6	2.5
SE-22	PEHA-S1MP	1.53	0.37	0.45	1.2/1	38.9	20.9	40.0	28.9	1.92	11.4	6.1	1.6
SE-23	PEHA-S1MP	1.53	0.50	0.56	0.8/1	35.5	18.0	34.5	24.9	1.92	7.9	6.6	1.04
SE-24	PEHA-SOMP	3.03	0.25	0.32	2.1/1	35.5	16.6	34.3	23.8	2.07	11.3	1.8	4.0
SE-25(a)	PEHA-SOMP	3.03	0.37	0.46	1.2/1	39.8	19.6	36.9	27.0	1.88	10.7	2.9	2.7
SE-25(b)	PEHA-SOMP	3.03	0.38	0.49	1.04/1	33.0	15.6	31.3	22.1	2.01	8.0	2.5	2.3
SE-26	PEHA-SOMP	3.03	0.50	0.60	0.66/1	35.5	17.4	35.4	24.7	2.04	6.9	3.5	1.5

- N.B.
- (1) Macromonomer $\bar{M}_n = \text{graft } \bar{M}_n$. Macromonomer conversions approximately 40% in all cases.
 - (2) Determined gravimetrically. In all cases total $[M] = 30\% \pm 1\%$ (w/v) on toluene; $[AIBN] = 0.75\% \text{ } 0.05$ (w/w) on monomer
 - (3) Determined by IR characterization of isolated graft copolymers
 - (4) Determined by GPC characterization of isolated graft copolymers.

seed/feed methods which have already been described in detail in section 3.4. Tables 4.30-4.33 show the reaction conditions used for each dispersion polymerization. Hexane was the diluent in all cases during the polymerization, both the monomer and initiator concentrations remained the same (ie, $20 \pm 0.5\%$ (w/w) and $1.0 \pm 0.05\%$ (w/w) respectively) and the polymerization temperature was constant at 342 K. Table 4.30 summarizes the one-stage polymerizations, table 4.31 summarizes dispersions obtained by seed/feed method 1 and tables 4.32 and 4.33 summarize the dispersions obtained by both seed/feed methods 2 and 3, since these produced essentially the same results. This will be further discussed in section 4.3.3. The objectives were to obtain discrete, spherical particles with a small size and a narrow size distribution. These were used as criteria to determine the most suitable polymerization method (section 4.3.3) and the most effective graft copolymer stabilizer (section 4.3.4). Having determined these, the effect of varying the steric stabilizer concentration on particle size was studied (section 4.3.5). Tables 4.30-4.33 also summarize the morphology of the particles obtained by TEM after subjecting each dispersion to several redispersion cycles in n-heptane, as described in section 3.4.4. In particular, particle sizes, shapes and aggregation were all monitored directly from micrographs. Particle sizes were estimated by measuring the diameters of at least 100 individual particles on various micrographs taken from different parts of the grid. \bar{D}_n is the number average particle size given by the equation

$$\bar{D}_n = \frac{\sum N_i D_i}{\sum N_i} \quad (4.27)$$

where N_i is the number of particles with diameter D_i .

An indication of the breadth of the particle size distribution was given by the ratio \bar{D}_s/\bar{D}_n , where \bar{D}_s is given by the equation

$$\bar{D}_s = \frac{\sum N_i (D_i)^2}{\sum N_i D_i} \quad (4.28)$$

TABLE 4.30

DISPERSION POLYMERIZATION OF MMA USING A ONE-STAGE METHOD^{a, b}

DISPERSION NO	PS-graft-PEHA TYPE	STERIC STABILIZER CONCENTRATION /%(w/w)	MONOMER CONVERSION /%(w/w)	MMA PARTICLES			
				APPEARANCE	SIZE RANGE/ μm	$\bar{D}_n/\mu\text{m}$	\bar{D}_w/\bar{D}_n
D6	SE-21	5.1	-	Dispersion flocculated during polymerization.	-	-	-
D7	SE-22	5.0	73	Network of aggregated particles. Little definition of particles within aggregates.	-	-	-
D9	SE-23	5.0	65	Particle aggregates. Non-spherical, bridged particles well-defined within aggregates.	0.7-0.9 (particles) ~ 8 (aggregates)	-	-
D8	SE-24	5.0	58	Particle aggregates. Non-spherical, bridged particles well-defined within aggregates.	0.2-1.0 (particles)	-	-
D4	SE-25(a)	5.0	66	Discrete, spherical particles.	generally 0.7-0.9 a few 0.3-0.5	0.74	1.05
D5	SE-26	5.0	68	Discrete, spherical particles.	Two ranges 0.6-0.8 0.1-0.3	0.45	1.39

N.B. (a) $[\text{MMA}] = 20 \pm 0.5\%(\text{w/w})$; $[\text{AIBN}] = 1.0 \pm 0.05\%(\text{w/w})$

Stabilizer, monomer and initiator concentrations are based on the total weight (including hexane).

(b) Stabilizer dissolved in monomer. Solution added to hexane at 342 K. Initiator added after 5 minutes.

Total polymerization time = 2 hours.

TABLE 4.31

DISPERSION POLYMERIZATION OF MMA USING SEED/FEED METHOD 1a, b

DISPERSION NO	PS-graft-PEHA TYPE	STERIC STABILIZER CONCENTRATION / %/w	MONOMER CONVERSION /%(w/w)	PMMA PARTICLES			
				APPEARANCE	SIZE RANGE/ μm	$\bar{D}_n/\mu\text{m}$	\bar{D}_w/\bar{D}_n
D2	SE-24	5.1	-	Dispersion flocculated during polymerization.	-	-	-
D3	SE-26	5.0	75	Discrete particles.	0.05-0.5	0.20	1.29

N.B. (a) Total concentrations, $[\text{MMA}] = 20 \pm 0.5\%(\text{w/w})$; $[\text{AIBN}] = 1.0 \pm 0.05\%(\text{w/w})$.

Stabilizer, monomer and initiator concentrations are based on the total weight of material (including hexane).

(b) Stabilizer and initiator dissolved in monomer.

20% of this solution added to hexane at 342 K and polymerized for 1 hour to form seed.

Remaining solution added as a feed in 4 shots at 30 minute intervals. Polymerized for a further 2 hours after final addition; total polymerization time 4.5 hours.

TABLE 4.32

DISPERSION POLYMERIZATION OF MMA USING SEED/FEED METHODS 2 AND 3a, b, c
 (i) APPROXIMATELY CONSTANT STABILIZER CONCENTRATION

DISPERSION NO	PS-graft-PEHA TYPE	STERIC STABILIZER CONCENTRATION /%(w/w)	METHOD	MONOMER CONVERSION /(w/w)	PMMA PARTICLES			
					APPEARANCE	SIZE RANGE/ μm	$\bar{D}_n/\mu\text{m}$	\bar{D}_w/\bar{D}_n
D15	SE-21	5.0	2		Dispersion flocculated during polymerization.	-	-	-
D21A	SE-21	5.0	3	-	Dispersion flocculated during polymerization.	-	-	-
D16	SE-22	5.0	2	-	Dispersion flocculated during polymerization.	-	-	-
D21B	SE-22	5.0	3	81	Particle aggregates. Poor resolution of fused particles within aggregates.	1-6 (aggregates)	-	-
D18	SE-23	5.0	2	63	Particle aggregates. Non-spherical, bridged particles well-defined within aggregates.	0.2-0.6 (particles)	-	-
D22	SE-23	5.0	3	70		2-6 (aggregates)	-	-
D14	SE-24	5.0	2	85	Some discrete particles. Some well-defined particle aggregates.	0.2-0.6 (particles)	-	-
D20	SE-24	5.0	3	70				
D12	SE-25(a)	5.0	2	70	Discrete particles	0.1-0.35	0.24	1.07
D11	SE-25(a)	5.0	3	69		0.1-0.3	0.21	1.08
D10	SE-25(a)	5.0	3	65		0.1-0.25	0.19	1.04
D13	SE-26	5.0	2	70	Discrete particles	0.2-0.45	0.30	1.09
D19	SE-26	4.8	3	80		0.1-0.4	0.31	1.09

N.B. (a) Total concentrations, [MMA] = $20 \pm 0.5\%$ (w/w), [AIBN] = $1.0 \pm 0.05\%$ (w/w). Stabilizer, monomer and initiator concentrations are based on the total weight of material (including hexane).

(b) SEED/FEED METHOD 2. Hexane + stabilizer overnight at room temp. Seed MMA added (40% (w/w) of total). Temperature raised to 342 K, seed AIBN added (40% (w/w) of total) and polymerized for 1 hour. Feed MMA + AIBN added in one shot, polymerized for a further 2 hours (total time = 3 hours).

(c) SEED/FEED METHOD 3. As (b), apart from feed method. Feed added in 6 separate shots separated by 30 minute intervals. After final shot, polymerized for a further 1.5 hours. Total polymerization time = 5 hours. NB. D10 is the same as D11, apart from MMA + AIBN in seed amounts to 20% (w/w) rather than 40% (w/w) of total.

TABLE 4.33

DISPERSION POLYMERIZATION OF MMA USING SEED/FEED METHOD 3a, b
(ii) VARYING STABILIZER CONCENTRATION

DISPERSION NO	PS-graft-PEHA TYPE	STERIC STABILIZER CONCENTRATION /%(w/w)	MONOMER CONVERSION /%(w/w)	PMMA PARTICLES			
				APPEARANCE	SIZE RANGE/ μm	$\bar{D}_n/\mu\text{m}$	\bar{D}_3/\bar{D}_n
D23	SE-25(b)	1.0	73	Generally discrete particles. A few aggregates containing a small number of well-defined, spherical particles which do not appear bridged.	0.5 - 0.85	0.75	1.02
D24	SE-25(b)	3.1	77	Discrete particles.	0.2 - 0.5	0.39	1.07
D26	SE-25(b)	4.7	72	Discrete particles.	0.15- 0.35	0.27	1.05
D25	SE-25(b)	6.8	70	Discrete particles.	0.1 - 0.3	0.21	1.05

N.B. (a) Total concentrations, [MMA] = 20 \pm 0.5%(w/w), [AIBN] = 1.0 \pm 0.05%(w/w). Stabilizer, monomer and initiator concentrations are based on the total weight of material (including hexane).

(b) SEED/FEED METHOD 3. Hexane + stabilizer overnight at room temp. Seed MMA added (40% (w/w) of total). Temperature raised to 342 K, seed AIBN added (40% (w/w) of total) & polymerized for 1 hour. Feed added in 6 shots separated by 30 minute intervals. After final shot, polymerized for a further 1.5 hours. Total polymerization time = 5 hours.

\bar{D}_n and \bar{D}_w/\bar{D}_n were only determined for those dispersions where unaggregated, discrete particles were produced. Such dispersions were also analysed by UV spectroscopy (see section 4.3.6). The accuracy of \bar{D}_n , \bar{D}_w and \bar{D}_w/\bar{D}_n can be questioned for a number of reasons. The soluble PEHA stabilizing layer which surrounds the particles collapses on to the particle surface when the dispersion medium is removed. However, this contribution to particle diameter can be neglected since this layer thickness is likely to represent less than 2% of the diameter of the smallest particles. Errors can also arise from electrical fluctuations in the microscope, which can generate up to 5% error in the recorded magnification. A more fundamental source of error might result from a change in the sample during preparation of the microscope grids. If the particles were significantly swollen in the dispersion medium, removal of the the medium might be expected to change the particle size. However, it is not expected that PMMA particles are swollen by hexane or heptane. Depolymerization of polymer particles has also been reported under the rather hostile conditions of high vacuum and electron bombardment within an electron microscope [61].

4.3.3 THE EFFECT OF DISPERSION POLYMERIZATION METHOD ON PARTICLE SIZE

A polymerization temperature of 342 K was chosen for all polymerizations for the following reasons. According to Waldbridge [9], when the anchoring component of the stabilizer strongly associates with itself, a higher reaction temperature is necessary for the stabilizer to be effective in the dispersion polymerization. It was thought that 342 K would be high enough to allow graft copolymer stabilizer molecules to leave micellar associates and move freely into the solution (see figure 2.7, section 2.2.3, equilibrium move towards single molecules), but not too high so that the stabilizer was weakly adsorbed on to particle surfaces. This temperature would also produce a good

rate of initiator decomposition. The stabilizer concentration in the polymerizations was generally 5%(w/w), apart from a few examples where this concentration was varied. This was chosen following the work of Taylor [17], who demonstrated that whilst 2% (w/w) of a polystyrene-block-poly(dimethylsiloxane) stabilizer (PS-block-PDMS) was sufficient in stabilizing PS particles, 5% (w/w) was necessary to stabilize PMMA particles. Therefore, higher concentrations were required when the anchor component of the stabilizer was different in chemical composition to the dispersed phase. Although this represents a relatively high concentration, it was found that only up to 60% of this stabilizer was actually incorporated. This will be discussed further in section 4.3.6.

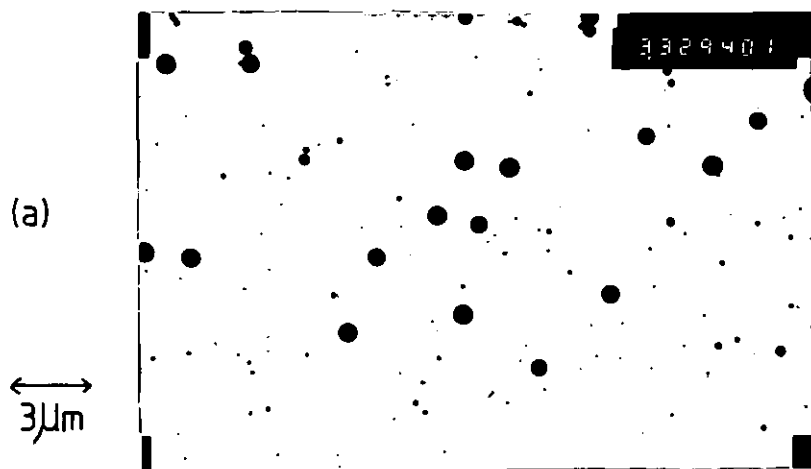
As described in section 2.2.4, dispersion polymerization begins in solution and growing oligomeric radicals associate with stabilizer. At a threshold molar mass, the oligomeric radicals precipitate and form particle nuclei which are prevented from flocculation by the action of the stabilizer. Since PMMA is very insoluble in aliphatic hydrocarbons such as hexane, the onset of particle formation is rapid and particle formation is normally completed very quickly. Once particles have formed, they absorb monomer from the diluent phase and polymerization within these particles follows bulk monomer kinetics [64]. Any radicals initiated in the diluent phase are then captured by existing particles before the radicals have reached the threshold molar mass required for precipitation. This suppresses solution polymerization and the formation of new particles. Therefore, provided that conditions do not change significantly, the number of particles should remain unchanged after initial particle formation is complete. Under such conditions, the formation of particles within a short time period and their subsequent growth without aggregation or renucleation should produce a uniform particle size. In this case, the sizes of the original nuclei control the final particle size. However, particle size was found to be markedly affected by the polymerization method. This

effect is best illustrated by comparing polymerizations where discrete particles were produced using the same stabilizer type and concentration. Figure 4.40 illustrates typical micrographs obtained from D5, D3 and D13 which were prepared using the one-stage, seed/feed 1 and seed/feed 2 methods respectively. The three dispersions were all prepared using stabilizer SE-26 at a concentration of 5.0% (w/w). In all micrographs shown in figure 4.40, the particles are spherical and discrete which suggests that uniform growth has occurred without aggregation. Comparing the average particle sizes produced, the one-stage method produced significantly larger particles (D5, $\bar{D}_n=0.45\mu\text{m}$) than either of the seed/feed methods (D3, $\bar{D}_n=0.20\mu\text{m}$ and D13, $\bar{D}_n=0.30\mu\text{m}$). The one-stage method (D5) produced essentially two ranges of particle sizes, namely, 0.7-0.8 μm and 0.1-0.3 μm . This suggests that renucleation occurred, i.e. a fresh crop of new particles was formed long after the first period of particle formation. Seed/feed method 1 (D3) produced a very wide range of particle sizes from 0.05 to 0.5 μm ($\bar{D}_s/\bar{D}_n = 1.29$). This suggests that particle formation continued over a long period of time, corresponding to a wide range of growth periods. However, seed/feed method 2 (D13) produced a fairly uniform particle size (range 0.2-0.45 μm , $\bar{D}_s/\bar{D}_n=1.08$). For this case, it does appear that particles were formed in a relatively short period of time and growth occurred without renucleation or aggregation. All of these differences can be explained either by changes in the solvency of the dispersion medium or the stabilizer concentration.

The process of particle formation is strongly influenced by the solvency of the medium for the polymer produced. For poor solvency, the threshold molar mass of the growing chain required for precipitation will be low and a high number of nuclei will be formed. At constant monomer concentration, each particle obtains less monomer and ends up smaller. However, for high solvency conditions, the threshold molar mass is higher and consequently, fewer nuclei are formed which grow larger. Since MMA is a solvent

FIGURE 4.40

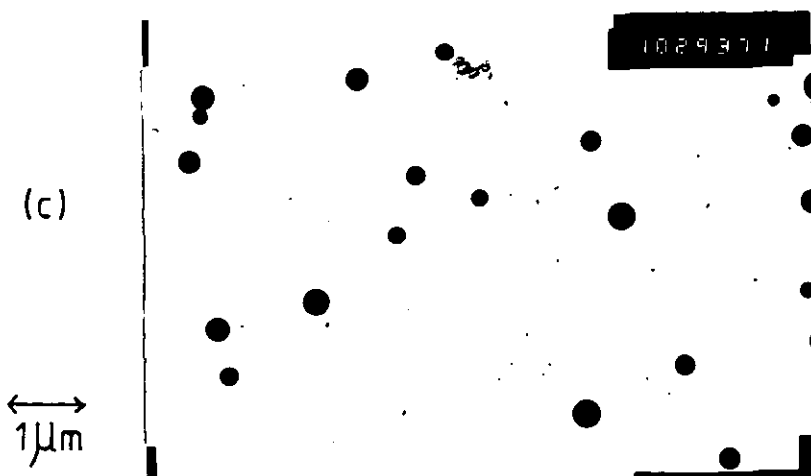
A COMPARISON OF PMMA PARTICLE MORPHOLOGY PRODUCED
BY DIFFERENT DISPERSION POLYMERIZATION METHODS
USING STABILIZER SE-26 (CONCENTRATION = 5.0%(w/w))



D5
ONE-STAGE



D3
SEED/FEED 1



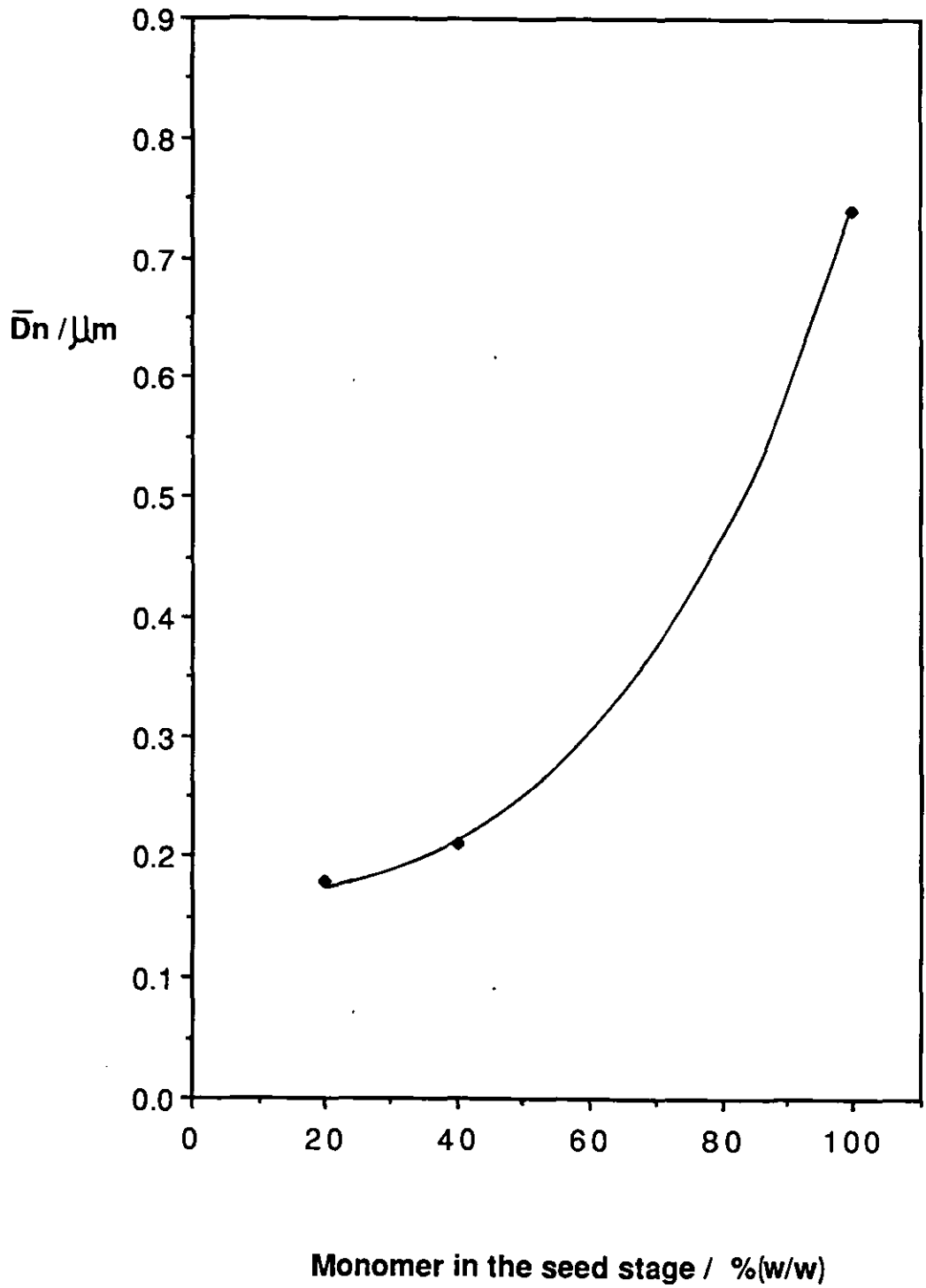
D13
SEED / FEED 2

for PMMA, higher monomer concentrations retard the onset of particle formation resulting in larger particles. This explains the larger particles produced by the one-stage process since at the beginning of the polymerization, the monomer concentration is significantly larger than in the seed/feed methods. However, there is also a further complicating factor in that solvency is likely to modify the operation of the stabilizer and its influence on the number of particles formed [9]. Higher solvency for the anchoring component probably reduces the tendency of the stabilizer to associate with the growing polymer chains during particle formation in addition to impairing the anchoring efficiency to particles already formed. Therefore, it is possible that instead of nucleation controlling final particle size that particle growth by coagulation controls the final particle size. This also explains the outcome of larger particles when the solvency of the medium is higher. For the one-stage polymerizations, the monomer concentration is high at the beginning of the polymerization and falls gradually as it is converted to polymer. Consequently, there is a reduction in the solvency of the medium and the conditions for precipitation of growing chains formed in solution change throughout the polymerization. Eventually, the solvency becomes poor enough for renucleation to occur later in the polymerization. An alternative explanation is that at the beginning of the polymerization, the anchoring efficiency of the stabilizer is impaired by the solvency conditions and this allows particles to aggregate forming larger particles. As polymerization proceeds, the anchoring efficiency improves and this causes renucleation, which is also favoured by the relatively low number of larger particles present. However, for seed/feed method 2 (D13), a small, fairly uniform particle size was produced, since the overall solvency of the medium for the particles and the anchoring component was lower and more consistent throughout the polymerization. Seed/feed method 3 produced essentially the same results as seed/feed method 2 (see table 4.32) although an example is not illustrated. This was surprising since in method 3, the feed of

monomer and initiator was added incrementally over a longer period of time. Therefore, the solvency of the medium was expected to be more consistent resulting in a narrower size distribution but this was clearly not the case. It is possible that there is a lower limit on the particle size uniformity as a result of the graft copolymer compositions; this is discussed further in section 4.3.4. The differences in the particle morphology produced by seed/feed method 1 in comparison to seed/feed methods 2 and 3 arise from the different procedures used in the addition of the stabilizer. In seed/feed method 1, the stabilizer was partitioned between the seed and the feed whereas in the other methods, all of the stabilizer was added in the seed. Method 1 produced a much broader particle size distribution as a result of the stabilizer concentration continually increasing as the feed was added. During the feed, the stabilizer concentration continually exceeds the amount required to protect the particles produced previously and this causes extensive renucleation throughout the polymerization. In summary, seed/feed methods 2 and 3 were preferred since smaller particles with a narrower size distribution were produced.

Generally, 40% (w/w) of the total monomer and initiator were used to form the seed in seed/feed polymerizations. Such a concentration was used in order to assist in solubilizing the stabilizers, since it was difficult to dissolve certain stabilizers in pure hexane (see section 4.3.4). However, one experiment was performed with a variable seed, namely D10 (table 4.32). The dependence of particle size on the percentage of total monomer in the seed stage is illustrated in figure 4.41. This compares the particle sizes of D10, D11 and D4 where the total monomer, initiator and stabilizer concentrations were identical. Although a degree of interpolation is required, it appears that particle size increases until a limiting value of $0.74\mu\text{m}$ is reached, equivalent to a one-stage process. Similar relationships have been achieved by Shakir [16] and Taylor [17] using block copolymer stabilizers. The reason for this effect is

FIGURE 4.41 THE EFFECT OF SEED MONOMER CONCENTRATION ON PMMA
PARTICLE SIZE IN DISPERSION POLYMERIZATION



due to the increase in the solvency of the medium with monomer concentration, which affects particle formation and the effectiveness of the stabilizer anchoring component as described earlier. It has been demonstrated that larger increases in particle size can be achieved when the solvency of the medium is high enough. In the stabilization of PMMA particles with poly(methyl methacrylate)-graft-poly(12-hydroxystearic acid) copolymers (PMMA-graft-PHSA), Antl et al [194] showed that particle size increased from 0.18-2.6 μ m as the monomer concentration was raised from 35-50% (w/w). For the dispersion polymerization of MMA in aliphatic hydrocarbons, particle growth is known to occur by the polymerization of absorbed monomer and polymerization follows bulk monomer kinetics. An auto-acceleration effect has often been observed and interpreted in terms of a diffusion controlled reaction of a polymeric radical trapped in a highly viscous polymer matrix (see theory section 2.2.5). However, Winnik et al [195] have shown that by adding solvents for PMMA particles prepared in aliphatic hydrocarbons, reaction rates were significantly slower. This was explained by two factors, an increasing amount of polymerization in solution followed by adsorption on to existing particles or solvent imbibed within particles reducing viscosity and thereby allowing an increased termination rate. Since the total monomer concentrations used here (20%(w/w)) are much lower than the solvent concentrations used by Winnik et al [195] (50%(w/w)), it is likely that most of the polymerization occurs in the polymer phase. Indeed, Shakir [16] has illustrated the existence of an autoacceleration effect for MMA dispersion polymerizations using exactly the same concentrations of reagents as this work, although a block copolymer stabilizer was used. In the present study, monomer conversions were high (60-80%, see tables 4.30-4.33) and unaffected by the monomer concentration at the beginning of the polymerization. Conversions were also independent of particle size (see table 4.33). This agrees with the work of Barrett and Thomas [64], confirming that there is no

dependence of polymerization rate on particle size.

4.3.4 THE EFFECT OF STABILIZER COMPOSITION ON PARTICLE MORPHOLOGY

The ability of graft copolymers to form micelles in a solvent which is selective for the backbone or grafts was discussed in section 2.2.3. It is thought that there is an equilibrium between unimer (molecularly dissolved copolymer) and micelles. Several experimental studies have shown that graft copolymers, in solvents selective for the grafts, form either micelles with a low association number <10 (ie. the number of molecules forming a micelle) or do not associate at all [59,196]. In the latter case, the graft copolymers assume a conformation of 'unimolecular micelles', in which the backbone forms a core and the grafts form a protective shell. An attempt was made at observing micelles of copolymer SE-26 by dissolving in hexane overnight at room temperature (5%(w/w)) and then using TEM to observe particles as for dispersions. Such a method has been used by Shakir [16] to observe block copolymer micelles in aliphatic hydrocarbons. However, it was found that a film formed on the grid rather than discrete particles. SE-26 was chosen since this copolymer was one of the more successful at producing discrete, unaggregated particles. A concentration of 5%(w/w) in hexane was chosen to mimic that used in dispersion polymerizations. Theoretically, PS-graft-PEHA copolymers in hexane should be capable of forming micelles with a PS core (insoluble backbone) and a PEHA shell of soluble grafts. Indeed, copolymers SE-25 and SE-26 both exhibited a bluish tint when dissolved in hexane. This is characteristic of very small scattering centres such as micelles. Unfortunately, this was not proved.

4.3.4.1 Copolymer stabilizers with graft lengths of $\bar{M}_n \approx 3000$ g.mol⁻¹

Figure 4.42 illustrates typical micrographs of particles obtained from dispersions D14, D12 and D13 which were obtained using seed/feed polymerization method 2, using graft copolymers SE-24, SE-25(a) and SE-26, respectively. As already discussed, seed/feed method 3 produced similar results for a given type of stabilizer. Figure 4.43 also illustrates particles obtained from dispersions D8, D4 and D5 which were also obtained using stabilizers SE-24, SE-25(a) and SE-26, respectively but produced using the one-stage method. The qualitative appearances of particles produced were dependent upon the stabilizer composition but independent of the polymerization method, although quantitatively the one-stage method consistently produced larger particles, as discussed previously in section 4.3.3. Stabilizers SE-25(a) (D12 and D4) and SE-26 (D13 and D5) produced discrete, spherical particles with similar, fairly uniform particle sizes. Therefore, it appears that uniform growth has occurred without aggregation processes. However, SE-24 (D14 and D8) produced aggregated particles with definite bridges. In addition, these particles were irregular in shape and also larger than those produced using SE-25 or SE-26. This suggests that the final aggregated particles appear to have grown by previous aggregation of even smaller particles. This can be explained by the different behaviour of the graft copolymers in the dispersion polymerization as a result of their different structures. As already discussed in sections 2.2.3 and 4.3.4, it is believed that there is an equilibrium between adsorbed stabilizer, single molecules and micelles. A careful balance between the anchor and soluble components is necessary for stabilizers to function effectively. For copolymers SE-25(a) and SE-26, it appears that the ASB is correct (ASB = 1.2/1 to 0.8/1) for the stabilizer to function effectively. There is sufficient insoluble component (40-55% (w/w) backbone $\bar{M}_n = 7-11 \times 10^3 \text{g.mol}^{-1}$) to provide effective adsorption to PMMA particles and good surface coverage but there

FIGURE 4.42

A COMPARISON OF PMMA PARTICLE MORPHOLOGY OBTAINED
FROM SEED/FEED DISPERSION POLYMERIZATION METHOD 2
USING STABILIZERS SE-24, SE-25(a)) AND SE-26
(CONCENTRATION = 5.0%(w/w))

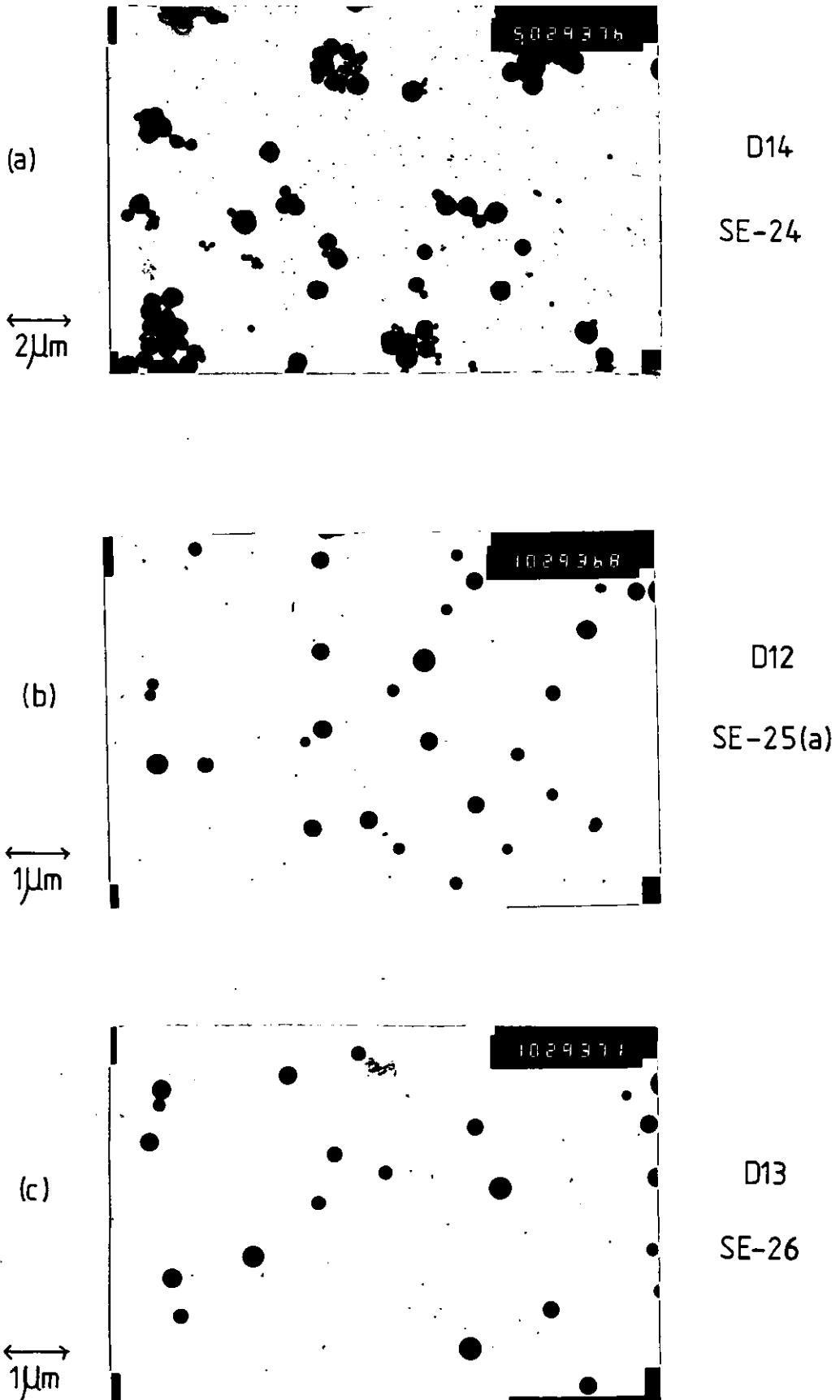
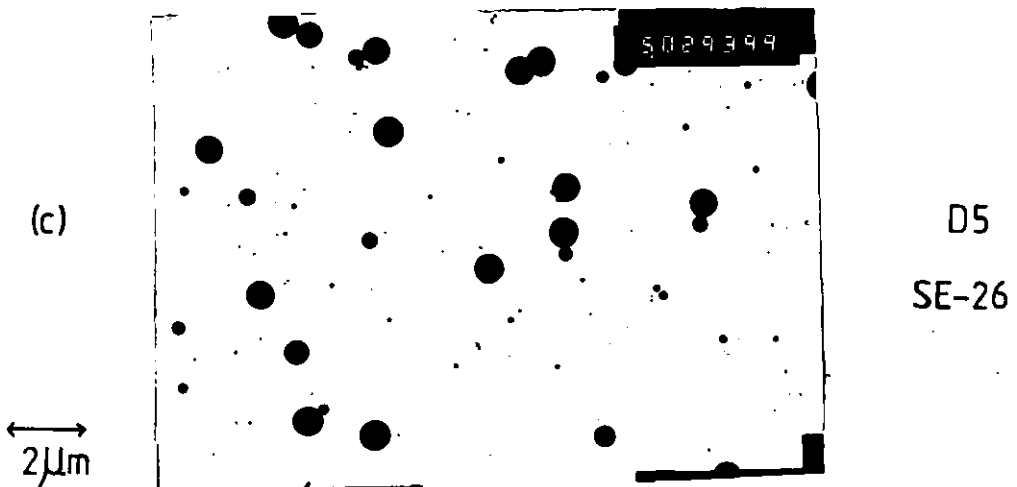
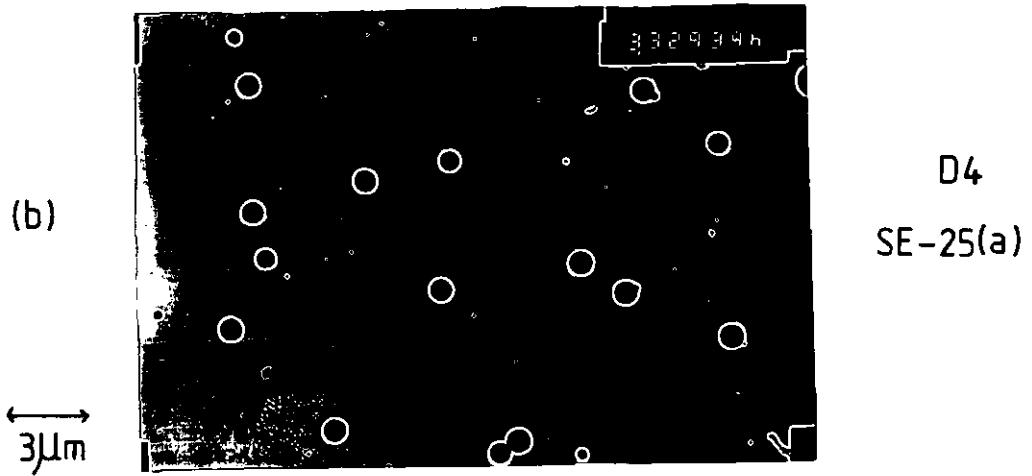
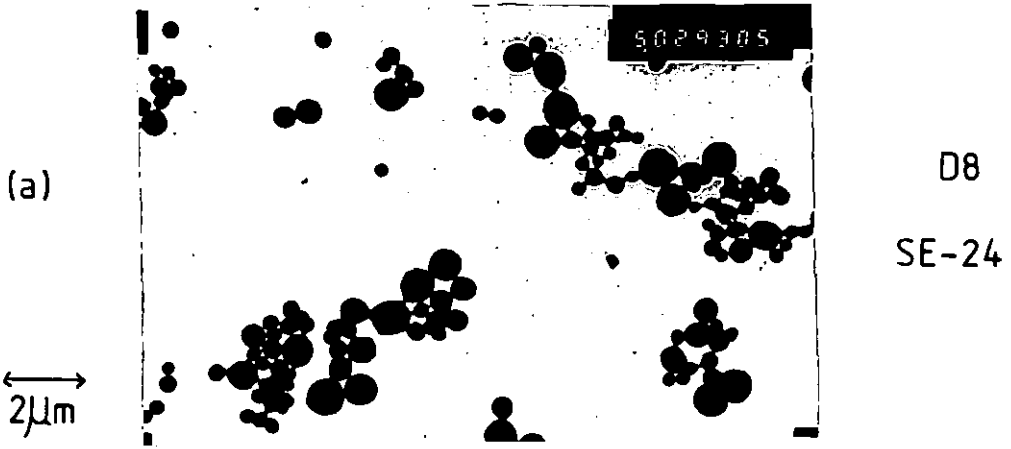


FIGURE 4.43 A COMPARISON OF PMMA PARTICLE MORPHOLOGY OBTAINED FROM THE ONE-STAGE DISPERSION POLYMERIZATION METHOD USING STABILIZERS SE-24, SE-25(a) AND SE-26 (CONCENTRATION = 5.0%(w/w))



is also sufficient soluble component (45-60%(w/w), $\bar{N}_g=2.9-3.5$) to allow copolymer molecules to dissociate from micelles into single molecules so that they can migrate to the particle surfaces. The length of soluble grafts also appears high enough to provide a thick enough steric barrier to prevent aggregation or flocculation. The particle sizes produced using stabilizers SE-25 and SE-26 were quite similar, despite differences in their compositions. For SE-26, the ASB was lower resulting in a lower backbone molar mass ($\bar{M}_n=6.9 \times 10^3 \text{g.mol}^{-1}$ cf. $10.7 \times 10^3 \text{g.mol}^{-1}$) and a higher number of grafts. Taylor [17] showed that the threshold molar mass for PS in dispersion polymerization media was approximately $1 \times 10^4 \text{g.mol}^{-1}$ and he proposed that PS anchoring components with molar masses lower than this would not be sufficiently insoluble in the dispersion medium to be effective. On this basis, the low backbone molar mass of SE-26 would be expected to seriously impair its anchoring efficiency resulting in significantly larger particles or even flocculation. Indeed, the backbone molar mass of SE-25 is a 'borderline' case. However, the fact that the backbones in both copolymers were effective anchoring components may be a result of the backbone compositions. As already discussed in section 4.2.4, although the copolymer compositions have been calculated assuming that each branching site X is part of the graft, the backbones are strictly poly(styrene-stat-methacrylate) copolymers with a very high styrene content. The average PS sequences are long and disrupted by methacrylate units at the branching points which arise from the original macromonomer end-groups. However, this small number of methacrylate units in the backbone is likely to be important in assisting the insolubility of the backbone in the dispersion medium. Since the methacrylate units are more compatible with the dispersed phase PMMA than the PS segments, this will also tend to assist the adsorption of the backbone as a result of specific interactions between the backbone branching points and the dispersed phase. For copolymer SE-26, there is a higher number of grafts per molecule on average and a shorter backbone chain length resulting in a slightly increased number of

methacrylate branching units and shorter average PS segment molar mass ($\bar{M}_n(\text{PS segment}) = 1.5 \times 10^3 \text{g.mol}^{-1}$ in SE-26 cf. $2.7 \times 10^3 \text{g.mol}^{-1}$ in SE-25(a)). The expected detrimental effect on adsorption of a reduction in backbone chain length is cancelled by the slight increase in methacrylate content of the backbone.

Copolymer SE-24 provided ineffective stabilization and the aggregation of particles can be attributed to a number of factors. As explained in section 2.1.3, the failure of stabilization can arise from poor solvency of the stabilizing chains, insufficient dimensions of the steric barrier, weak adsorption of the stabilizer to the particles or incomplete surface coverage. The success of stabilizers SE-25(a) and SE-26 illustrates that the solvency of the medium is good for the stabilizing chains and that the molar mass of the soluble component is sufficient to provide an effective steric barrier. Weak adsorption of the stabilizer can also be discounted, since the backbone molar mass in SE-24 is higher than either SE-25(a) or SE-26. This should provide an increased insolubility providing a greater driving force for adsorption. (There are, however, a lower average number of grafts and hence a lower average number of methacrylate branching sites on the backbone). Therefore, it is probable that the aggregation of particles results from incomplete coverage of the particle surfaces. The ASB is too large (2.1/1, 68% (w/w) backbone) which causes the stabilizer equilibrium to favour micellization. When PMMA radicals grow to the threshold molar mass required for precipitation, they are probably restricted from entering into the core of a micelle because of the incompatibility of PS and PMMA [191]. Consequently, nucleation occurs in the dispersion medium. Concomitantly, the stabilizer is restricted from dissociating into single molecules, thereby preventing sufficient copolymer reaching the nuclei. This results in insufficient surface coverage, producing bald spots on the particles, allowing them to bridge and aggregate. However, the copolymer does not appear irreversibly micellized, since this would lead to severe

flocculation. It was noted that there appears to be two aggregation processes, one in the early stages for small particles and one in the latter stages for larger particles. The first can be explained as a result of the surface area initially being too high for the available copolymer to cover. Later in the polymerization, there is less free monomer available resulting in an increased stabilizer insolubility, restricting further dissociation of copolymer and resulting in further aggregation. The fact that the ASB was too large for SE-24 was confirmed by the difficulty obtained in dissolving it in the dispersion medium in comparison to SE-25(a) and SE-26. Solutions of copolymers SE-25(a) and SE-26 were essentially transparent in hexane even at room temperature but exhibited a bluish tint, indicative of the presence of small scattering centres, such as micelles. In direct contrast, SE-24 was swollen by hexane at room temperature but not properly dissolved. The solubility was assisted by the addition of seed monomer and raising the temperature to 342 K although the medium was opaque before initiator was added.

4.3.4.2 Copolymer stabilizers with graft lengths of $\bar{M}_n \approx 1500$ g.mol⁻¹

Figure 4.44 illustrates typical micrographs of particles obtained from dispersions D21A, D21B and D22 obtained by seed/feed method 3 using stabilizers SE-21, SE-22 and SE-23, respectively. Similar results were obtained by method 2 for the corresponding stabilizers (see table 4.32). Figure 4.45 also illustrates particles obtained from dispersions D6, D7 and D9 which also utilized SE-21 SE-22 and SE-23 but which were produced using the one-stage method. As in section 4.3.4.1, the qualitative appearances of particles were dependent on the stabilizer composition but independent of the polymerization method used, although quantitatively the one-stage method produced consistently larger particles. In summary, graft copolymers SE-

21, 22 and 23 were all inefficient as stabilizers and at best, particle aggregates were obtained. Particles flocculated using SE-21 before polymerization was terminated. Generally, particles were produced using SE-22 and SE-23 but sedimentation occurred within a few minutes for these dispersions as a result of the aggregated particles produced. For SE-22, the aggregated particles were coalesced and poorly defined. Although a distinct improvement in the definition of particles within aggregates was evident using SE-23, particle bridging was still significant. As explained in the previous section, there are a number of reasons why stabilization can fail. Failure due to weak adsorption can be neglected, since the ASB and the length of the backbone in SE-23 are similar to SE-26, which was found to give effective stabilization. Following the discussion in section 4.3.4.1, adsorption of SE-23 should be assisted in comparison to SE-26 as a result of more branching methacrylate units and a lower PS segment length (see table 4.29). Poor solvency of the stabilizing chains can also be neglected since hexane is a good solvent for PEHA, and the fact that there is some steric barrier is evident from the fact that complete flocculation is prevented. However, it appears that the dimensions of the steric barrier are insufficient, allowing particles to aggregate. It is also possible that aggregation could be caused by incomplete surface coverage as a result of the stabilizer ASB being too high, with the stabilizer equilibrium favouring micellization as explained for stabilizer SE-24. However, copolymer SE-23 was soluble in the dispersion medium at the polymerization temperature with solutions being virtually transparent and this effect is likely to be of secondary importance for this stabilizer. In contrast, copolymers SE-21 and SE-22 were quite insoluble in hexane at room temperature and with the addition of seed monomer, significant quantities remained undissolved. This is a result of the higher ASB, longer backbones and less grafts per molecule in comparison to SE-23. Once the polymerization temperature was attained and before initiator was added, the solubility increased but the dispersion medium appeared significantly turbid. It seems likely

that for these stabilizers, incomplete surface coverage provides an additional mechanism to that of insufficient steric barrier, thereby causing a reduction in the effectiveness of the stabilizers. The effect is more severe for SE-21, which has the highest ASB. SE-21 and SE-22 had identical ASB values to SE-24 and SE-25 respectively (ASB=2.1/1 and 1.2/1 respectively) but were more insoluble in the dispersion media. This is somewhat surprising since SE-21 and SE-22 have a higher number of grafts (graft $\bar{M}_n=1530\text{g.mol}^{-1}$) in comparison to SE-24 and SE-25 (graft $\bar{M}_n=3030\text{g.mol}^{-1}$). The decreased solubility must be caused by the shorter graft chain lengths. It is possible that graft molar masses of $\bar{M}_n=1530\text{g.mol}^{-1}$ are insufficient in length to form a soluble layer around the backbone core, making micelle formation difficult.

In summary, PS-graft-PEHA copolymers with graft $\bar{M}_n=1530\text{g.mol}^{-1}$ were unsuccessful in producing discrete, spherical PMMA particles. This is in contrast to the work of Barrett et al [8,9] who showed that PMMA-graft-PHSA copolymers with graft $\bar{M}_n=1500\text{g.mol}^{-1}$ were effective in the stabilization of PMMA particles. This can be attributed to a difference in the dimensions of the steric barrier provided by the different soluble components. For PEHA chains, a large proportion of the molar mass exists in short branches whereas in PHSA, most of the molar mass resides in the main chain. Therefore in commonly good solvents, this suggests that the end-to-end distance of PEHA chains will be shorter than PHSA chains with equivalent molar masses. When adsorbed at interfaces, PEHA stabilizing chains provide a narrower steric barrier than PHSA chains with the same molar mass. However, PS-graft-PEHA copolymers with graft lengths of $\bar{M}_n=3030\text{g.mol}^{-1}$ produced discrete particles provided that the ASB was correct. Vincent [60] suggested that the most efficient stabilizers should have an ASB ratio within the range 3.0/1 to 0.33/1. For the stabilization of PMMA particles with PS-block-PDMS copolymer stabilizers, Dawkins and Taylor [197] showed that stable particles could be produced, provided that the ASB was in

the range 4.0/1 to 0.5/1. For the PS-graft-PEHA copolymers reported in the present work, the lowest ASB used was 0.8/1 (SE-26). This lies in both ranges referred to above. It is possible that lower ASB's could be used to provide stabilization but this was not investigated since copolymers with higher graft contents were difficult to purify (see section 4.2.2). The upper limit of the ASB was significantly lower than those found by Vincent [60] and Dawkins and Taylor [197], lying between 1.2/1 (SE-25(a) produced discrete particles) and 2.1/1 (SE-24 produced aggregated particles). This could be a result of the relatively low molar mass of the soluble components since Dawkins and Taylor [197] also showed that PDMS stabilizing chains with higher molar masses can stabilize larger surface areas on PMMA particles. Indeed, it has also been shown experimentally [198] that long tails or stabilizing chains are more effective in stabilizing particles than shorter chains. Therefore, the polydispersity of the PEHA grafts will have an important effect. The grafts in the effective stabilizers arise from macromonomer PEHA-50MP which has $\bar{M}_n^* = 3.03 \times 10^3 \text{ g.mol}^{-1}$ and $\bar{M}_w/\bar{M}_n = 1.53$ (see section 4.1.3.2). When PMMA particles covered with surface layers of these PEHA chains approach one another, the initial interaction will arise between stabilizing chains with significantly higher molar masses than the number average. Undoubtedly, these longer chains will play an important role in preventing flocculation. It must also be emphasized that the overall PS-graft-PEHA graft copolymer molecules are polydisperse with respect to molar masses and are likely to be significantly heterogeneous with respect to chemical composition and physical architecture, as already discussed in section 4.2.4. Both of these factors may result in a lower limit for the size distribution of particles obtained by using these copolymers as stabilizers. Individual copolymer molecules within the same sample can be expected to behave slightly differently in the dispersion medium, thereby making the production of monodisperse particles difficult to achieve. The graft copolymers provide stabilization despite the fact that the backbones are of a different chemical nature to the dispersed phase. The

compatibility of the copolymer backbones with the dispersed phase is likely to be assisted by a number of factors. The presence of monomer acts as a solvent and swells both the dispersed phase particles and the stabilizer backbones, which decreases the anchoring energy. Also, the anchoring component molar masses are low ($\bar{M}_n(\text{backbone})=6.7-11 \times 10^3 \text{g.mol}^{-1}$) and this increases compatibility when compared to higher molar mass analogues. As already discussed, compatibility is further assisted by the fact that the branching methacrylate units in the copolymer backbones provide specific interactions with the dispersed phase. This also enhances insolubility of the backbone in the dispersion medium and this can explain why such low backbone molar masses are effective at anchoring.

4.3.5 THE EFFECT OF STABILIZER CONCENTRATION ON PARTICLE SIZE

This was investigated using copolymer SE-25(b) (one of the most effective stabilizers) and polymerization method seed/feed 3 (one of the preferred methods). Stabilizer concentrations were varied from 1.0 to 6.8% (w/w) and all concentrations produced spherical particles (indicating uniform growth) with fairly narrow particle size ranges and distributions. The dispersed phase particle polydispersity was unaffected by the stabilizer concentration used, as summarized previously in table 4.33. All concentrations used produced discrete particles, apart from the lowest concentration of 1% (w/w). Although most particles were discrete in this case, a few particles formed very small aggregates. This suggests that there was insufficient stabilizer present for complete surface coverage at this concentration. Therefore, the minimum stabilizer concentration required to prevent particle aggregation lies somewhere in the range 1-3% (w/w). Figure 4.46 demonstrates the effect of different concentrations of SE-25(b) copolymer on the mean particle diameter of the PMMA dispersed phase. As the stabilizer concentration increases, smaller particles are produced. This can be predicted by the mechanism of

particle formation (section 2.2.4) since the stabilizer concentration is one of the most important factors controlling nucleation. As already discussed in section 2.2.4, association between the stabilizer and growing chains raises the probability of nucleation by causing precipitation to occur at lower molar masses. Therefore, increasing the stabilizer concentration produces an increased number of nuclei. This results in smaller final particles provided that growth is unaffected by aggregation processes. For smaller nuclei, the rate of precipitation is faster and there is a larger surface area to be covered and both can lead to aggregation. However, the increased stabilizer concentration prevents this by causing a higher rate of stabilizer adsorption and an increase in the surface coverage. Figure 4.46 also suggests that there is a lower limit to the particle size obtained at higher concentrations. This is possibly an equivalent to the critical micelle concentration in aqueous systems [20].

Barrett and Thomas [8] first developed an expression of the form

$$D = Kc_s^{-a} \quad (4.29)$$

for the relationship between particle diameter D and stabilizer concentration c_s , where both K and a are constants. Figure 4.47 illustrates the relationship between D and c_s on a double logarithmic plot, which expresses equation 4.29 in a linear form. From the slope of this relationship, $a = 0.63$ for the PS-graft-PEHA stabilizer SE-25(b). The exponent a has been determined for other stabilizers in the dispersion polymerization of MMA in aliphatic hydrocarbons. Shakir [16] reported that $a = 0.98$ for polystyrene-block-[poly(ethylene-co-propylene)] stabilizers, Dawkins and Taylor [17,197] found that $a = 0.77$ for PS-block-PDMS stabilizers and Susoliak and Barton [199] showed that $a = 0.36-0.46$ for polyisoprene-block-polystyrene-block-polyisoprene stabilizers. Although all these stabilizers are block copolymers, they are similar to the present case in that anchoring is essentially provided by a PS anchor component. However, the

FIGURE 4.46

THE EFFECT OF PS-graft-PEHA STABILIZER
CONCENTRATION ON PARTICLE SIZE OF PMMA DISPERSIONS

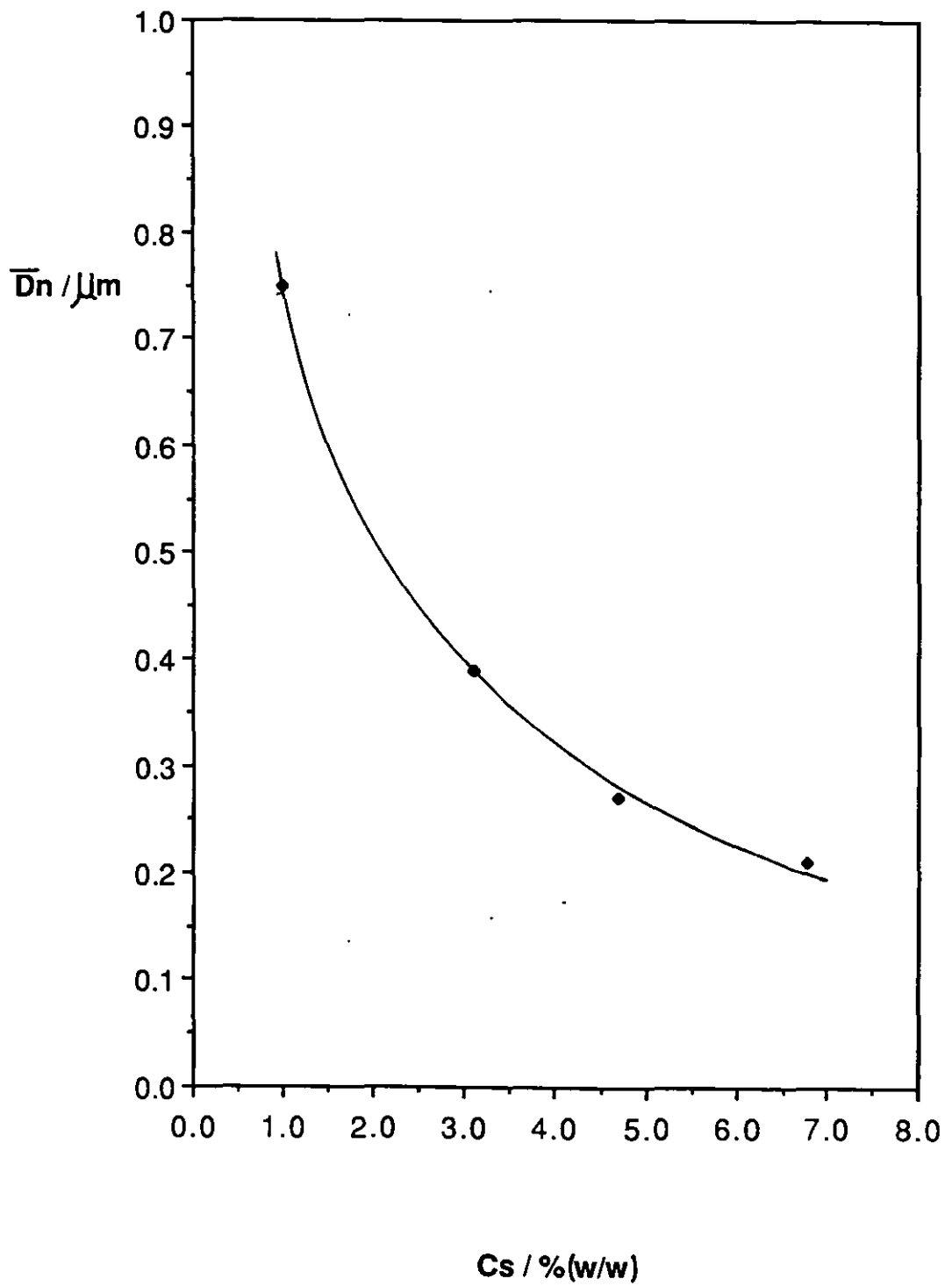
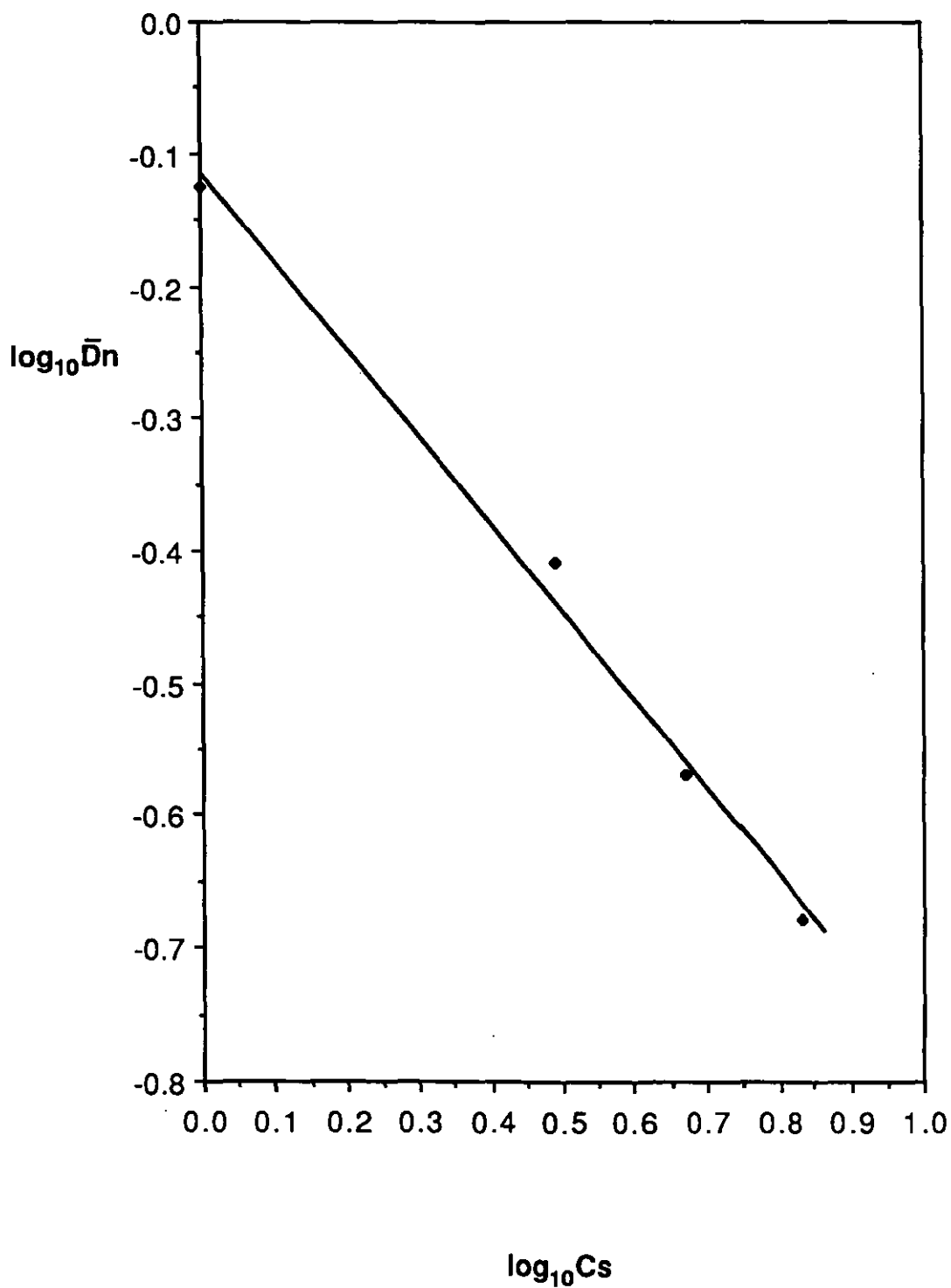


FIGURE 4.47 DOUBLE LOGARITHMIC PLOT OF PMMA PARTICLE SIZE
VERSUS PS-graft-PEHA STABILIZER CONCENTRATION



exponent for copolymer SE-25(b) most closely resembles $a = 0.5-0.6$ determined by Barrett and Thomas [8] for graft copolymers containing PHSA grafts and various backbones.

4.3.6 PARTICLE SURFACE COVERAGE

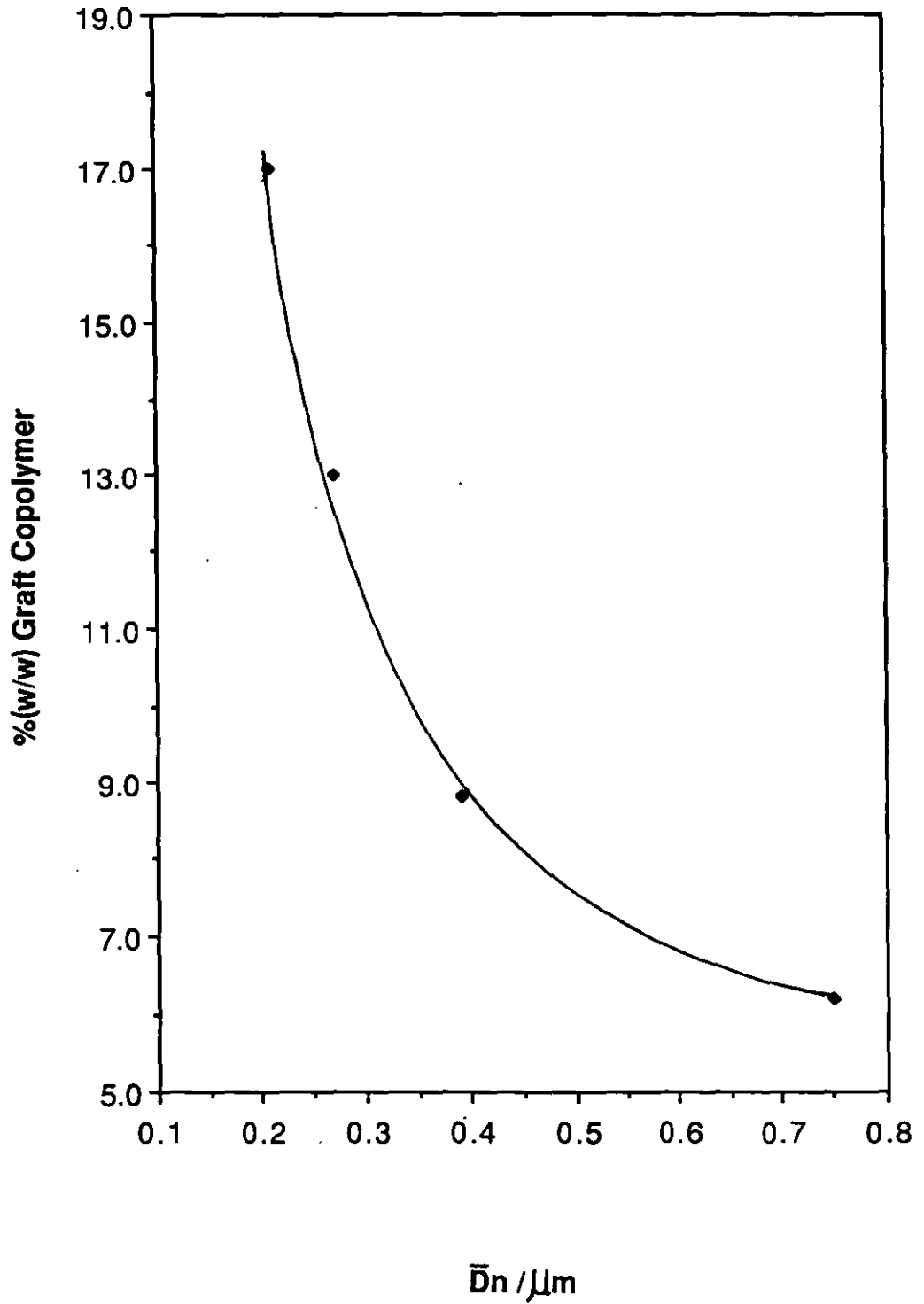
Table 4.34 shows the percentage of graft copolymer stabilizer for those PMMA dispersions where discrete particles with narrow size distributions were obtained ($\bar{D}_w/\bar{D}_n < 1.10$). These values were calculated from UV spectroscopy performed on redispersed and dried dispersion samples in chloroform, as described in section 3.5.7. The copolymer contents depend upon particle size and vary from 6.2-17.0% (w/w). Figure 4.48 clearly illustrates for copolymer SE-25(b) that the percentage of graft copolymer increases as the particle size decreases. On the basis of graft copolymer to monomer in the original dispersions and considering monomer conversions, the graft copolymer contents of the dispersed phase represent less than 60% of the stabilizer originally available in the polymerization. Higher concentrations were required than necessary since the adsorption mechanism is not 100% efficient and this may also be due to the different chemical natures of the dispersed phase and the copolymer anchoring components. The surface area A occupied by each stabilizing PEHA chain was then calculated from the graft copolymer content of the particles and the average particle size \bar{D}_n . It was assumed that the copolymers only occupied the surfaces of the particles, that the anchoring component did not extend significantly into the dispersion medium and that each PEHA chain was terminally adsorbed at the particle surface. By further assuming that each PEHA chain was anchored at the centre of a regular hexagon of area A , the mean separation distance d between adjacent PEHA chains was calculated. The results for A and d are also presented in table 4.34. These suggest that, providing discrete particles are produced, A and d are approximately constant for stabilizing chains with $\bar{M}_n=3030\text{g.mol}^{-1}$,

TABLE 4.34

SURFACE COVERAGE DATA FOR PMMA DISPERSIONS WITH
DISCRETE PARTICLES ($\bar{D}_w/\bar{D}_n \leq 1.10$)

DISPERSION	COPOLYMER STABILIZER	$\bar{D}_n/\mu\text{m}$	COPOLYMER CONTENTS / % (w/w)	$A/(\text{nm})^2$	d/nm
D10	SE-25(a)	0.19	15.3	1.90	1.48
D11	SE-25(a)	0.21	15.1	1.75	1.42
D12	SE-25(a)	0.24	11.6	1.98	1.51
D13	SE-26	0.30	9.4	1.49	1.31
D19	SE-26	0.32	12.9	1.05	1.10
D23	SE-25(b)	0.75	6.2	1.12	1.14
D24	SE-25(b)	0.39	8.8	1.50	1.32
D26	SE-25(b)	0.27	13.0	1.47	1.30
D25	SE-25(b)	0.21	17.0	1.47	1.30

FIGURE 4.48 THE VARIATION OF ADSORBED PS-graft-PEHA STABILIZER CONCENTRATION WITH PMMA DISPERSED PARTICLE SIZE



with no obvious dependence on particle size. This implies that total surface coverage may be assumed for most dispersions. The only exceptions are D19 and D23. Dispersion D23 contains the lowest stabilizer concentration. As already discussed in section 4.3.5, some particles were found to be aggregated. The low surface area covered by each stabilizing chain can be explained in this case by incomplete surface coverage due to the lack of sufficient stabilizer. A and d are similar for copolymer stabilizers SE-25(a), SE-25(b) and SE-26. The only identical structural feature in these copolymers is the length of the grafts and therefore, this appears to control A and d. This is in good agreement with the work of Dawkins and Taylor [197] when studying PMMA dispersions stabilized by PS-block-PDMS copolymers. They found that A increased with an increasing molar mass of the stabilizing chains but was independent of the anchoring component molar mass. For the stabilization of PMMA particles with PS-block-PDMS copolymers containing stabilizing PDMS chains with $\bar{M}_n = 3.2 \times 10^3 \text{g.mol}^{-1}$, Taylor [17] found that $A = 6.4 \text{nm}^2$ and $d = 2.7 \text{nm}$. In the present case, the stabilizing PEHA chains occupy a lower surface area and are more closely packed ($A = 1.5$ to 2.0nm^2 and $d = 1.3$ to 1.5nm). However, these values agree quite well with those reported by Barrett et al [8,9] for PMMA particles stabilized with PMMA-graft-PHSA copolymers. For PHSA stabilizing chains with $\bar{M}_n \approx 1500 \text{g.mol}^{-1}$, it was found that $A = 3.0 \text{nm}^2$ and $d = 1.7 \text{nm}$. This similarity is likely to be a result of PEHA chains with $\bar{M}_n \approx 3000 \text{g.mol}^{-1}$ having a similar end-to-end distance in aliphatic hydrocarbons to PHSA chains with $\bar{M}_n \approx 1500 \text{g.mol}^{-1}$, as previously discussed in section 4.3.4.2.

4.3.7 DISPERSION STABILITY

Dispersions with small, discrete particles were the most stable. However, even these samples did not exhibit long-term stability at room temperature and sedimentation began to occur over a few days. Therefore, it appears that although the stabilizers were

initially effective in providing stabilization, desorption of the stabilizer occurred with time. This is most probably the result of the low anchoring component molar masses since they are likely to be near the limit for precipitation (see section 4.3.4). This desorption also suggests that the stabilizer molecules were anchored by a physical adsorption mechanism and had not been grafted onto the particle surfaces by a chain transfer mechanism. This is not surprising since the chain transfer constant C_p for growing PMMA radicals with PS is of the order of 10^{-4} [171] and C_p for growing PMMA radicals with PEHA is likely to be of the same order of magnitude. In studies of block copolymers stabilizing PMMA particles, it has been shown that PMMA dispersions are very stable over long periods of time at temperatures below the T_g of PMMA, even when a solvent is added for the anchor component [200,201]. This suggests that PS blocks are firmly anchored within the hard PMMA matrix despite their incompatibility and this has been confirmed by neutron scattering. However, in the present case, the stability is only short term and this implies that the stabilizers are only anchored at the surface mainly in trains with only occasional loops protruding into the particles. Desorption of the stabilizer can then readily occur if the anchoring is weak and flocculation can then occur, since there is no reservoir of stabilizer to retain the surface coverage.

Although no controlled flocculation studies were achieved, the addition of ethanol to stirred dispersions at room temperature was found to encourage rapid flocculation. Since ethanol is a non-solvent for the stabilizing PEHA chains, this implies that the mechanism is steric stabilization. However, it was not established whether this flocculation occurred near the θ -conditions for the PEHA chains.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

5.1 CONCLUSIONS

Carboxyl-terminated PMMA and PEHA prepolymers with molar masses of $\bar{M}_n \sim 1500$ and 3000 g.mol^{-1} were synthesized by free-radical polymerization using ACVA and TGA as matched initiator and chain transfer agent, respectively. These prepolymers were characterized thoroughly by EGA, IR, ^1H NMR and GPC. The molar masses of the prepolymers were readily controlled by the feed ratio of chain transfer agent to monomer but careful purification was required in order to remove impurities and prevent significant fractionation. In most cases, the chain transfer agent concentration was deliberately chosen to be far greater than the initiator concentration in order to maximize the number of chains produced by chain transfer reactions. Consequently, the carboxyl-terminated prepolymers were found to be monofunctional, within experimental error. These prepolymers were converted to methacrylate-terminated macromonomers via acyl chloride terminated intermediates. IR qualitatively showed the appearance and disappearance of the various functional groups. The macromonomers were also characterized by IR, ^1H NMR and GPC. The molar masses of the macromonomers were found to be almost identical to those of their respective carboxyl-terminated prepolymers, indicating that subsequent reactions only altered the nature of the end-groups. The macromonomer chains were also found to be approximately monofunctional, within experimental error.

PS-graft-PMMA and PS-graft-PEHA copolymers, with graft lengths of $\bar{M}_n \sim 1500$ and 3000 g.mol^{-1} , were synthesized by the free-radical copolymerization of styrene (M_1) with the methacrylate-terminated PMMA or PEHA macromonomers (M_2), respectively. Conditions were altered so that the molar masses of copolymers were significantly different from the molar masses of the macromonomer precursors in order to enable GPC to distinguish between them. Dual detector GPC showed that macromonomer conversions were independent of

comonomer feed compositions. The minimum macromonomer conversion was ~15% and the maximum feed concentration of macromonomer was 50% (w/w) due to problems encountered in purifying copolymers with large proportions of unreacted macromonomers. GPC also enabled the monitoring of the purification method to remove unreacted macromonomers. "Blank" polymerization experiments with carboxyl-terminated prepolymers showed that the macromonomers were incorporated by copolymerization of the terminal unsaturation rather than by transfer reactions involving the PMMA or PEHA segments. Purified copolymers were characterized by TLC, GPC, IR and ^1H NMR. TLC showed that polystyrene homopolymer contamination was negligible in all cases. The choice of developer in this characterization method was found to be critical in order to prevent overestimation of the homopolymer produced. The molar masses and polydispersities of graft copolymers and their fluctuations with conversion, were found to be similar to PS homopolymers produced under analogous conditions.

By applying the Jaacks simplification, the Finemann-Ross method and the Kelen-Tüdös method to copolymerization data, the styrene reactivity ratio (r_1) was determined for each set of copolymerizations. The values of r_1 did not appear to depend significantly on the method of estimation. Macromonomer reactivities were obtained by comparing reciprocal values of r_1 to the copolymerization of conventional methacrylates with styrene. In the limits investigated, the macromonomer reactivities toward propagating chains with terminal styrene units were found to be independent of the macromonomer chain length and the type of polymer chain. Macromonomer reactivities were also found not to be significantly different from conventional methacrylates. Therefore, the macromonomer reactivities were controlled by the end-group and were unaffected by possible excluded volume, incompatibility and solvent effects resulting from the influence of the macromonomer chain. It was realized that the method used to determine r_1 only produced

approximate estimates. Values of r_2 could not be determined as a result of the large difference between the styrene and macromonomer mole fractions in the feed and the copolymer.

The ability of macromonomers to behave like conventional methacrylates enabled facile control of graft copolymer composition. All graft copolymer compositions could be controlled in the same manner, irrespective of macromonomer composition or molar mass. Copolymerized styrene essentially produced the backbone of the graft copolymers, whereas copolymerized macromonomer resulted in grafts. The molar masses of grafts were controlled by the molar mass of the macromonomer copolymerized. A number of parameters were controlled by the feed composition. An increase in the macromonomer feed concentration produced an increase in the MMA or EHA content of the copolymer with a corresponding increase in the average number of grafts per molecule. Since the total monomer concentration remained constant, this produced a decrease in the styrene concentration in the feed, resulting in a decreased styrene content in the copolymer and a decreasing backbone molar mass. The backbones were strictly poly(styrene-stat-methacrylate) copolymers with high styrene contents, the methacrylate components arising from the copolymerized macromonomer end-groups. The average PS segment lengths between grafts was found to be inversely proportional to the number of grafts per molecule. The conversion chemical heterogeneity was small and there was only a small composition drift between copolymers prepared from identical feed compositions but to different conversions.

PMMA particles were prepared by free-radical dispersion polymerization using PS-graft-PEHA copolymers as steric stabilizers. Particle morphology and size were estimated by TEM. Particle morphology was found to be strongly influenced by stabilizer composition. Copolymer stabilizers with graft lengths of $\bar{M}_n \sim 1500 \text{ g.mol}^{-1}$ were inefficient as stabilizers, producing particle aggregates or even flocculation. It was thought that

this was mainly a result of this chain length providing too thin a steric barrier to prevent particles coming into contact. However, copolymers with graft lengths of $\bar{M}_n \sim 3000$ g.mol⁻¹ provided effective stabilization and produced discrete particles, provided that the ASB was correct (1.2/1 to 0.8/1). These stabilizing chains provided a thick enough steric barrier to prevent particle aggregation. The upper limit of the ASB producing discrete particles was in the range 1.2/1 to 2.1/1. It is probable that the minimum ASB was lower than 0.8/1, but such copolymers were not used since they were difficult to purify. For copolymers producing discrete particles, particle size and polydispersity varied, depending on the polymerization method. Smaller particle sizes were obtained using seed/feed methods when compared to the one-stage method as a result of the lower free monomer concentrations decreasing the solvency of the medium for the polymer produced. Of the three seed/feed methods compared, methods 2 and 3 were preferred since small particles with a narrow size distribution were obtained. Seed/feed method 1 produced a broad particle size distribution since the stabilizer was divided between the seed and the feed, causing renucleation throughout the polymerization. The mean particle size was greatly influenced by the concentration of PS-graft-PEHA copolymer (in systems where discrete particles were produced). The minimum stabilizer concentration required to produce discrete particles was in the range 1-3% (w/w). Smaller particles were obtained as the concentration of stabilizer was increased and there was more stabilizer associated with these smaller particles. The surface coverage of discrete polymer particles was calculated and it was represented as the surface area A occupied or stabilized by each PEHA chain. The mean separation distance d between adjacent PEHA chains was also calculated assuming hexagonal close packing at the particle-liquid interface. A and d were generally constant with no dependence on particle size and total surface coverage may be assumed for the dispersions. For dispersions with discrete particles, rapid flocculation was induced by adding ethanol, a non-solvent for the

stabilizing PEHA chains. This suggests that the mechanism was steric stabilization with the stabilization being provided by a surface layer of PEHA. During the course of the dispersion polymerization, the nuclei formed adsorbed graft copolymer from the dispersion medium. The driving force for this adsorption was the insolubility of the graft copolymer backbone. This was essentially polystyrene with a small number of branching methacrylate units, which may also have provided specific interactions with the dispersed phase. The stability of the dispersions was only short-term (a few days) and this was likely to be a result of the low backbone molar masses being close to the threshold molar mass required for insolubility in the polymerization medium.

5.2 RECOMMENDATIONS FOR FURTHER WORK

The present work has provided a method for preparing PS-graft-PEHA copolymers suitable for the steric stabilization of PMMA dispersions. Stabilizing PEHA chains with molar masses of $\bar{M}_n \sim 3000\text{g.mol}^{-1}$ provided layers of sufficient thickness to prevent flocculation and backbone molar masses of approximately $7 \cdot 10 \times 10^3\text{g.mol}^{-1}$ were sufficient for short-term stability. However, further work is required to improve the understanding of the behaviour of these dispersions. The formation of micelles by these copolymers and micellar dimensions should be studied and Small Angle X-ray Scattering would be suitable for this [202,203]. Controlled flocculation studies on dispersions could be performed by adding a non-solvent for the stabilizing chains, in order to determine the critical flocculation volume and the critical flocculation temperature. This could then be related to the θ -conditions for the stabilizing chains in order to confirm that the steric stabilization mechanism is operative. The conformation of both the anchoring and soluble components of the

adsorbed stabilizer is of interest. Rheological studies could be performed in order to obtain surface layer thicknesses which could then be compared to end-to-end distances of PEHA chains in solution obtained by solution viscosities of free PEHA chains. Such studies have been performed by Shakir [16] and Taylor [17] on block copolymer stabilizers. Neutron scattering could be used to study the conformation of anchoring components using the principles applied by Dawkins et al [200,201] to PMMA particles stabilized by block copolymers.

For the PS-graft-PEHA and PS-graft-PMMA copolymers prepared from the copolymerization of styrene (M_1) with macromonomers (M_2), only r_1 was determined as a result of the high molar concentration of M_1 in comparison to M_2 . It would be interesting to determine r_2 in order to discover the macromonomer reactivity towards polymer radicals with terminal macromonomer units. Values of r_2 could be determined if the molar feed concentration of macromonomer was high enough but the copolymer compositions produced could not be measured directly since large amounts of unreacted macromonomer cannot be removed. In such cases, copolymer compositions would have to be measured indirectly by measuring macromonomer and comonomer conversions accurately. It would also be interesting to compare the effect on PMMA dispersions of using PS-graft-PEHA stabilizers with higher backbone and graft molar masses. This would involve preparing and copolymerizing macromonomers with molar masses $\bar{M}_n \geq 3000 \text{g.mol}^{-1}$. Characterization of these macromonomers would be more difficult and more inaccurate as a result of the lower concentration of polymerizable end-groups. The overall graft copolymer molar masses would necessarily have to be higher in order for GPC to discriminate between product and unreacted macromonomer. This would be of interest, since the copolymerization of macromonomers with higher molar masses producing copolymers with higher backbone molar masses may reduce the macromonomer reactivity as a result of excluded volume, incompatibility or solvent effects associated with the increased

polymer chain length. This would have implications on controlling graft copolymer compositions.

Rather than use preformed graft copolymers as stabilizers, PEHA macromonomers could be used directly in the dispersion polymerization as stabilizer precursors, with PMMA-graft-PEHA copolymers being formed in situ. The anchor components would then have the same composition as the dispersed phase. Such methods have been used by Barrett et al [8,9] and Pelton et al [204] for other graft copolymers formed in situ during the dispersion polymerization of MMA. However, conditions would have to be carefully controlled, since it has been shown here that the ASB is critical for the stabilizers to act effectively. It would also be difficult to characterize graft copolymers prepared in situ.

This work has illustrated that PS-graft-PEHA copolymers with well-defined compositions can be prepared from equally well-defined PEHA macromonomers. Moreover, the graft copolymer structures can be readily controlled. It has also been shown that, provided the structure is correct, the graft copolymers are capable of stabilizing particles which have different chemical compositions to the anchoring component, ie. one can rely upon the insolubility of the graft copolymer backbone in the dispersion medium to provide adsorption. As stated in the introduction (section 1), the ultimate objective of this research programme was to produce well-characterized secondary stabilizers capable of stabilizing and controlling PVC primary particle size during the suspension polymerization of VCM. PEHA grafts represent potentially suitable soluble components in stabilizers for the stabilization of PVC particles swollen by VCM. However, a PS backbone is unlikely to be suitable as an anchoring component since it is too soluble in VCM [19]. Potentially suitable anchoring components include PVC, poly(styrene-co-acrylonitrile) or polyvinylidene chloride. Therefore, the knowledge obtained from PEHA macromonomer synthesis and

copolymerization could be applied to produce poly(vinyl chloride)-graft-poly(2-ethyl hexyl acrylate) (PVC-graft-PEHA) poly(styrene-co-acrylonitrile)-graft-poly(2-ethyl hexyl acrylate) or poly(vinylidene chloride)-graft-poly(2-ethyl hexyl acrylate) copolymers, containing backbones as anchoring components for PVC particles and grafts as soluble components in VCM. In a similar manner to this work, methacrylate branching units arising from copolymerized methacrylate-terminated macromonomers would be expected to provide specific interactions with PVC particles, since low molar mass PMMA is compatible with PVC [205]. The present work suggests that such graft copolymer stabilizers should have an ASB of approximately 1/1, a minimum PEHA graft molar mass of $\bar{M}_n=3.0 \times 10^3 \text{g.mol}^{-1}$ and a minimum anchoring component molar mass $\bar{M}_n=7-10 \times 10^3 \text{g.mol}^{-1}$. However, unpublished results have suggested that the true solution copolymerization of VCM is difficult to achieve [15] and preformed PVC-graft-PEHA copolymers with controlled compositions will be difficult to produce.

Following the work of an earlier recommendation, it may also be possible to use PEHA macromonomers directly in VCM suspension polymerizations to produce PVC-graft-PEHA copolymer stabilizers in situ. However, these copolymers would be more difficult to characterize and their compositions more difficult to control than preformed graft copolymers.

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