

1984

A small-angle neutron scattering investigation of aggregation in polystyrene above the gel point

Jeffrey G. Weissman
Lehigh University

Follow this and additional works at: <https://preserve.lehigh.edu/etd>

 Part of the [Chemical Engineering Commons](#)

Recommended Citation

Weissman, Jeffrey G., "A small-angle neutron scattering investigation of aggregation in polystyrene above the gel point" (1984). *Theses and Dissertations*. 5169.
<https://preserve.lehigh.edu/etd/5169>

This Thesis is brought to you for free and open access by Lehigh Preserve. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Lehigh Preserve. For more information, please contact preserve@lehigh.edu.

3301
/

A SMALL-ANGLE NEUTRON SCATTERING INVESTIGATION OF
AGGREGATION IN POLYSTYRENE ABOVE THE GEL POINT

Jeffrey G. Weissman
Department of Chemical Engineering
Lehigh University
Bethlehem, PA 18015

Research Report submitted in accordance with requirements
in completion of the M. S. degree in Chemical Engineering

Certificate of Approval

Approved and recommended for acceptance as a Research Report in partial fulfillment of the requirements for the degree of Master of Science.

8/21/84

date

J. H. Jenkins
professor in charge

John C. Chen
department chairman

ACKNOWLEDGEMENTS

The author wishes to express his gratitude for the assistance and guidance recieved from Dr. Sperling, and to Ana Maria Fernandez and Marc Linné for their helpful comments and suggestions.

This work was made possible from financial support through the Polymers Program of the National Science Foundation, Grant No. DMR-8405053. SANS experiments were performed at NCSASR, funded by NSF Grant No. DMR-7724458 through interagency agreement No. 40-637-77 with DOE.

In addition, the author wishes to acknowledge the generous support of Stauffer Chemical Company through their summer intern program and the Stauffer Chemical Fellowship.

ABSTRACT

Polystyrene was photopolymerized by bulk, free-radical methods to yield a material in which mid-range conversions, fraction II, were deuterated. The initial portion, fraction I, was crosslinked with one mole percent divinyl benzene. Fractions II and III were either linear or crosslinked. The synthesis was conducted in such a manner as to minimize disturbances in the chain conformations.

All of the compositions with fraction II greater than four mole percent were found to have unusually high molecular weights and radii of gyration, apparently due to aggregation, when studied by small-angle neutron scattering (SANS). SANS gave weight-average molecular weights between 110,000 and 760,000 gms/mole for fraction II, while GPC indicated molecular weights from 110,000 to 240,000 gms/mole, yielding aggregation numbers of one to five, which increased with the size of fraction II. The aggregation is thought to be caused by the presence of "excluded volume" arising from previously polymerized fraction I. This leads to a model suggesting a non-random distribution of labeled polymer, which results in several chains scattering like one larger chain.

CHAPTER 1

INTRODUCTION

Background

Small-angle neutron scattering (SANS) is a powerful tool in the study of polymer chain conformation and morphology (1-3). SANS takes advantage of the strong difference in coherent scattering between hydrogen and deuterium, permitting determination of molecular weights and radii of gyration, as well as structural and morphological features of suitably labeled polymers. The inherent assumption in the technique is that no difference in the behavior of the protonated and deuterated portions exists, permitting the study of labeled chains identical to their hydrogenated (ordinary) counter parts.

Recently, Fernandez et al (7,8) synthesized polystyrene/polydeuterostyrene/polystyrene (PSH/PSD/PSH) networks for SANS experiments. The samples were prepared by inserting a fraction of labeled monomer at a mid-range point in the polymerization. The networks contained one mole percent divinylbenzene (DVB), and were made using free-radical bulk polymerization techniques. The synthesis was conducted in such a manner as to minimize disturbances in the chain conformations. This created a portion of labeled polymer molecules at a specific conversion range after the gelation. Abnormally high R_g and M_w values were obtained, attributed to aggregation of lower molecular weight chains.

The proposed mechanism for this aggregation was related to the synthesis method by assuming that chains formed at about the same time should tend to crosslink with other contemporaneously synthesized chains. There was hypothesized to be a greater probability of unreacted crosslink sites occurring in freshly made chains. The extra crosslink sites provided for non-random contacts of the labeled portions, resulting in the apparent aggregation.

The present work was intended to continue the research begun by Fernandez et al. If the crosslinking agent were to be removed from the deuterated portion, then the chains might have less reason to aggregate. Samples were made by a similar method, but with several modifications. The first part, fraction I, was always crosslinked (x), while the labeled portion, fraction II, was either crosslinked or linear (l). The reaction was carried to 100% conversion with fraction III, which again was either crosslinked or linear. Three series of specimens were made : xxx, xlx, and xll, in which the conversion of fraction II was varied. In all these series, only the mid-conversion range was deuterated, permitting the study of the conformation of the chains in just that particular region.

Theory

As SANS theory has been discussed in detail

elsewhere (1-3, 9-15), only a brief overview will be given here. The probability that a neutron will be scattered through a solid angle Ω is given by the scattering cross-section $d\Sigma/d\Omega$, per unit volume. For polymers containing labeled portions, the scattering cross-section is given by

$$\left[\frac{d\Sigma}{d\Omega}(K) \right]^{-1} = \frac{1}{C_N M_w} [S(K)]^{-1} \dots \dots \dots (1)$$

where C_N is the sample constant given by

$$C_N = \frac{(a_H - a_D)^2 N_A \rho (1-X) X}{m_D^2} \dots \dots \dots (2)$$

and $S(K)$ is the single chain form factor. The Debye form for a random coil is given by

$$S(K) = \frac{2}{R_g^4 K^4} \left\{ R_g^2 K^2 - [1 - \exp(-R_g^2 K^2)] \right\} \dots \dots \dots (3)$$

K is the wave vector and is equivalent to $4\pi/\lambda \sin\theta$. The quantity λ is the neutron wavelength and 2θ is the angle of scatter. a_H and a_D are the scattering lengths of hydrogenated and deuterated structural units in the polymer, N_A is Avogadro's number, ρ represents the polymer density, X is the concentration of the deuterated species in the polymer, and m_D is the deuterated mer molecular weight. The value of R_g in these equations is the z-average.

In the Guinier region, where $R_g^2 K^2 < 1$, equation (3) can be simplified, substitution into equation (1) yields the basic SANS equation for polymers:

$$\left[\frac{d\Sigma}{d\Omega}(K) \right]^{-1} = \frac{1}{C_N M_w} \left(1 + \frac{K^2 R_g^z}{3} \right) \dots \dots \dots (4)$$

$d\Sigma/d\Omega(K)$ is directly proportional to scattering intensity $I(K)$ and can be obtained by converting from $I(K)$ using suitable machine constants (16). By measuring intensity verses K for a sample, M_w and R_g^z may be obtained through a Zimm plot ($[d\Sigma/d\Omega(K)]^{-1}$ vs. K^2) of equation 4, where the molecular weight is given by

$$M_w = \frac{1}{C_N} \frac{d\Sigma}{d\Omega}(0) \dots \dots \dots (5)$$

and $d\Sigma/d\Omega(0)$ is the intercept of the plot. The quantity R_g^z is given by

$$R_g^z = \left[3 C_N M_w (\text{slope}) \right]^{1/2} \dots \dots \dots (6)$$

R_g^w can be found from

$$R_g^w = \left(\frac{M_w}{M_z} \right)^{1/2} R_g^z \dots \dots \dots (7)$$

where M_w and M_z are the weight and z-averaged molecular weights. The value of $d\Sigma/d\Omega(K)$ must be corrected by removal of incoherent scattering intensity by subtracting scattering from the appropriate blank, leaving only the coherent intensities, as discussed below.

EXPERIMENTAL

Synthesis

The goal was to synthesize a polystyrene/polydeuterostyrene/polystyrene network such that the labeled polymer would be inserted at a certain mid-range

conversion, and in such a way as not to disturb the conformation of the polymer chains already in place. The net effect was to have chains formed during a certain conversion interval labeled. This was accomplished based on method "A" of Fernandez et al (7,8). All synthesis were conducted in glass molds placed vertically in an ultraviolet light reaction chamber kept at room temperature. The molds consisted of two glass plates, 4" x 4" x 1/4" each, between which were placed two 10 micron Mylar films. Between the Mylar sheets was placed a cut 'O'-ring, typically VITON (90 durometer, 1.5mm diameter), with the opening directed upwards to allow for addition of monomer solution. The components were assembled sandwich fashion and clamped together using six to eight 1/2" binder clips placed strategically around the glass plate edges. Two 2" 'C'-clamps were used to hold the mold vertically. Leakage from the mold was minimum.

Styrene monomer (Fischer) and deuterated styrene monomer (Cambridge Isotope Labs) were purified by passing the monomers through a chromatography column packed with neutral alumina (80-200 mesh, Fischer). Technical grade DVB (K & K Rare & Fine Chemicals) and analytic grade benzoin (Kodak) were used as received. The initiator (benzoin) concentration was kept constant at 0.4 wt%, and crosslinker (DVB) kept at 1.0 mole%, after adjusting for

the 55% concentration of the DVB. Both were based on styrene monomer weight.

Fraction I was prepared by filling the mold with the styrene/DVB/benzoin mixture and allowing polymerization to proceed to the desired conversion, usually 40-50%. The sample was demolded and dried in a vacuum chamber, at room temperature, for 1-2 days. Conversions were determined gravimetrically from the swollen and dried weights.

Fraction II, consisting of the labeled polymer, was prepared by swelling the dried the fraction I samples to the original weight, before evaporation with a monomer mixture consisting of deuterated styrene and benzoin, with or without DVB. The samples were allowed to equilibrate for one day in a closed container, at which point equilibrium was assumed to have been reached. The reswollen samples were then placed into the UV chamber and allowed to polymerize for an additional conversion period. Polymerization of fraction II proceeded from four to 20 percent, taking 0.5 to 4 hours. The samples were demolded and dried as before.

Fraction III was prepared in the same way as fraction II, with the exception that protonated (normal) styrene monomer was used, as in fraction I. Fraction III was polymerized for at least 36 hours, at which point the

total conversion was in excess of 98%. The finished samples were dried in a vacuum chamber for 1-2 days to remove all unreacted monomer.

Several blanks were prepared to determine incoherent scattering levels in the SANS experiments. One type consisted of a random copolymer of styrene and deuterated styrene, at the appropriate weight percent, polymerized to 100% conversion in the molds. Another type of blank was made from pure styrene monomer plus initiator. A third type of blank was prepared by following the synthesis method outlined above, but in which for fractions I, II, and III, the monomer consisted of solutions of styrene and deuterated styrene, thus also producing a randomly labeled polymer.

For the purpose of preparing conversion vs. time and molecular weight vs. conversion curves, linear polystyrene was synthesized systematically for a full range of conversions obtainable. At specific conversions polymer was recovered by first dissolving the partly polymerized material in THF, then precipitating into excess methanol and drying.

Equipment

Molecular weights were determined using a Waters Gel Permeation Chromatograph, GPC, calibrated to high resolution with narrow molecular weight distribution

polystyrene standards. Some molecular weights were verified with intrinsic viscosity measurements.

Small-angle neutron scattering experiments were made using the 5 meter SANS instrument available at the National Center for Small Angle Scattering Research (NCSASR) at the Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee. The incident neutron beam had a wavelength of 4.82 Å, with source slits of 2 cm and sample slits of 0.9 cm. The detector was a 18 x 17 cm. two-dimensional array with 0.3 x 0.3 cm. elements. The sample to detector distance was fixed at 4.6 meters. All data was corrected for detector sensitivity and background. Measurements were made for 3 hours per sample, typically yielding about 50,000-100,000 net counts above background. Since the SANS instrument had an absolute calibration, intensities were directly convertible to scattering cross-sections, and to molecular weights (5).

The K values over which the data were taken ranged from 0.007Å to 0.080Å. On comparison of this range with the R_g^2 values (Results), it is seen that $K^2 R_g^2$ is usually greater than one for the data taken, ranging from 0.3 to 3.3. However, the linearity of the data obtained suggests that it still yields the correct results; a small systematic error may be present. The error in R_g^2 and M_w^{SANS} is estimated to be between 10 and 20% for

all the samples.

RESULTS

Conversion vs. time and molecular weight vs. conversion curves are given in Figures 1 and 2, respectively, for linear polystyrene. The molecular weight increases linearly with conversion, from $M_w = 40,000$ initially, up to about 70,000 gms/mole at 55% conversion, and then increases at an increasing rate with the onset of the Trommsdorf effect. The weight-averaged molecular weight of the final product was near 300,000 gms/mole. These results are similar to that obtained by other workers at this laboratory using similar synthesis methods (7,17,18). All obtained M_w of about 300,000 gms/mole for polystyrene at 100% conversion, indicating a high degree of repeatability in the experimental method.

In order to determine the molecular weight of the inserted fraction II, the instantaneous molecular weight is needed. The molecular weight data was converted into instantaneous molecular weights according to Robertson (19) and James and Piirma (20):

$$M_w^p = M_w^{0-p} + p \frac{dM_w^{0-p}}{dp} \dots \dots \dots (8)$$

where p is the conversion of interest. The instantaneous molecular weight is found by adding to the overall molecular weight (M_w^{0-p}) the quantity corresponding to the

slope of the M_w vs. p curve (dM_w^0/dp) at the conversion of interest multiplied by p . The result of this calculation is given in Figure 2.

The instantaneous molecular weight is significantly greater than the overall molecular weight at the same conversion, and increases much faster. M_w^0 above about 65% conversion thus becomes inaccurate due to the steepness of the curve.

Twelve samples were prepared for this study, for which the distribution of the fractions are shown in Table I. The instantaneous molecular weights were calculated for fraction II by taking M_w^0 at the midpoint conversion of fraction II (conversion of fraction I plus half the conversion of fraction II). Sperling et al (17) found that the main chain molecular weight in crosslinked polystyrene is the same as that for linear polystyrene synthesized under the same conditions. This result indicates that the small amounts of crosslinker used have little effect on the primary molecular weight distribution; so molecular weights obtained for linear polystyrene are applicable to crosslinked polymers.

SANS Results

Molecular weight data. Weight average molecular weights and z-averaged radii of gyration determined by

SANS are presented in Table II. Incoherent scattering was removed by the appropriate blank as discussed in Appendix I. A typical $d\Sigma/d\Omega(K)$ vs. K plot and the corresponding Zimm plot for determination of M_w^{SANS} and R_g^2 are given in Figures 3 and 4.

Molecular weights from GPC and SANS are shown in Table II. Weight-average radii of gyration were calculated from R_g^2 by equation (7), using GPC data for values of M_w and M_z . These values, together with $R_g^w / \sqrt{M_w^{SANS}}$ are also given in Table II.

The average value of $R_g^w / \sqrt{M_w^{SANS}}$ is 0.28 ± 0.04 , which is well within error of the known value of 0.275 for polystyrene (21,22). The molecular weights obtained from SANS and from GPC are significantly different, the SANS result being one to five times greater than the GPC result. The aggregation number, N , can be defined as the ratio of M_w^{SANS} to M_w^{GPC} .

Figure 5 shows N increasing approximately linearly with mole percent of fraction II above about four mole percent. The different types of samples; xxx, xlx, and xll all follow the same trend. The quantity N appears approach unity as the size of fraction II goes below four mole percent.

Comparison to previous data. The present results are

compared with those obtained by Fernandez et al (7,8), for samples prepared by the same technique, in Tables III and IV. Both Fernandez et al and the present work show significant aggregation and almost the same ratio of $R_g^w / \sqrt{M_w^{SANS}}$, but in the previous work, N approaches one for increasing size of fraction II and approaches a very large value (about 40) as fraction II weight approaches zero. The data of Fernandez et al were corrected for molecular weight mismatch according to the method of Boue et al (12) and Crist et al (23), where:

$$M_w = M_{w(app)} \left[1 - \frac{X \Delta w}{1 - \Delta w} \right] \dots \dots \dots (9)$$

$$R_g^z = R_{g(app)}^z \left[1 + \frac{X \Delta z}{1 + (1-X) \Delta w} \right] \dots \dots \dots (10)$$

and where

$$N_{wh} = N_{wd} (1 + \Delta w) \dots \dots \dots (11)$$

$$N_{zh} = N_{zd} (1 + \Delta z) \dots \dots \dots (12)$$

N_{wh} , N_{wd} , N_{zh} , and N_{zd} are the weight and z-averaged degrees of polymerization for the hydrogenated and deuterated polymers, and X is the mole fraction of deuterated polymer. Trial calculations indicate the correction to be about 5% for samples A-L, which is less than the experimental error. Thus this correction was not done for the present data, in part due to the apparent small correction involved, and in part due to the ambiguity of selecting degree of polymerization data.

DISCUSSION

The present data shows that samples containing greater than about four to six mole percent of fraction II appear to be aggregated. These mid-range labeled compositions had values of N , the aggregation number, increasing from one to five as the size of fraction II increased. The following sections will discuss the reasons for this behavior.

Fernandez et al (7,8) were the first to show aggregation in these types of samples. However, they found a radically different dependence of aggregation number on fraction II concentration. Also, Fernandez et al found a higher range of aggregation numbers, from one to 35. The most important differences in the two synthetic procedures is that the current samples (A-L) all have fraction I conversions from 43-58%, while those of Fernandez et al all lie above 60%. Table IV compares the two sets of data. For the larger fraction I specimens there is significantly less open volume for fraction II to polymerize in. This smaller polymerization volume empirically should lead to greater degrees of aggregation since the same volume of fraction II is occupying less total space, which was found.

Proposed mechanism of aggregation The aggregation number N increases with increasing size of fraction II. The Occam's Razor principle suggests a mass effect, with increasing size of fraction II triggering an increased

response to whatever underlying mechanism causes the aggregation.

Several other cases of aggregation in SANS experiments have been reported in the literature, most noticeably the segregation of PEH/PED blends, as demonstrated by Schelten et al (4,9,10,24). In samples slow cooled from the melt, PED tends to segregate from PEH due to differential crystallization temperatures, resulting in a non-random distribution of PED, which in turn leads to unusually high values of M_w and R_g . Schelten pointed out the important result that the effect was apparently noticeable for even small deviations from a statistical blend.

In a completely different experiment, Guenet and Picot (25) studied the rejection of atactic PS in a crystallizing isotactic PS matrix. As the degree of crystallinity was increased, the labeled atactic PSD showed increasing degrees of clustering as the chains were forced into decreasing amorphous volumes. The immediate cause of aggregation was an increasing degree of non-randomness in the labeled chain distribution. In both cases the authors noted that clustering can occur if even one contact between labeled chains above statistical occurred; two non-random adjacent chains can give an apparent molecular weight twice that of the single chain molecular weight.

In accordance with the above results, it is proposed that the apparent aggregation of the samples studied arises from the labeled chains being excluded from some region of the bulk, causing a slightly non-random distribution of the labeled chains. Several mechanisms can be proposed to explain this.

The effect may be a result of artifacts introduced by the synthesis method. When fraction II was swelled into crosslinked fraction I, the fresh monomer may have been excluded from certain regions due to incomplete or inefficient swelling, resulting in fraction I not returning to its originally partly polymerized state as before the first evaporation of monomer. This may have been repeated when fraction III was prepared. One could conceive of the emplaced chains of either fraction I or fraction II "sticking" together, caused the observed aggregation. With higher conversions of fraction II, the effect would be more pronounced.

This possibility cannot be totally ruled out, but seems doubtful in view of circumstantial evidence. Styrene is a good solvent for polystyrene, and presumably also for deuterated polystyrene. In blends of PSH and PSD, two groups, Wignall et al (21) and Cotton et al (22) both found normal results, indicating no thermodynamic incompatibilities in the system. There is no reason to assume that insufficient time was allowed for swelling

equilibrium to be obtained (26,27).

Some mechanisms considered by Fernandez et al (7,8) to explain their data included the possibility that the chains were not aggregated, but were actually one continuous chain; caused either by very low termination rate or from a high degree of chain transfer. This may seem reasonable as the quantity $R_p^w / \sqrt{M_w^{SAHS}}$ corresponds to that of a random coil for all the samples (Table II). However, this possibility is unlikely considering the polymerization conditions. Fraction II contains fresh initiator and crosslinker when swollen into fraction I, the effects of which would serve to lower M_w and decrease the possibility of chain transfer.

The working hypothesis developed by Fernandez et al to explain their results relied on the fact that fraction II contained crosslinks. They proposed that pendant vinyl groups (PVGs) (i.e. potential crosslink sites) served as the means to provide for non-random contact points. In fraction II there is a higher probability that a chain crosslinks with another just formed chain rather than with previous (fraction I) or later (fraction III) chains. This is because of the greater probability of unreacted PVG's in the just polymerized portion of fraction II. Consequently, the labeled fraction II chains tend to be aggregated due to the crosslinking in fraction II.

Figure 5 shows no real difference in the apparent aggregation trend of the three types of samples (xxx, xlx, xll). Any effects of crosslinks in fractions II or fraction III appears to be negligible. The observed aggregation is due to the presence of crosslinking in fraction I or perhaps some other factor. The mechanism of Fernandez et al, that of crosslinks present in fraction II causing the observed aggregation, does not account for the apparent aggregation observed in the xlx and xll samples in the conversion range studied.

Inhomogenities in free radical copolymerizations.

Numerous authors have discussed the presence of inhomogenities in crosslinked polymers, including resins and condensation polymers (28-35). Vinyl/divinyl copolymerizations are thought to form inhomogenities before the gel-point is reached (36-38). This type of polymerization was recently modeled by Boots and Pandey using the kinetic gelation model (39). The presence and causes of inhomogenities in the styrene/DVB system has been extensively studied (40-46), the results of which will be used to explain the trends of the data.

Although many have tried to apply the results of Flory and Stockmayer to predict the gel point of styrene/DVB copolymers (47,48), but have consistently found that gel point predictions were a magnitude too small for low crosslink concentrations (45,46). In fact,

Stockmeyer was the first to point out the styrene/DVB is not ideal, as one of the basic assumptions of the gelation theory is equal reactivities of all the double bonds in the system; however, the reactivity of DVB is much greater than that of styrene (48).

This marked difference in reactivities is responsible for the appearance of inhomogeneities in styrene/DVB copolymers. The presently accepted polymerization mechanism, as applied to these copolymers, is as follows (36,42,44,45). While there is a conventional buildup of a network through interchain crosslinking, as predicted by the Flory theory, intrachain reactions predominate. At the beginning of the copolymerization, significantly more DVB reacts, which leads to a high probability of "back-biting" reactions, producing tightly crosslinked regions (gel-balls) at low conversions. There is a greater concentration of divinyl monomer in the polymer than what would be expected from the monomer feed ratio. The structure of the polymer just before the gel point, at about 13% conversion for one mole percent crosslinker (45,46), consists of densely crosslinked regions interspersed in a more or less continuous network of much lower crosslink density. Due to the tightness of the gel-balls, there are significant numbers of PVGs that were unable to react within these regions, as well as trapped radicals.

The situation is compounded by the fact that commercial DVB is a mixture of roughly 35% meta-DVB and 20% para-DVB. The remainder is mostly ethyl styrene. p-DVB reacts somewhat faster than m-DVB, increasing the driving force towards inhomogeneities. For both the meta and para isomers, the unreacted second vinyl group has the same reactivity as the styrene double bond (39,40,43,44,46). The structure of fraction I at about 40-50% conversion is imagined to consist of regions of tightly crosslinked polymer containing mainly p-DVB as the crosslinker, with trapped PVGs. Connecting these regions will be linear and branched sequences containing both m-DVB and p-DVB, with a significant number of unreacted PVGs available for further reaction. This model has been qualitatively verified by Guillot (38), who found that pendant chains are encapsulated in crosslink "islands" while the network is still growing, and that polymerization occurs just outside the boundaries of the gel (high crosslinked) regions. He also states that m-DVB tends to react later, forming PVGs around these regions. This is similar to a result of Rigbi (49). Boots and Pandey (39) present figures which show, for ten percent divinyl crosslinker and 44% conversion, significant aggregation, as calculated by the kinetic gelation model. In their case, a significant

number of PVGs are present on the "edges" of the aggregates, as well as trapped within.

When fraction II monomer mixture, consisting of the labeled monomer, is swelled into the dried fraction I, the regions of high crosslink density are relatively unavailable, excluding fraction II from polymerizing in certain regions. Fraction II is envisioned as being slightly non-random from this cause, accounting for the observed aggregation. While the unavailable volume for fraction II was not calculated, it can be estimated to be sufficient (perhaps 20-30% of the swollen volume) to force the polymerizing fraction II chains into non-random spatial configurations. This effect would be enhanced by an increase in the number of fraction II chains as found experimentally (Figure 5). The effect of PVGs in fraction I or fraction II, if any, is not apparent. An increase in fraction I size will cause a corresponding increase in excluded volume* leading to higher states of apparent aggregation, as observed qualitatively by Fernandez et al (7,8).

*Note that the use of "excluded volume" in this context - unswellable or inaccessible polymer regions due to crosslink density variations - should not be confused with the definition used in many theories in which "excluded volume" is defined as the fact that a given polymer molecule excludes others or itself from occupying its immediate place in space (47), although the concepts are similar. In this case "excluded volume" refers to supermolecular regions.

The notion of "gel-balls" caused by the higher reactivity of the DVB may account for the differences in the dependence of N on fraction II size. If the viscosity of the medium is high enough, perhaps new "gel-balls" are formed when fresh DVB is added along with deuterated styrene in fraction II. This leads to the inverse dependence noted by Fernandez et al. However, if the effect is concentration related, the apparent aggregation increases with fraction II size. These two mechanisms may be competing, with factors such as internal viscosity and internal diffusion constants playing important roles, related to the conversion of fraction I.

IPN model. Another approach to the understanding of the results is modeling the system based on homo-IPN's (50). In a paper by Siegfried et al (51) concerning the mechanical properties of PS/PS homo-IPN's, they noted that network I controls the physical and mechanical properties of the IPN. Network II was seen to form less continuous domains and behave like a filler. In the present case, fraction I behaves like network I. The presence of network I is then excluded volume, forcing network II (fraction II) into restricted regions - and causing aggregation of the labeled chains. This model would not have to depend on the presence of microgels and inhomogenities in fraction I, although their presence

would enhance the effect. Another point to be made is that in IPN's network I is polymerized to 100% conversion, and then swelled with monomer II. Network I chains in the finished IPN are extended. This is not the case for fraction I, but the similarities remain.

Conformation of the aggregated chains. As noted in Table II, all of the samples had $R_g^w / \sqrt{M_w^{SANS}}$ values within experimental error of the θ -solvent value of 0.275. For polymers in the bulk state, good agreement with θ -solvent values have been found for many systems (see 1-3). If the above mechanism for aggregation is accepted, then an aggregate of about 4 chains, as in samples I, J, K, L, must consist of a random coil, as the $R_g^w / \sqrt{M_w^{SANS}}$ values behave like a single chain. Schelten et al (9) and Guenet and Picot (25) have calculated Kratky plots ($K^2 I$ vs. K in form) for clustering or interpenetration of labeled chains. These plots show maxima at moderate K values, the height of which increases and moves to smaller K values with increasing clustering (N). The form of these plots, which are based on the random coil model (Gaussian chain distribution), are similar to plots of the experimental data, as shown in Figure 6.

The agreement in Figure 6 may support the proposed aggregation mechanism. Clustering due to excluded volume will lead to an interpenetration of the labeled chains above what is statistically expected. Apparently, the

aggregates still behave like a random coil, as $R_g^w / \sqrt{M_w^{SANS}}$ is similar to that value for single chains, although the aggregate consists of several chains. The apparent aggregation number may not correspond to the actual number of labeled molecules in the aggregate, but may only be an indication of the degree of aggregation and non-randomness in fraction II.

CONCLUSION

Polystyrene crosslinked with one mole percent divinylbenzene showed apparent aggregation through SANS measurements of chains labeled at the mid-conversion range. In the conversion range of 40-55%, aggregation numbers of one to five were found, increasing with increasing size of the labeled portion. The aggregation number does not depend on the presence or absence of crosslinker in fraction II, the labeled portion, or in the polymer at higher conversions, fraction III.

The aggregation is postulated to be due to the presence of excluded volume, leading to a non-random distribution of polymer chains formed later. The excluded volume is thought to contain inhomogeneities which consist of regions of higher crosslink density, and may be considered as "tight" gel-balls. This causes polymerizing chains to be restricted in the potential volume they can occupy, and hence appear aggregated in

SANS measurements of abnormally high molecular weights and radii of gyration.

At least two series of further experiments are planned. In one, the conversion of fraction I would be varied. As fraction I size increases, the state of aggregation should also increase for similar sized fraction II's. This has been shown tentatively by this work and the previous study (7,8). The difficulty of preparing low conversion fraction I samples may limit the usefulness of this experiment. In another series, the amount of crosslinker could be varied from zero (111 case) up to perhaps 10-20%. Questions to be resolved include the dependence of the "excluded volume" mechanism on crosslinker. Will the absence of crosslinker eliminate the observed aggregation in the full conversion range, and how will the aggregation depend on crosslinker concentration and on size of fraction II in different conversion ranges.

The importance of their presence of inhomogeneities lies in their effect on the physical and mechanical properties of the resulting polymer. The present results might explain why certain polymers exhibit lower than expected strength. Inhomogeneities serve as stress concentrators and failure sites. If the mechanisms of their formation can be completely elucidated, then perhaps stronger or tougher polymers can be produced

REFERENCES

1. J. S. Higgins and R. S. Stein, J. Appl. Cryst. 11 346 (1978).
2. A. Maconnachie and R. W. Richards, Polymer 19 739 (1978).
3. L. H. Sperling, Polym. Eng. Sci. 24 1 (1984).
4. J. Schelten, G. D. Wignall, D. G. H. Ballard, and W. Schmatz, Colloid & Polym. Sci. 252 749 (1974).
5. H. Benoit, D. Decker, R. Duplessix, C. Picot, P. Rempp, J. P. Cotton B. Farnoux, G. Jannick, and R. Ober, J. Polym. Sci. Polym. Phys. Ed. 14 2119 (1976).
6. D. Y. Yoon and P. J. Flory, Macromolecules 9 294 (1976).
7. A. M. Fernandez, J. M. Widmaier, L. H. Sperling, and G. D. Wignall, accepted, Polymer.
8. L. H. Sperling, A. M. Fernandez, and G. D. Wignall, ACS Sym. Ser. 243 71 (1984).
9. J. Schelten, G. D. Wignall, D. G. H. Ballard, and

- G. W. Longnan, Polymer 18 1111 (1977).
10. J. Schelten, A. Zinken, and D. G. H. Ballard,
Colloid & Polym Sci. 259 260 (1981).
11. H. Benoit, private communication.
12. F. Boue, M. Nierlich, and L. Leibler, Polymer 23 29
(1982).
13. L. Leibler and H. Benoit, Polymer 22 195 (1981).
14. G. Allen, Makromol. Chem. Suppl. 3 335 (1979).
15. H. Benoit, J. Koberstein, and L. Leibler, Makromol.
Chem. Suppl. 4 85 (1981).
16. User Notes, National Center for Small-Angle
Scattering Research, September, 1983.
17. L. H. Sperling, K. B. Ferguson, J. A. Manson, E. M.
Corwin, and D. L. Siegfried, Macromolecules 9
743 (1976).
18. J. K. Yeo, L. H. Sperling, and D. A. Thomas, Polymer
24 307 (1983).
19. E. R. Robertson, Trans. Faraday Soc. 67 1929 (1956).

20. H. L. James and I. Piirma, ACS Sym. Ser. 24 197 (1975).
21. G. D. Wignall, D. G. H. Ballard, and J. Schelten, European Polym. J. 10 861 (1974).
22. J. P. Cotton, D. Decker, H. Benoit, B. Farnoux, J. S. Higgins, G. Jannick, R. Ober, C. Picot, and J. desCloizeaux, Macromolecules 7 863 (1974).
23. B. Crist, W. W. Graessley, and G. D. Wignall, Polymer 23 1561 (1982).
24. J. Schelten, G. D. Wignall, and D. G. H. Ballard, Polymer 15 682 (1974).
25. J. M. Guenet and C. Picot, Macromolecules 14 309 (1981).
26. E. A. Collins, J. Bares, and F. W. Billmeyer, "Experiments in Polymer Science," John Wiley & Sons, 1973.
27. F. Rodriguez, "Principles of Polymer Systems," 2nd ed., McGraw-Hill, 1982.
28. S. C. Misra, J. A. Manson, and L. H. Sperling, ACS

Sym. Ser. 114 157 (1979).

29. S. S. Labana, S. Newman, and A. J. Chomppf, in "Polymer Networks," ed. A. J. Chomppf and S. Newman, Plenum , 1971, p. 453.
30. E. G. Booalek, E. R. Moore, S. S. Levy, and C. C. Lee, J. Appl. Polym. Sci. 3 625 (1964).
31. K. Dusek, in "Developments in Polymerizations - 3," R. N. Haward, ed., Applied Science Publications, London, 1982.
32. K. Dusek, J. Plestil, F. Lednicky, and S. Lunick, Polymer 19 393 (1978).
33. K. Dusek and M. Ilavský, Polym. Eng. Sci. 19 393 (1978).
34. D. H. Solomon, B. C. Loft, and J. D. Swift, J. Appl. Polym. Sci. 11 1593 (1967).
35. L. Gallacher and F. A. Bettelnein, J. Polym. Sci. 58 697 (1962).
36. K. Dusek, in "Polymer Networks," ed. A. J. Chomppf and S. Newman, Plenum , 1971, p.245.

37. W. Klonowski, Rheol. Acta. 18 673 (1979).
38. J. Guillot, Makromol. Chem. 183 619 (1982).
39. H. M. J. Boots and R. B. Pandey, Polym. Bull. 11 415 (1984).
40. M. Barthelin, G. Boissier, and J. Dubois, Makromol. Chem. 182 2075 (1981).
41. P. W. Kwant, J. Polym. Sci. Polym. Chem. Ed. 17 1331 (1979).
42. R. H. Wiley and E. E. Sale, J. Polym. Sci. 42 491 (1960).
43. R. H. Wiley, S. Rao, J. Jin, and K. S. Kim, J. Macromol. Sci.-Chem. A4 1453 (1970).
44. G. Schwachula, J. Polym. Sci. Sym. 53 107 (1975).
45. B. T. Storey, J. Polym. Sci. Part A 3 265 (1965).
46. J. Malinsky, J. Klaban, and K. Dusek, J. Macromol. Sci.-Chem. A5 1071 (1971).
47. P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, 1953.

48. W. H. Stockmeyer, J. Chem. Phys. 12 125 (1944).

49. Z. Rigbi, in "Polymer Networks," ed: A. J. Chomppf and S. Newman, Plenum, 1971, p. 245.

50. L. H. Sperling, "Interpenetrating Polymer Networks," Plenum, 1981, p. 49.

51. D. L. Siegfried, D. A. Thomas, and L. H. Sperling, Macromolecules 12 586 (1979).

APPENDIX I

Choice of blanks. Blanks consisting of both protonated PS and randomly deuterated PS, at the appropriate weight percent, were used to measure incoherent scattering background (11). In addition, incoherent backgrounds were also removed by calculating the average intensity a randomly deuterated blank should produce and using the result for correction of scattering intensities.

A $d\Sigma/d\Omega(K)$ vs. K plot for a blank shows some increase in scattering intensities at very low angles, below $K = 0.008\text{\AA}$, probably due to void scattering. Whether or not these voids are also present in the samples is unknown, although void scattering has been reported to be only 1% of total incoherent scattering (12). Consequently, average incoherent scattering was calculated for each blank by averaging $d\Sigma/d\Omega(K)$ at higher K values, and the appropriate quantity subtracted.

The results of the different correction methods is given in Tables A1 and A2 for two samples. There is no difference, within experimental error, between the random copolymer blank and the average level subtractions. While $d\Sigma/d\Omega(0)$ values and hence molecular weights are consistently lower (but still within error) for the protonated blank, R_g^z values are slightly lower. The quantity $R_g^w / \sqrt{M_w^{SANS}}$, which has been determined to be 0.275

for a PS random coil by SANS and other methods (3,21,22) agrees with the experimental value for the deuterated blanks, but is slightly lower for the hydrogenated blanks. Incoherent scattering was corrected by subtracting the appropriate randomly deuterated blank or the corresponding average incoherent scattering level for all the samples, both methods yielding identical results. The difference between the deuterated and protonated blanks is within experimental error, although subtraction of incoherent intensities with the deuterated blank is more correct.

TABLE CAPTIONS

Table I : Polystyrene network type and fraction distribution.

Table II : Results of GPC and SANS and calculated values for polystyrene.

Table III : Summary of results obtained by Fernandez et al (7,8) for polystyrene networks.

Table IV : Comparison of main results of Fernandez et al (7,8) with present results for polystyrene.

Table A1 : Comparison of results obtainable for several blanks, as shown for sample F.

Table A2 : Comparison of results obtainable for several blanks, as shown for sample G.

Table I : Polystyrene network type and fraction weight distribution

SAMPLE IDENTIFICATION	TYPE	WEIGHT CONVERSION OF FRACTION			MOLE FRACTION
		<u>I</u>	<u>II</u>	<u>III</u>	<u>II</u>
A	xxx	.433	.041	.526	.044
B	xxx	.428	.048	.524	.052
C	x1x	.576	.076	.348	.081
D	xxx	.500	.083	.417	.089
E	x11	.512	.086	.402	.092
F	x1x	.494	.099	.407	.106
G	x1x	.447	.117	.436	.125
H	x11	.559	.141	.300	.150
I	x1x	.472	.165	.363	.175
J	xxx	.464	.179	.357	.190
K	x1x	.463	.188	.349	.200
L	x11	.450	.202	.348	.214

Table II : Results of GPC and SANS and calculated values for polystyrene.

SAMPLE	M_W^P (GPC)(a) (gms/mole)	M_W^{SANS} (a) (gms/mole)	N (b)	R_g^Z (a) (Å)	R_g^W (b) (Å)	$\frac{R_g^W}{\sqrt{M_W^{SANS}}}$ (b)
A	110,000	180,000	1.6	126	105	0.25
B	110,000	110,000	1.0	130	106	0.32
C	200,000	230,000	1.2	140	114	0.24
D	150,000	210,000	1.4	200	160	0.35
E	160,000	290,000	1.8	150	122	0.23
F	150,000	340,000	2.3	161	144	0.28
G	130,000	330,000	2.5	189	154	0.27
H	240,000	470,000	2.0	243	198	0.29
I	150,000	590,000	3.9	224	183	0.24
J	150,000	760,000	4.8	334	278	0.32
K	160,000	520,000	3.3	241	197	0.27
L	150,000	580,000	3.9	244	199	0.26

(a) Experimentally determined.

(b) Calculated values.

Table III : Summary of results obtained by
Fernandez et al (7,8) for
polystyrene networks.

SAMPLE NUMBER	WEIGHT FRACTION			N*
	I	II	III	
2	.799	.201	.000	1 ⁺
5	.750	.139	.111	4
7	.600	.139	.261	11
4	.750	.102	.148	15
6	.600	.100	.300	16
3	.750	.054	.196	34

* Molecular weight mismatch corrected (see eqs. 9-12).

+ This sample was affected by the Tromsdorff effect,
and its molecular weight is known with less
certainty than the other samples of Fernandez et al.

Table IV : Comparison of main results of Fernandez et al (7,8) with present results for polystyrene.

	<u>Fernandez</u>	<u>Present Work</u>
Percent conversion at beginning of fraction II	60-85	40-55
Types of networks studied	xxx	xxx, xlx, xll
SANS blank	PSH	PSH/PSD random copolymers
Molecular weight mismatch correction	0-30 %	small and ignored
Range in N	1-35	1-5
Dependance of N on mole-% fraction II	decreases with increasing fraction II	first none, then increasing with fraction II
$R_g^W / \sqrt{M_W^{SANS}}$	0.31±0.09	0.28±0.04

Table A1 : Comparison of results obtainable for several blanks, as shown for sample F

blank type	$\frac{d\Sigma}{d\Omega}$ (cm^{-1})	R_g^Z (\AA)	$\frac{R_g^W}{\sqrt{M_w^{\text{SANS}}}}$
PSH	35±4	176±14	0.255
PSH/PSD random copolymer (90/10 wt%)	37±4	197±15	0.276
average level of (90/10) copolymer blank	39±4	203±18	0.277

sample F : 9.8 wt% fraction II

Table A2 : Comparison of results obtainable for several blanks, as shown for sample G.

<u>blank type</u>	$\frac{d\Sigma}{d\Omega}$ (cm^{-1})	R_g^Z (\AA)	$\frac{R_g^W}{\sqrt{M_w \text{ SANS}}}$
PSH	45±4	185±11	0.254
PSH/PSD random copolymer (87/13 wt%)	44±4	190±13	0.264
average level of (87/13) copolymer blank	42±4	189±13	0.268
sample G : 11.7 wt% fraction II			

FIGURE CAPTIONS

Figure 1 : Experimental conversion vs. time curve for bulk, free-radical polymerization of polystyrene.

Figure 2 : Experimental weight- and number- average molecular weight and calculated weight-average instantaneous molecular weight vs. conversion curves for polystyrene polymerizations.

▲ : M_n , ● : M_w .

Figure 3 : $[d\Sigma/d\Omega(K)]/C_N$ vs. $K = (4\pi/\lambda)\sin\theta$ for sample K.

Figure 4 : Zimm plot for sample K.

Figure 5 : Aggregation number N vs. mole-% of fraction II.

Figure 6 : Comparison of Kratky plots for samples B, G, and L (bottom) with those calculated by Guenet and Picot (25) (top), for interpenetrating random coils. Numbers correspond to aggregation number N.

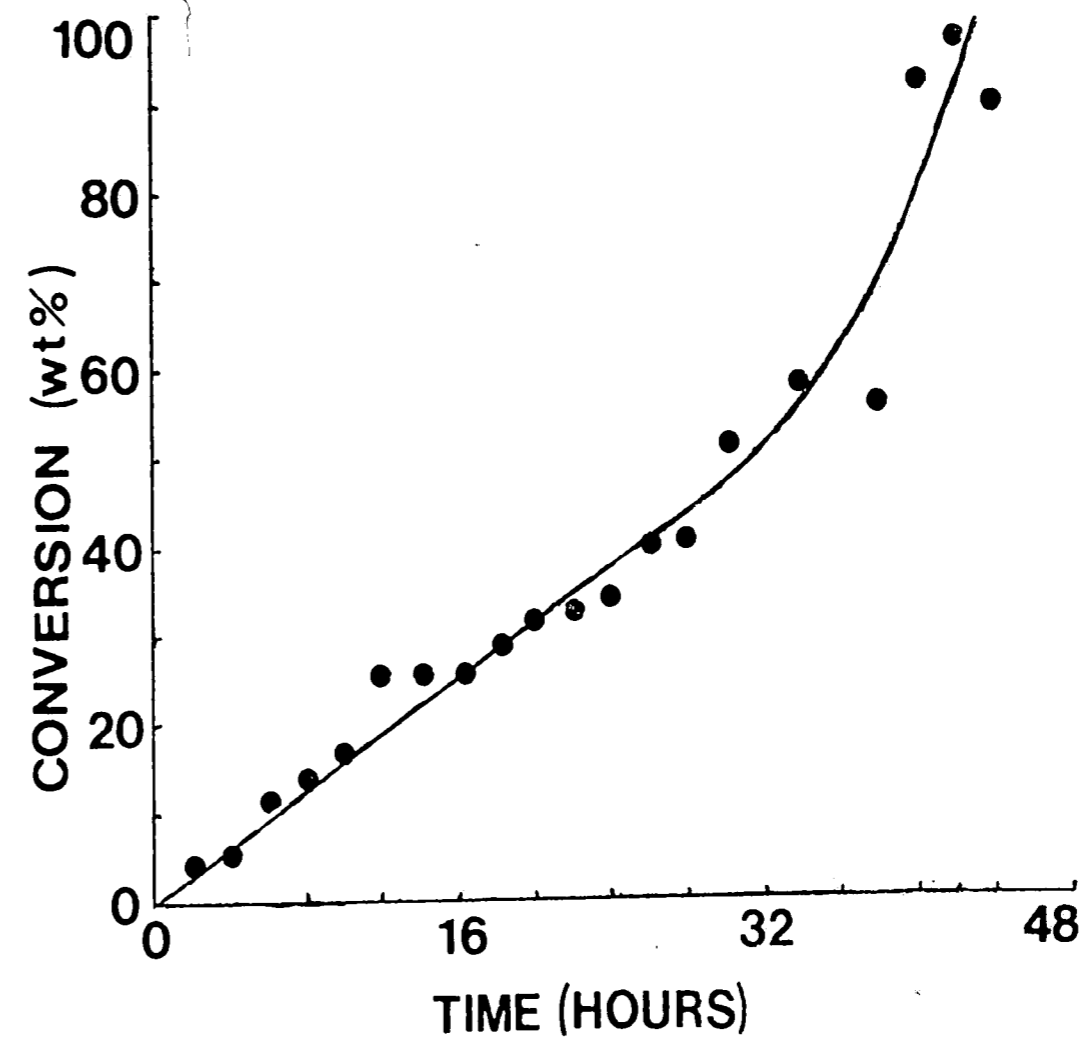


FIGURE 1

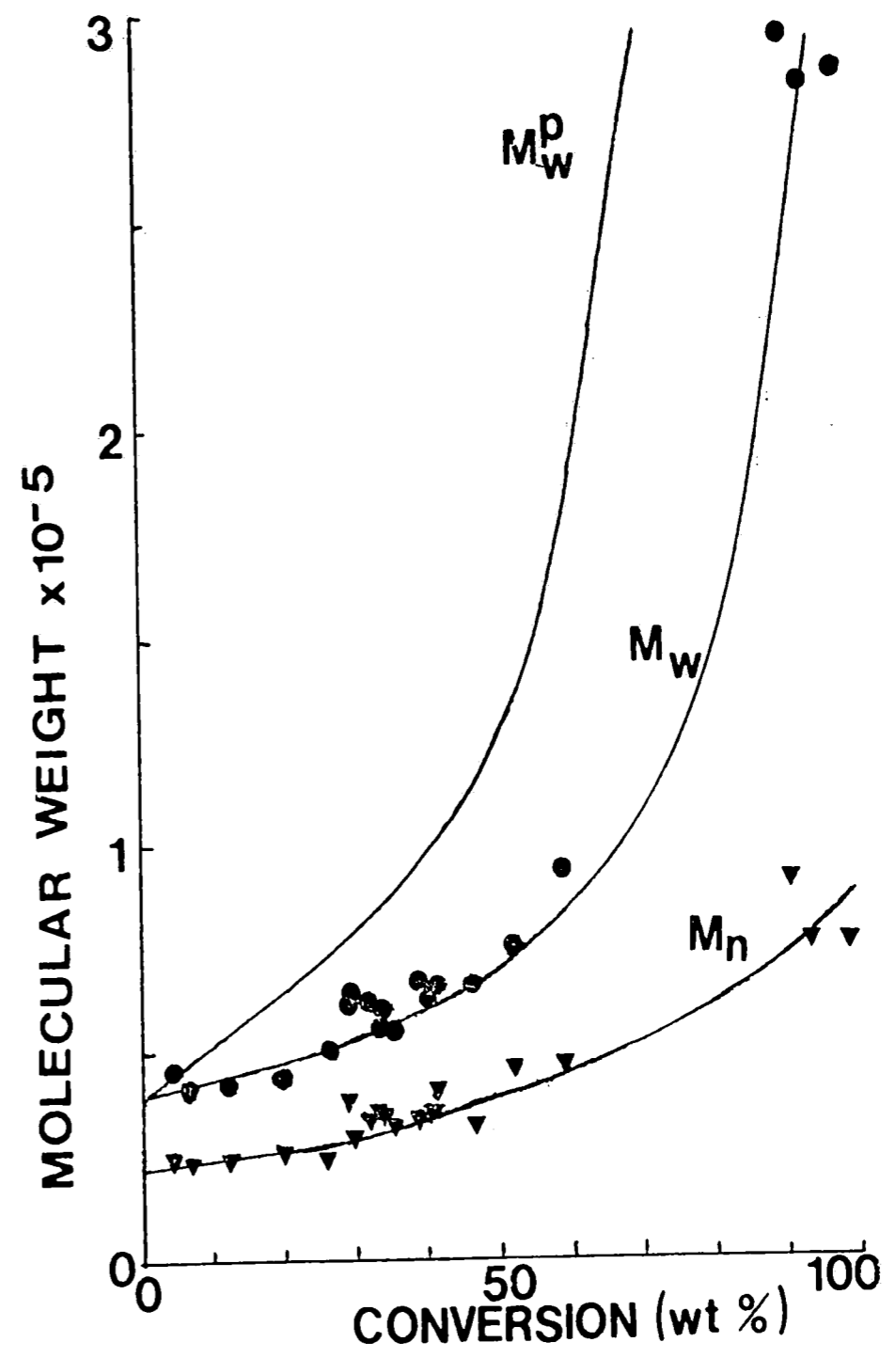


FIGURE 2

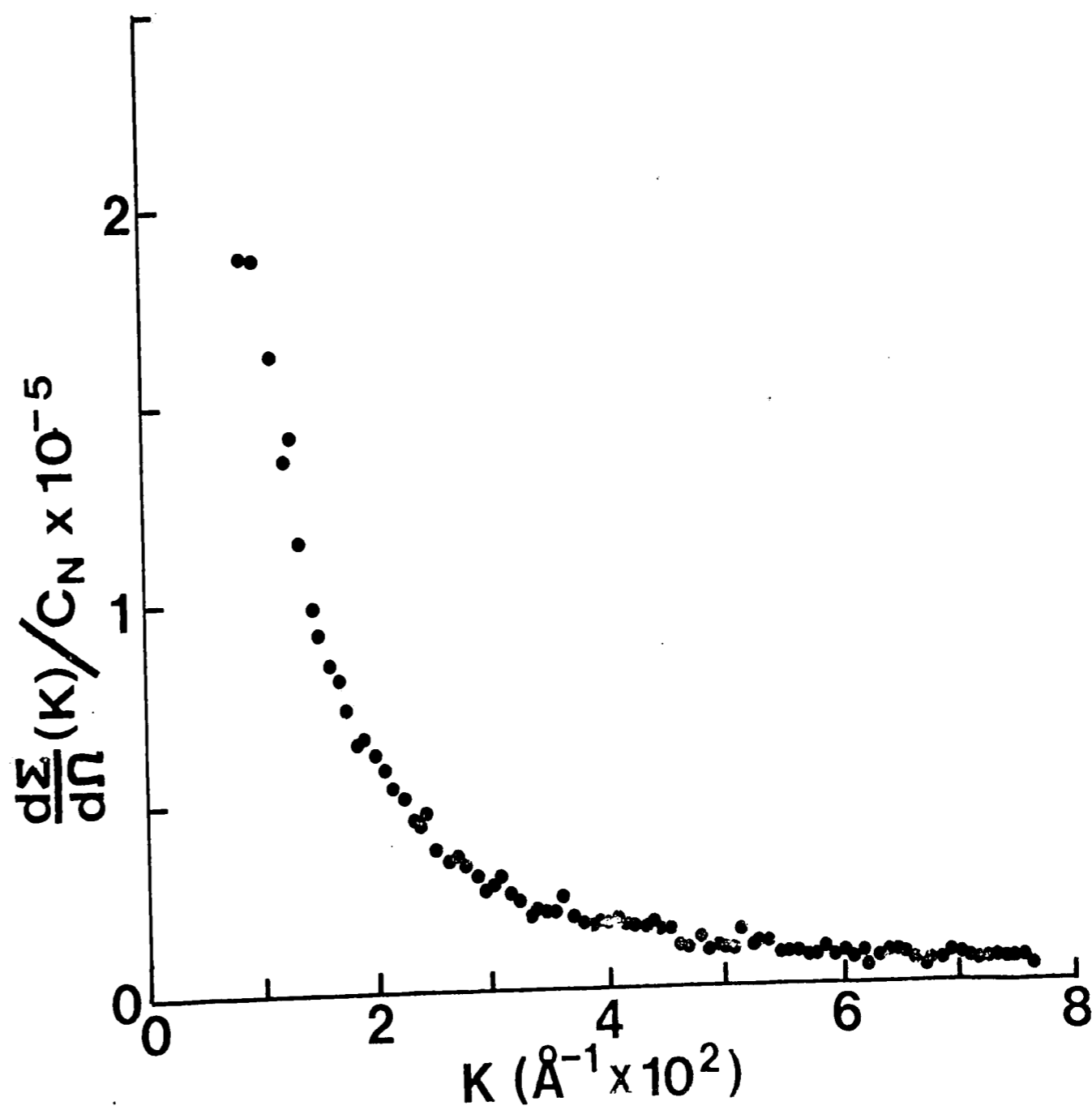


FIGURE 3

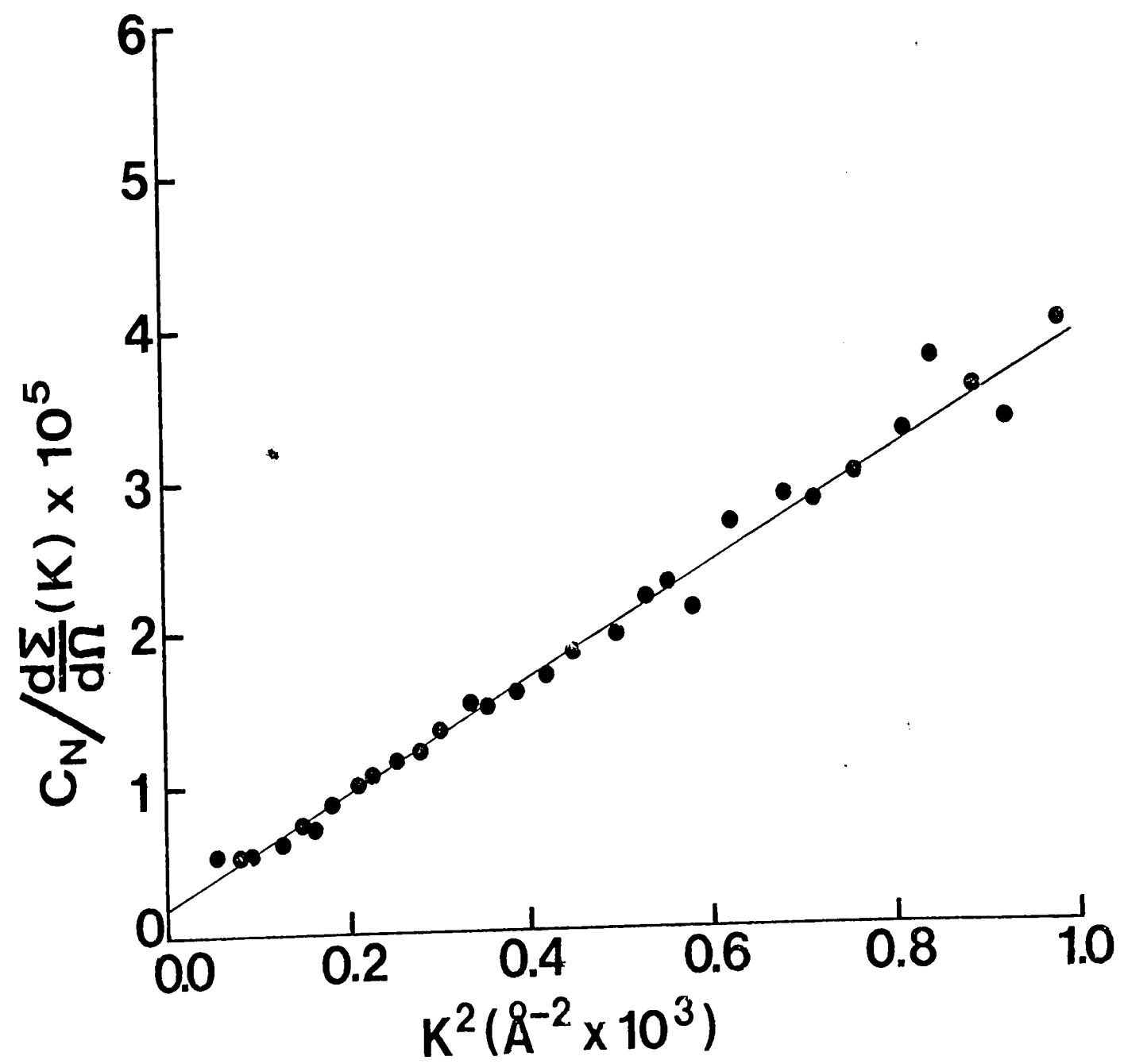


FIGURE 4

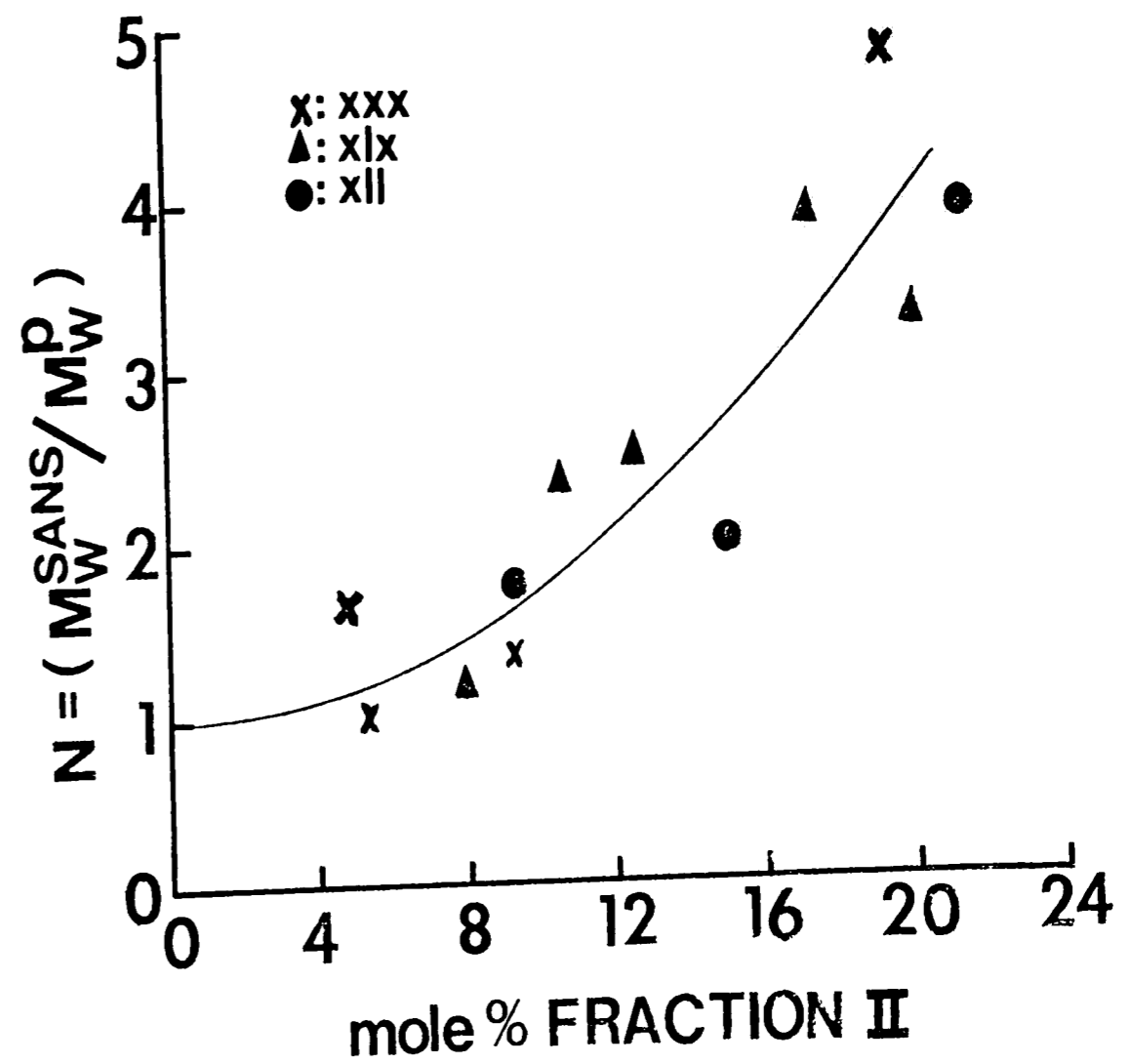


FIGURE 5

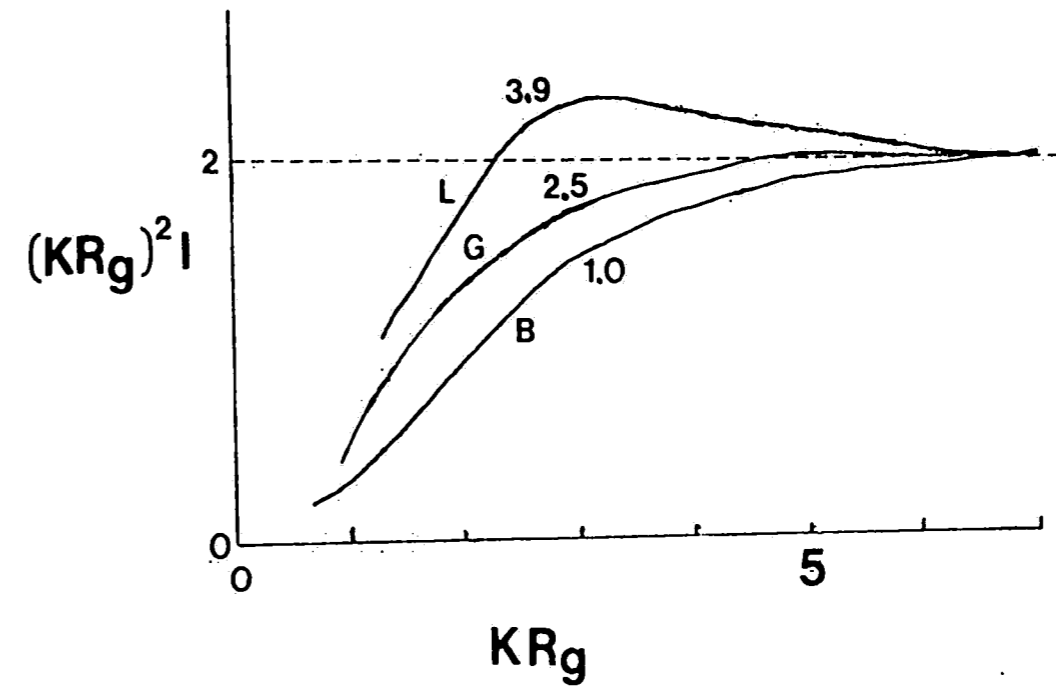
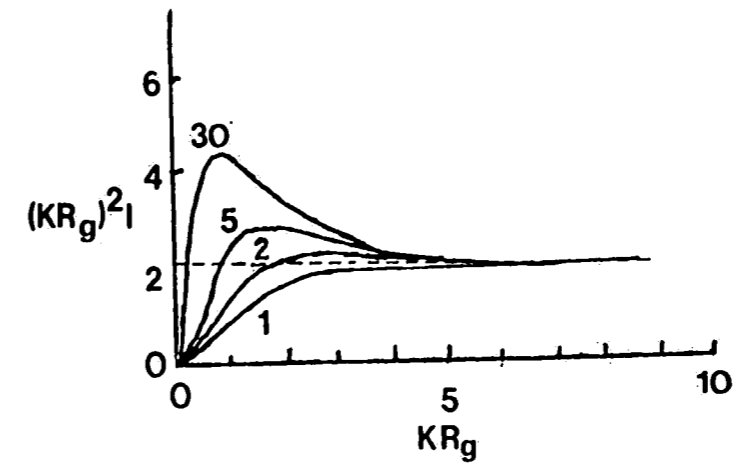


FIGURE 6

CHAPTER 2

DATA INTERPRETATION

SANS Data

As seen in figure 4, the points at the lowest K values are not quite linear. These points (usually only the first and second) had considerable error, and were routinely discarded before calculating the slope and intercept of the plot. Upon careful examination of the remaining points, a slight curvature may be noted. This is more apparent in Zimm plots for some of the other samples. Because of this curvature, the intercept can be greatly effected by what set of points are taken to draw a straight line through the data. As an example, if points 3-15 are chosen, the intercept, $I(0)$, may have a value of 10.0; while if points 5-15 are taken, the intercept could increase to 11.0 or 12.0; and if points 10-20 are taken, the intercept may rise to a value of 20.0. Thus by judicial choice of points in the Zimm plot, the data can appear as one chooses. As already noted in the experimental section of Chapter 1, most of the data was above the Guinier region. Consequently, the points corresponding to the lowest K values (i.e. 3-10) were used in calculating all of the data, thus giving the lowest molecular weights. While this procedure was considered correct, it should be kept in mind that M_w^{SANS} could actually be significantly higher, depending on the interpretation of the data. This could have some consequences in the interpretation of what is happening

inside the samples.

Instantaneous Molecular Weights

On comparison of the instantaneous molecular weight (M_w^P) curve of Fernandez et al (7,8) with that of this study (Figure 1), a significant difference is observed. While the curve of Fernandez et al increases slowly until about 90% conversion, then rises rapidly; the curve in Figure 1 is seen to increase much more quickly, and rise rapidly above 50% conversion. Fernandez et al was able to obtain M_w^P values up to 90% conversion, while they could only be obtained up to 65% conversion in this study.

The reason for the difference may lie in the synthesis procedure of the linear PS used in determining the molecular weight (M_n , M_w , and M_w^P) curves. In this study, as described in Chapter 1, the linear PS was made in the same way as the samples. Fernandez reports (private communication) that the PS used for their study was synthesized in glass vials. As discussed in most basic transport phenomena texts (see chapters on dimensional analysis), geometrical similarity is an important constraint in comparing two systems. As glass vials are not similar to glass molds in several respects, the applicability of results obtained from PS polymerized in glass vials to characterization of samples made in

glass molds must be questioned.

Attempting to calculate aggregation numbers for Fernandez et al's data using the M_w^P curve in Figure 1 fails, as M_w^P cannot be obtained in the conversion range of samples 2-7. Qualitatively the M_w^P 's may be on the order of 500,000 to 1,000,000, which would imply that the states of aggregation of Fernandez et al's data is only $N = 1$ to 5. These numbers agree with that found for the present samples, as shown in figure 5, although the trend and exact placement of the recalculated N values remains unknown. Obviously one has to be careful in interpreting molecular weight data and determining the applicability of the results to various systems.

Predictions of the Excluded Volume Model

If the experiments described in the conclusion of Chapter 1 should be completed, the following results may be found. As crosslinker concentration is varied, aggregation number should change. Keeping the size of fraction I and II constant, aggregation will increase with increasing crosslinker concentration. As more crosslinker is present in the system, the "gel-balls" get tighter and more extensive, as shown experimentally by the lowering of the gel-point with increased crosslinker concentration (i.e. 45,46). As volume exclusion increases, more aggregation will occur, leading to higher apparent molecular weights from SANS. No aggregation

will be observed in the zero crosslinker case. As all chains are free to occupy any part of the bulk, not being restrained by crosslinks, there is no excluded volume, thus fraction II will be random, and SANS will give normal results. This, in essence, is what the excluded volume model states : that aggregation is due solely to the unavailability of regions in the polymer, by whatever cause, to a certain set of polymer chains. In this case, densely crosslinked regions excluded later polymerizing chains from penetrating their areas, causing the non-randomness of the system.

Likewise, in the case of varying fraction I conversion, aggregation is expected to increase with increasing fraction I conversion, above and probably below the gel point as well. As fraction I size increases, so does the extent of excluded volume and consequently aggregation. The exact dependence of aggregation on fraction I size is not clear, but it may increase linearly with fraction I size, then level off above a certain conversion. This will have to be determined experimentally.

In another experiment, the nature of the gel balls can be examined. By deuterating fraction I, and polymerizing up to a variety of conversions, SANS may be able to determine the size and shape of the "excluded volume". (In this case, fraction III is not needed).

Below the gel point, aggregation of fraction I will increase linearly with size of fraction I, as the growth of the gel balls below the gel point is assumed to be linear, or perhaps slightly decreasing with extent of conversion. Above the gel point, aggregation may stay constant or decrease, as the "gel balls" (now tightly crosslinked regions) become larger and more diffuse.