1720 *Macromolecules* 1985, *18*, 1720–1727

Small-Angle Neutron Scattering Determination of Nonrandomness in Cross-Linked Polystyrene at Midrange Conversions

J. G. Weissman[†] and L. H. Sperling*

Polymer Science and Engineering Program, Department of Chemical Engineering, Materials Research Center No. 32, Lehigh University, Bethlehem, Pennsylvania 18015.

Received October 16, 1984

ABSTRACT: Polystyrene was photopolymerized by bulk, free-radical methods in a three-step synthesis to yield a sample containing a portion of deuterated chains at a specific conversion of interest. The initial portion of protonated polystyrene, fraction I, was cross-linked with 1 mol % divinylbenzene and polymerized up to conversions of 40–50%. The unreacted monomer was replaced with deuterated styrene monomer, and fraction II was polymerized for an additional 4–20% conversion. Fraction III was again protonated, which brought the total conversion to 100%. Fractions II and III were either linear or cross-linked. All of the compositions with fraction II greater than 4 wt % were found to have unusually high molecular weights and radii of gyration when studied by small-angle neutron scattering (SANS). SANS gave weight-average molecular weights between 110 000 and 760 000 for fraction II, while GPC indicated molecular weights from 110 000 to 240 000, yielding an apparent enhancement of SANS molecular weight of up to 5 times the GPC value. The enhancement was thought to be caused by the presence of "excluded volume" arising from previously inhomogeneously polymerized cross-linked fraction I and leads to a model suggesting a nonrandom distribution of labeled polymer, which results in several chains scattering like one large chain.

Introduction

Background. Small-angle neutron scattering (SANS) is a powerful tool in the study of polymer chain conformation and morphology.[1-6] 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 with their protonated (ordinary) counterparts.

Recently, Fernandez et al.[7,8] synthesized polystyrene/poly(deuteriostyrene)/polystyrene (PSH/PSD/PSH) networks for SANS experiments. The samples were prepared by inserting a fraction of labeled monomer at a midrange point in the polymerization. The networks contained 1 mol % divinylbenzene (DVB) and were made by 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 norandomness of lower molecular weight chains.

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

The present work was intended to continue the research begun by Fernandez et al. If the cross-linking agent were to be removed from the deuterated portion, then the chains might have less reason to be nonrandom. Samples were made by a similar method, but with several modifications. The first part, fraction I, was always cross-linked (x), while the labeled portion, fraction II, was either cross-linked or linear (l). The reaction was carried to 100% conversion with fraction III, which again was either cross-linked 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

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

where C_N is the sample constant given by

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

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

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

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 protonated 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 $R_g^2 K^2 < 1$, eq 3 can be simplified; substitution into eq 1 yields the basic SANS equation for polymers:

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

$d\Sigma(K)/d\Omega$ 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 vs. K for a sample, M_w and R_g^z may be obtained through a

---

[†] Present address: Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, PA 15213.

Zimm plot ($[\mathrm{d}\Sigma(K)/\mathrm{d}\Omega]^{-1}$ vs. K^2) of eq 4, where the molecular weight is given by

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

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

$$R_g^z = [3C_N M_w(\mathrm{slope})]^{1/2} \qquad (6)$$

R_g^w can be found from

$$R_g^w = (M_w/M_z)^{1/2}R_g^z \qquad (7)$$

where M_w and M_z are the weight- and z-average molecular weights.[17-22] The value of $\mathrm{d}\Sigma(K)/\mathrm{d}\Omega$ must be corrected by removal of incoherent scattering intensity by subtracting scattering from the appropriate blank, leaving only the coherent intensities, as discussed below.

It must be pointed out that the correlation function of the deuterated species and the protonated species will, in general, be different if the molecular weights of the two species are different. The molecular weight mismatch can be corrected by using the method of Boue et al.[12] and Crist et al.[23] where

$$M_w = M_w(\mathrm{app})\left[1 - \frac{X\Delta w}{1-\Delta w}\right] \qquad (8)$$

$$R_g^2 = R_g^2(\mathrm{app})\left[1 + \frac{X\Delta z}{1+(1-X)\Delta w}\right] \qquad (9)$$

and where

$$N_{wH} = N_{wD}(1+\Delta w) \qquad (10)$$

$$N_{zH} = N_{zD}(1+\Delta z) \qquad (11)$$

N_{wH}, N_{wD}, N_{zH}, and N_{zD} are the weight- and z-average degrees of polymerization for the protonated and deuterated polymers and X is the mole fraction of deuterated polymer.

Experimental Section

Synthesis. The goal was to synthesize a polystyrene/poly(deuteriostyrene)/polystyrene network such that the labeled polymer would be inserted at a certain midrange conversion and in such 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 syntheses 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 in. × 4 in. × $^1/_4$ in. each, between which were placed two 10-μm Mylar films. Between the Mylar sheets was placed a cut O-ring, typically Viton (90 durometer, 1.5-mm diameter), with the opening directed upward to allow for addition of monomer solution. The components were assembled sandwich fashion and clamped together with 6–8 $^1/_2$-in. binder clips placed strategically around the glass plate edges. Two, 2-in. C-clamps were used to hold the mold vertically. Leakage from the mold was minimal.

Styrene monomer (Fisher) and deuterated styrene monomer (Cambridge Isotope Labs) were purified by passing the monomers through a chromatography column packed with neutral alumina (80–200 mesh, Fisher). Technical grade DVB (K&K Rare and Fine Chemicals) and analytic grade benzoin (Kodak) were used as received. The initiator (benzoin) concentration was kept constant at 0.4 wt %, and the cross-linker (DVB) concentration was kept at 1.0 mol %, 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 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 1 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 4% to 20%, taking 0.5–4 h. 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 h, 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 and then precipitating into excess methanol and drying.

Equipment. Molecular weights were determined with 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 conducted on the 5-m SANS instrument available at the National Center for Small Angle Scattering Research (NCSASR) at Oak Ridge National Laboratory (ORNL), Oak Ridge, TN. 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 an 18 × 17 cm two-dimensional array with 0.3 × 0.3 cm elements. The sample-to-detector distance was fixed at 4.6 m. All data were corrected for detector sensitivity and background. Measurements were made for 3 h 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 0.007 to 0.080 Å. On comparison of this range with the R_g^z values (see Results), it is seen that $K^2R_g^2$ is usually greater than 1 for the data taken, ranging from 0.8 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^z 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 to about 70 000 at 55% conversion, and then increases at an increasing rate with the onset of the Trommsdorff effect. The weight-average molecular weight of the final product was near 300 000. 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 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

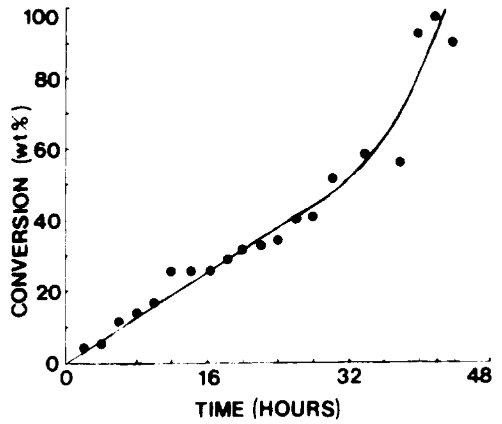

Figure 1. Experimental conversion vs. time curve for bulk, free-radical polymerization of polystyrene.

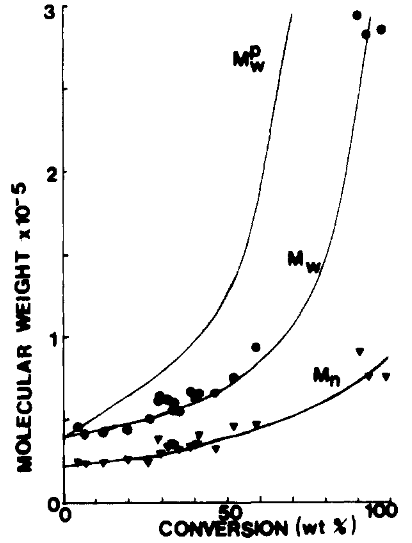

Figure 2. Experimental weight- and number-average molecular weights and calculated weight-average instantaneous molecular weight vs. conversion curves for polystyrene polymerizations: (▲) M_n; (●) M_w.

needed. The molecular weight data were converted into instantaneous molecular weights according to Robertson[19] and James and Piirma:[20]

$$M_w^p = M_w^{0-p} + p\frac{dM_w^{0-p}}{dp} \tag{12}$$

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-p}/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^p 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 is shown in Table I. The instantaneous molecular weights were calculated for fraction II by taking M_w^p 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 cross-linked polystyrene is the same as that for linear polystyrene synthesized under the same conditions. This result indicates that the small amounts of cross-linker used have little effect on the primary molecular weight distribution; so molecular weights obtained for linear polystyrene are applicable to cross-linked polymers.

Table I
Polystyrene Network Type and Fraction Weight Distribution

sample	type	wt conv of fraction I	wt conv of fraction II	wt conv of fraction III	mol fraction II
A	xxx	0.433	0.041	0.526	0.044
B	xxx	0.428	0.048	0.524	0.052
C	xlx	0.576	0.076	0.348	0.081
D	xxx	0.500	0.083	0.417	0.089
E	xll	0.512	0.086	0.402	0.092
F	xlx	0.494	0.099	0.407	0.106
G	xlx	0.447	0.117	0.436	0.125
H	xll	0.559	0.141	0.300	0.150
I	xlx	0.472	0.165	0.363	0.175
J	xxx	0.464	0.179	0.357	0.190
K	xlx	0.463	0.188	0.349	0.200
L	xll	0.450	0.202	0.348	0.214

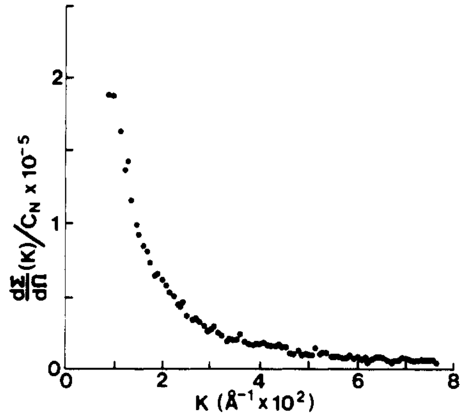

Figure 3. $[d\Sigma(K)/d\Omega]/C_N$ vs. $K = (4\pi/\lambda)\sin\theta$ for sample *K*.

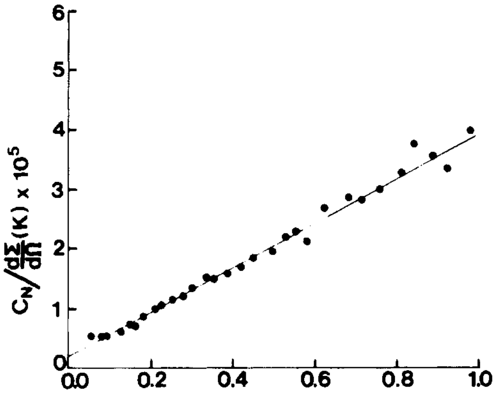

Figure 4. Zimm plot for sample *K*.

SANS Results. Molecular Weight Data. Weight-average molecular weights and z-average 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 $d\Sigma(K)/d\Omega$ vs. K plot and the corresponding Zimm plot for determination of M_w^{SANS} and R_g^z 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^z by eq 7, using GPC data for values of M_w and M_z. These values, together with $R_g^w/(M_w^{SANS})^{1/2}$ are also given in Table II.

The average value of $R_g^w/(M_w^{SANS})^{1/2}$ is 0.28 ± 0.04, which is well within error of the known value of 0.275 for

Table II
Results of GPC and SANS and Calculated Values for Polystyrene

sample	type	M_w^P(GPC)[a]	M_w^{SANS} [a]	N[b]	R_g^z,[a] Å	R_g^w,[b] Å	$R_g^w/(M_w^{SANS})^{1/2}$ [b]
A	xxx	110 000	180 000	1.6	126	105	0.25
B	xxx	110 000	110 000	1.0	130	106	0.32
C	xlx	200 000	230 000	1.2	140	114	0.24
D	xxx	150 000	210 000	1.4	200	160	0.35
E	xll	160 000	290 000	1.8	150	122	0.23
F	xlx	150 000	340 000	2.3	161	144	0.28
G	xlx	130 000	330 000	2.5	189	154	0.27
H	xll	240 000	470 000	2.0	243	198	0.29
I	xlx	150 000	590 000	3.9	224	183	0.24
J	xxx	150 000	760 000	4.8	334	278	0.32
K	xlx	160 000	520 000	3.3	241	197	0.27
L	xll	150 000	580 000	3.9	244	199	0.26

[a] Experimentally determined. [b] Calculated values.

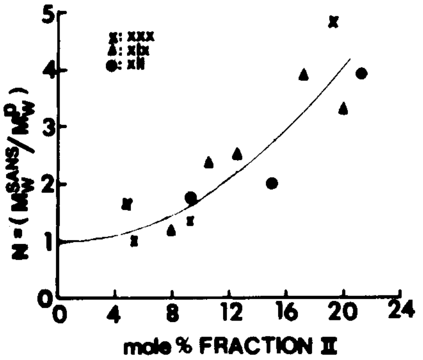

Figure 5. Aggregation number N vs. mole percent of fraction II.

polystyrene.[21,27] The molecular weights obtained from SANS and from GPC are significantly different, the SANS result being 1–5 times greater than the GPC result. The nonrandomness number, N, can be defined as the ratio of M_w^{SANS} to M_w^P(GPC).

Figure 5 shows N increasing approximately linearly with mole percent of fraction II above about 4 mol %. The different types of samples, xxx, xlx, and xll, all follow the same trend. The quantity N appears to approach unity as the size of fraction II goes below 4 mol %.

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 nonrandomness and almost the same ratio of $R_g^w/(M_w^{SANS})^{1/2}$, but in the previous work, N approaches 1 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] eq 8–11.

Both instantaneous and cumulative averages were studied, and the correction was found to be 5% or less for all samples. The total error estimated for the experimental molecular weight determinations is of the order of 10%, and hence the correction of Boue et al.[12] was not applied. Also, since the apparent molecular weight caused by the nonrandomness was much higher in some cases, there is some ambiguity in selecting the degree of polymerization data for this correction. However, even if the worst case is assumed, the correction is still of the order of 10%, far smaller than the nonrandomness effect found.

Table III
Summary of Results Obtained by Fernandez et al.[7,8] for Polystyrene Networks

	wt fraction			
sample	I	II	III	N[a]
2	0.799	0.201	0.000	1[b]
5	0.750	0.139	0.111	4
7	0.600	0.139	0.261	11
4	0.750	0.102	0.148	15
6	0.600	0.100	0.300	16
3	0.750	0.054	0.196	34

[a] Molecular weight mismatch corrected (see eq 8–11). [b] 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

	Fernandez	present work
% 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
mol wt mismatch correction	0–30%	small and ignored
range in N	1–35	1–5
dependence of N on mol % fraction II	decreases with increasing fraction II	first none and then increasing with fraction II
$R_g^w/(M_w^{SANS})^{1/2}$	0.31 ± 0.09	0.28 ± 0.04

Discussion

The present data show that samples containing greater than about 4–6 mol % of fraction II appear to be nonrandom. These midrange-labeled compositions had values of N, the nonrandomness number, increasing from 1 to 5 as the size of fraction II increased. The following sections discuss the reasons for this behavior.

Fernandez et al.[7,8] were the first to show nonrandomness in these types of samples. However, they found a radically different dependence of the nonrandomness number on fraction II concentration. Also, Fernandez et al. found a higher range of nonrandomness numbers, from 1 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% to 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 nonrandomness since the same volume of fraction II is occupying less total space, which was found.

Proposed Mechanism of Nonrandomness. The nonrandomness 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 nonrandomness.

Several other cases of nonrandomness 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 nonrandom 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 nonrandomness was an increasing degree of nonrandomness 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 nonrandom 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 increase in molecular weight of the samples studied arises from the labeled chains being excluded from some region of the bulk, causing a slightly nonrandom 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 cross-linked 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 increase. 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 incompatabilities 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 clustered 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 $R_g^{w}/(M_w^{SANS})^{1/2}$ 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 cross-linker 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 cross-links. They proposed that pendant vinyl groups (PVGs) (i.e., potential cross-link sites) served as the means to provide for nonrandom contact points. In fraction II there is a higher probability that a chain cross-links 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 PVGs in the just-polymerized portion of fraction II. Consequently, the labeled fraction II chains tends to be clustered due to the cross-linking in fraction II.

Figure 5 shows no real difference in the apparent nonrandomness number of the three types of samples (xxx, xlx, xll). Any effects of cross-links in fractions II or fraction III appear to be negligible. The observed clustering is due to the presence of cross-linking in fraction I or perhaps some other factor. The mechanism of Fernandez et al., that of cross-links present in fraction II causing the observed apparent increase in molecular weight, does not account for the apparent increase observed in the xlx and xll samples in the conversion range studied.

Inhomogeneities in Free-Radical Copolymerizations. Numerous authors have discussed the presence of inhomogeneities in cross-linked polymers, including resins and condensation polymers.[28-35] Vinyl/divinyl copolymerizations are thought to form inhomogeneities 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 inhomogeneities in the styrene/DVB system have 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] gel point predictions have consistently been found to be a magnitude too small for low cross-link concentrations.[45,46] In fact, Stockmayer was the first to point out that 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 cross-linking, 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 cross-linked 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 1 mol % cross-linker,[45,46] consists of densely cross-linked regions interspersed in a more or less continuous network of much lower cross-link density. Due to the tightness of the gel balls, there are significant numbers of PVGs that are 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% *m*-DVB and 20% *p*-DVB. The remainder is mostly ethylstyrene. *p*-DVB reacts somewhat faster than *m*-DVB, increasing the driving force toward 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 around 40–50% conversion is imagined to consist of regions of tightly cross-linked polymer containing mainly *p*-DVB as the cross-linker, 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 cross-link "islands" while the network is still growing and that polymerization occurs just outside the boundaries of the gel (high cross-linked) 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 that show, for 10% divinyl cross-linker 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-cross-link density are relatively unavailable, excluding fraction II from polymerizing in certain regions. Fraction II is envisioned as being slightly nonrandom from this cause, accounting for the observed apparent molecular weight increase. 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 nonrandom 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,[52] leading to higher states of apparent aggregation, as observed qualitatively by Fernandez et al.[7,8]

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-IPNs.[50] In a paper by Siegfried et al.[51] concerning the mechanical properties of PS/PS homo-IPNs, 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 inhomogeneities in fraction I, although their presence would enhance the effect. Another point to be made is that in IPNs, 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 Segregated Chains. As noted in Table II, all of the samples had $R_g^w/(M_w^{\mathrm{SANS}})^{1/2}$ 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 ref 1–3). If the above mechanism for aggregation is accepted, then an aggregate of about 4 chains, as in samples I–L, must consist of a random coil, as the $R_g^w/(M_w^{\mathrm{SANS}})^{1/2}$ values behave like that of a single chain. Schelten et al.[9] and Guenet and Picot[25] have calculated Kratky plots ($(KR_g)^2I$ vs. KR_g 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), is similar to plots of the experimental data, as shown in Figure 6.

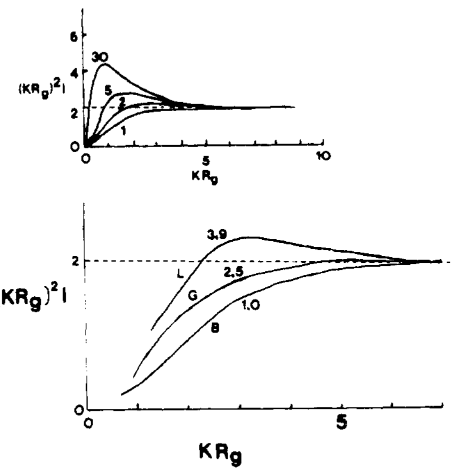

Figure 6. Comparison of Kratky plots for samples B, G, and L (bottom) with those calculated by Guenet and Picot[25] (top) for interpenetrating random coils. Numbers correspond to aggregation number N.

The agreement in Figure 6 may support the proposed nonrandomness 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 $R_g^w/(M_w^{\mathrm{SANS}})^{1/2}$ is similar to the 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 nonrandomness in fraction II.

Finally, it appears that the theory available for the exact interpretation of cross-linked and nonrandom systems is still embryonic. These results point to important new understanding of networks but cannot be characterized beyond the simple nonrandomness number for lack of exact theory. However, noting the rapid state of development of the field, it may be hoped that such a theory will be forthcoming shortly.

Conclusions

Polystyrene cross-linked with 1 mol % divinylbenzene showed apparent increases in molecular weight through SANS measurements of chains labeled at the mid-conversion range. In the conversion range 40–55%, nonrandomness numbers of 1–5 were found, increasing with increasing size of the labeled portion. The nonrandomness number does not depend on the presence or absence of cross-linker in fraction II, the labeled portion, or the polymer at higher conversions, fraction III.

The apparent molecular weight increase is postulated to be due to the presence of excluded volume, leading to a nonrandom distribution of polymer chains formed later. The excluded volume is thought to contain inhomogeneities that consist of regions of higher cross-link density and

Table V
Comparison of Results Obtainable for Several Blanks As Shown for Sample F[a]

blank type	$d\Sigma/d\Omega$, cm^{-1}	R_g^z, Å	$R_g^w/(M_w^{SANS})^{1/2}$
PSH	35 ± 4	176 ± 14	0.255
PSH/PSD random copolymer (90/10 wt %)	37 ± 4	197 ± 15	0.276
av level of 90/10 copolymer blank	39 ± 4	203 ± 18	0.277

[a] Sample F: 9.8 wt % fraction II.

Table VI
Comparison of Results Obtainable for Several Blanks As Shown for Sample G[a]

blank type	$d\Sigma/d\Omega$, cm^{-1}	R_g^z, Å	$R_g^w/(M_w^{SANS})^{1/2}$
PSH	45 ± 4	185 ± 11	0.254
PSH/PSD random copolymer (87/13 wt %)	44 ± 4	190 ± 13	0.264
av level of 87/13 copolymer blank	42 ± 4	189 ± 13	0.268

[a] Sample G: 11.7 wt % fraction II.

may be considered as "tight" gel balls. This causes polymerizing chains to be restricted in the potential volume they can occupy and hence appear segregated in SANS observations 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 cross-linker could be varied from 0 (lll case) up to perhaps 10–20%. Questions to be resolved include the dependence of the "excluded volume" mechanism on cross-linker. Will the absence of cross-linker eliminate the observed segregation in the full conversion range, and how will the molecular weight increase depend on cross-linker 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.

Acknowledgment. We acknowledge 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. We thank Dr. G. D. Wignall of the Oak Ridge National Laboratories for many helpful discussions and assistance with the neutron scattering experiments.

Appendix

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 $d\Sigma/d\Omega$ vs. K plot for a blank shows some increase in scattering intensities at very low angles, below $K = 0.008$ Å, 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 $d\Sigma(K)/d\Omega$ at higher K values, and the appropriate quantity was subtracted.

The results of the different correction methods are given in Tables V and VI for two samples. There is no difference, within experimental error, between the random copolymer blank and the average level subtractions. While $d\Sigma(0)/d\Omega$ 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 $R_g^w/(M_w^{SANS})^{1/2}$, 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 protonated 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.

Registry No. neutron, 12586-31-1; (divinylbenzene)·(styrene) (copolymer), 9003-70-7; (deuteriostyrene)·(styrene) (copolymer), 97655-09-9; (divinylbenzene)·(deuteriostyrene)·(styrene) (copolymer), 97655-10-2.

References and Notes

(1) J. S. Higgins and R. S. Stein, *J. Appl. Crystallogr.* 11, 346 (1978).
(2) A. Maconnachie and R. W. Richards, *Polymer*, **19**, 739 *Crystallogr.*,
(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. Jannink, 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, *Polymer*, **25**, 1718 (1984).
(8) L. H. Sperling, A. M. Fernandez, and G. D. Wignall, *ACS Symp. Ser.*, **No. 243**, 71 (1984).
(9) J. Schelten, G. D. Wignall, and D. G. H. Ballard, and G. W. Longman, *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. Leiber 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, Sept 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 Symp. Ser.*, **No. 24**, 197 (1975).
(21) G. D. Wignall, D. G. H. Ballard, and J. Schelten, *Eur. Polym. J.*, **10**, 861 (1974).
(22) J. P. Cotton, D. Decker, H. Benoit, B. Farnoux, J. S. Higgins, G. Jannink, R. Ober, C. Picot, and J. des Cloizeaux, *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).

Macromolecules 1985, *18*, 1727-1736

(26) E. A. Collins, J. Bares, and F. W. Billmeyer, "Experiments in Polymer Science", Wiley, New York, 1973.
(27) F. Rodriguez, "Principles of Polymer Systems", 2nd ed., McGraw-Hill, New York, 1982.
(28) S. C. Misra, J. A. Manson, and L. H. Sperling, *ACS Symp. Ser.*, **No. 114**, 157 (1979).
(29) S. S. Labana, S. Newman, and A. J. Chompff, in "Polymer Networks", A. J. Chompff and S. Newman, Eds., Plenum Press, New York, 1971, p 453.
(30) E. G. Bobalek, E. R. Moore, S. S. Levy, and C. C. Lee, *J. Appl. Polym. Sci.*, **8**, 625 (1964).
(31) K. Dusek, in "Developments in Polymerizations", Vol. 3, R. N. Haward, Ed., Applied Science Publishers, London, 1982.
(32) K. Dusek, J. Plestil, F. Lednicky, and S. Lunick, *Polymer*, **19**, 393 (1978).
(33) K. Dusek and M. Ilavsky, *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. Bettelheim, *J. Polym. Sci.*, **58**, 697 (1962).
(36) K. Dusek, in "Polymer Networks", A. J. Chompff and S. Newman, Eds., Plenum Press, New York, 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., Polym. Symp.*, **No. 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 University Press, Ithaca, NY, 1953.
(48) W. H. Stockmayer, *J. Chem. Phys.*, **12**, 125 (1944).
(49) Z. Rigbi, in "Polymer Networks", A. J. Chompff and S. Newman, Eds., Plenum Press, New York, 1971, p 245.
(50) L. H. Sperling, "Interpentrating Polymer Networks and Related Materials", Plenum Press, New York, 1981, p 49.
(51) D. L. Siegfried, D. A. Thomas, and L. H. Sperling, *Macromolecules*, **12**, 586 (1979).
(52) Note that the use of "excluded volume" in this context—unswellable or inaccessible polymer regions due to cross-link 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.

Chain Conformation in Medium and High Ester Content Polyether–Polyester Block Copolymers: A Small-Angle Neutron Scattering Study

John A. Miller, J. Michael McKenna,[†] Gerfried Pruckmayr,[†] J. Ernest Epperson,[‡] and Stuart L. Cooper*

Department of Chemical Engineering, University of Wisconsin, Madison, Wisconsin 53706.
Received December 11, 1984

ABSTRACT: The conformation of the polyether soft segment, the polyester hard segment, and the entire chain was measured as a function of temperature in two series of polyether–polyester multiblock copolymers using small-angle neutron scattering. At room temperature, the average soft segment was found to be in a slightly expanded random coil conformation, although some of the segments are probably extended. The measured soft-segment radius of gyration decreased somewhat as the sample was heated. This behavior was attributed to the presence of fewer taut soft segments due to the relaxation of stresses in the material as the chains become more mobile above the glass transition temperature of the hard segments. The crystallized hard segments exhibited a chain-folded structure at room temperature. The measured fold length was 3–4 hard-segment units long. The hard-segment radius of gyration increased substantially as the temperature was increased. This is attributed to the unfolding of some segments by a melting and recrystallization of the highly folded segments and to new hard segments crystallizing out of the amorphous phase into an extended crystalline conformation. The radius of gyration of the whole chain decreased as the temperature was increased between 25 and 150 °C. The reason for this is unclear, although it may be due to the relaxation of the stresses introduced into the system by molding the sample below the hard-segment crystalline melting temperature. Above 160 °C, the crystallization of new hard-segment material becomes an important process, along with lamellar thickening. These processes cause the radius of gyration of the whole chain to increase.

Introduction

Polyether–polyester block copolymers are segmented thermoplastic elastomers that exhibit excellent physical properties and chemical resistance. They are marketed by E. I. du Pont de Nemours and Co. under the trade name of Hytrel. Polyether–polyesters exhibit a two-phase microstructure, which is responsible for their superior mechanical characteristics. The two phases present in Hytrel systems are an amorphous phase and a crystalline or semicrystalline phase. The amorphous phase, also called the soft phase, consists of a mixture of polyether and polyester segments, which are also known as the soft and hard segments, respectively. The crystalline phase consists almost exclusively of crystallized polyester segments. The service temperature of the material lies between the glass transition temperature of the soft phase and the crystalline melting temperature of the hard phase. The microstructure of these materials at intermediate polyester compositions features a soft, rubbery matrix filled with a hard, reinforcing phase that acts as a physical cross-linker. The major driving force for phase separation in the polyether–polyester systems is the crystallization of the hard polyester segments. Any contribution to the driving force due to the incompatibility of the ester and ether segments is smaller in magnitude, unlike the situation in polyurethane block copolymers, where the driving force is usually dominated by intersegmental repulsion. Chemical structure and processing conditions are also known to

---

[†] E. I. du Pont de Nemours and Co., Wilmington, DE 19898.
[‡] Argonne National Laboratory, Argonne, IL 60439.

0024-9297/85/2218-1727$01.50/0