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SMALL-ANGLE NEUTRON SCATTERING FROM POLYSTYRENE-DVB NETWORKS
CONTAINING A DELTA FRACTION OF DEUTERATED POLYSTYRENE:
EVIDENCE FOR AGGREGATION DURING POLYMERIZATION

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INTRODUCTION

Before the introduction of small-angle neutron scattering (SANS), polymer chain conformation studies were restricted to light-scattering and small-angle X-ray (SAXS) instrumentation, usually conducted in dilute solution. Under Flory θ -conditions (1), most polymer chains were shown to be random coils. While scientists of that day theorized that the conformation of polymer chains in an amorphous bulk polymer were similar to that which existed under Flory θ -conditions, there was only limited direct experimental evidence in support of this theory (2). In recent years, SANS has been shown to be an appropriate technique to study directly the chain conformation and dynamics of flexible polymer molecules in the bulk state (3-6). Generally, SANS data has been consistent with the existence of random coils in the bulk state (3,7), although Benoit et al. (8-10) have shown that on extension, the chain ends appear to extend more than the control section, leading to non-Gaussian statistics.

In general, the samples analyzed by SANS technique are materials formed by an hydrogenated polymer matrix in which a small concentration of isotopically labeled (deuterated) polymer molecules are dispersed or "diluted". This method takes advantage of the contrast between the hydrogenated and the deuterated molecules due to the differences in the coherent scattering length of deuterium ($b_D = 0.66 \cdot 10^{-12}$ cm) and hydrogen ($b_H = -0.37 \cdot 10^{-12}$ cm) atoms.

The present samples were based on an hydrogenated polystyrene matrix in which was synthesized a small fraction of labeled (deuterated) polystyrene chains. Contrary to the previous practice of blending in the deuterated fractions (3-10), the present deuterated delta fractions were synthesized in place by free radical mechanisms.

THEORY

The principles of neutron scattering theory as applied to the solution of polymer problems has been described in a number of papers and review articles (3-11). In this paper the notation used is that of the National Center for SANS research User's Guide (12).

The coherent intensity in a SANS experiment is described by the cross section $d\Sigma/d\Omega$, which is the probability that a neutron will be scattered into a solid angle, Ω , for unit volume of the sample. This cross section, which is normally used to express the neutron scattering power of a sample, is identical with the Rayleigh ratio, R , used for light-scattering. One formulation of the basic scattering equation (4,13) reads:

$$\left[\frac{d\Sigma}{d\Omega} (k) \right]^{-1} = \frac{1}{K_N M_w} \left[S(k) \right]^{-1} \quad (1)$$

Where M_w is the weight-average molecular weight of the polymer, K_N is a calibration constant given by

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$$K_N = \frac{(a_H - a_D)^2 N_0 \rho (1-X)X}{M_p^2} \quad (2)$$

where a_H and a_D are the scattering length of a normal (hydrogenated) and deuterated (labeled) monomer structural unit, ρ is the density of the polymer, X is the mole fraction of labeled chains, M_p is the monomer mass and N_0 is the Avogadro's number.

$S(k)$ is the single form chain factor [identical with the $P(\theta)$ function used in light scattering], which describes the conformation of an individual labeled chain. This molecular structure factor becomes independent of particle shape as the angle of scatter θ approaches zero, and under these limiting conditions Guinier region ($k^2 R_g^2 < 1$) becomes a measure of the radius of gyration, R_g .

After rearranging, equation (1) becomes:

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

K is equal to $4\pi\lambda^{-1} \sin \theta$, where λ is the wave length of the neutron radiation and 2θ is the angle of scatter. Thus, the mean square radius of gyration, R_g^2 , and the polymer molecular weight, M_w , may be obtained from the slope and intercept respectively of the Zimm plot of $[d\Sigma/d\Omega (K)]^{-1}$ vs. K^2 .

The values of M_w and R_g^2 were evaluated after appropriate subtraction of the scattering from an unlabeled polymer matrix (blank) from the samples containing different fractions of labeled molecules.

In the above derivation, it was assumed that the labeled molecules are fully deuterated. Thus, considering the structural units of the hydrogenated and deuterated polystyrenes as C_8H_8 and C_8D_8 , respectively, the values of a_H and a_D are: $a_H = 2.328 \cdot 10^{-12}$ cm, and $a_D = 10.656 \cdot 10^{-12}$ cm.

EXPERIMENTAL SECTION

Synthesis

In the following, the synthesis of the homopolymer PS-DVB networks will be described, including two different methods for inserting a delta fraction of deuterated primary network chains within this network during the polymerization.

Method A. This synthesis involves three steps; in each of them a free radical bulk polymerization was performed.

Step I: Polymerization of the first portion, hydrogenated-polystyrene gel. A monomer mixture composed of styrene, benzoin and divinylbenzene was exposed to U.V. light. The initiator concentration was 0.4% by weight and the cross-linking agent concentration was 1 mole %, both percentages were based on monomer weight. After 12-16 hours of U.V. exposure the prepolymer was viscous enough to be poured into a mold, its conversion being about 10-15%. Then, the sample was exposed to U.V. light again until approximately 24-30 hours, total. The polystyrene network was then sufficiently gelled to be removed from the mold and was dried in a vacuum oven for 24 hours at room temperature followed by 48 hours at 60°C, to remove remaining unreacted monomer. The final conversion, corresponding to about 60-70% was gravimetrically calculated.

Step II: Polymerization of deuterated styrene as the delta fraction.

Small samples of the hydrogenated polystyrene networks (60-70% conversion) from step I were swelled with deuterated styrene monomer, divinylbenzene and benzoin mixture to exactly the weight existing before the evaporation of hydrogenated monomer was begun. The swollen gel was placed in a mold and again exposed to U.V. light. After a certain extent of conversion, the polymer gel was again removed from the mold and dried in a vacuum oven. The added conversions reached ranged from 5 to 20%.

Step III: Polymerization of hydrogenated styrene to complete reaction.

The dry network from Step II was reswollen again with hydrogenated styrene, divinylbenzene and benzoin to replace the deuterated monomer removed at the end of the second step. The swollen gel was once more placed in a mold and exposed to U.V. light until completion of the reaction.

The reason for replacing the monomer removed so exactly was to prevent the chain conformation within the already formed material from being disturbed. All the polymerizations were carried out in glass plate molds with a 1 mm. rubbery O-ring, and covered with polyethyleneterephthalate (PET) films, to prevent adhesion. The final size of the samples was approximately 1 cm x 1 cm x 1 mm.

Method B. This technique is suitable for labeling at the beginning of a polymerization. In a glass vial, deuterated styrene and DVB were polymerized via benzoin and U.V. light. This reaction was stopped before the gel point (~5-8% conversion), and the polymer precipitated into methanol. After drying, the branched polydeuterostyrene was dissolved in (hydrogenated) styrene monomer, DVB, and benzoin. The mixture was then poured into the mold and exposed to U.V. light for 36 hours. This method permits an exact amount of polydeuterostyrene to be incorporated, and to be characterized before being incorporated into the network. Of course, all samples were also prepared without a deuterated fraction, for purposes of H-PS blank subtractions.

For purposes of molecular weight characterization, polystyrene was also made in the identical fashion as described above, but without any crosslinker.

Instrumental

The molecular weights of linear, bulk polystyrene, with its reaction stopped at various levels of conversion were obtained using a Waters Gel Permeation Chromatography instrument calibrated with narrow molecular weight distribution polystyrenes. The intrinsic viscosities were determined on a Ubbelohde-type viscometer using toluene as the solvent.

The neutron experiments were performed on the 30-m SANS facility (12,13) at the National Center for Small Angle Scattering Research (Oak Ridge National Laboratory). The incident neutron radiation had a wave length of $\lambda = 4.75 \text{ \AA}$, collimated by source slits (1-2 cm diameter) and sample slits (0.5-1.0 cm diameter) separated by a distance of 7.5 m. The area detector ($64 \times 64 \text{ cm}^2$) with 1 cm^2 element size was mounted on rails inside a 20 m vacuum flight path and positioned at sample detector distances (SDD) of 16.02 and 18.5 meters.

RESULTS

The molecular weights of linear bulk polystyrene, prepared by free radical methods without DVB, are shown in Table I. Both GPC and intrinsic viscosity methods were employed. The former shows the molecular weight distribution, which shows M_w/M_n running about 3 or 4 to one.

Viscosity molecular weights of near 3×10^5 gms/mole for linear PS and acrylic acid anhydride crosslinked and hydrolyzed (decrosslinked) PS were previously observed from similar syntheses (14).

Table I shows the values of M_v after polymerization to various levels of conversion. While the data shows a relatively flat plateau until after at least 74% conversion, followed by a rise, the data of interest are the values of M for the individual delta fractions. Assuming for purposes of calculation that $M_v \approx M_w$, the relationship between M_w and its fractions may be written:

$$M_w = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i} \quad (4)$$

$$M_w = \left(\sum_{i=1}^j w_i M_i + \sum_{i=j}^k w_i M_i + \sum_{i=k}^l w_i M_i + \dots \right) / \sum_{i=1}^{\infty} w_i \quad (5)$$

where w_i is the weight fraction of any particular portion having a molecular weight M_i . The delta fraction values are also shown in Table I. While this analysis lacks depth, it illustrates the progression in molecular weight throughout the polymerization.

Figure 1 illustrates the results of the SANS experiment on Sample No. 1, which contained 2% of deuterated PS introduced at the beginning of the polymerization, Method B. Using equation (3), the slope of a plot of $(I - I_0)^{-1}$ [proportional to $(d\epsilon/d\Omega)^{-1}$] vs K^2 yielded the radius of gyration, R_g . The intercept, again using equation (3), yielded M_w . Values are shown in Table II.

The several values of R_g and M_w determined by SANS for the various delta fractions are shown in Table II. It is immediately observed that the samples prepared by Method A have molecular weights several times higher than expected from the corresponding values in Table I. Interestingly, the molecular weights in Table II increase with the size of the delta fraction.

DISCUSSION AND CONCLUSIONS

Sample No. 1 yielded a molecular weight of about 70,000 gms/mole, and a Z-average radius of gyration of 121 Å. While we have not corrected for polydispersity of molecular weights, and mismatch of the D and H bearing molecules, these results were in the range expected for single molecules dispersed in a polymer whether in network form or not. These results are similar to those found for a linear PS at Flory- θ conditions. Thus the extent of branching in this sample was thought to be rather low. The other samples, on the other hand, yielded molecular weights in the neighborhood of one to two millions, see Table II. Data in Table I suggest that the delta fraction of polystyrene of interest has a molecular weight of about 50,000-72,000 gms/mole, depending on position. These results are strongly suggestive of aggregation. The aggregation of chains formed during a given interval of conversion has long been suspected (15-18), and some data, particularly electron microscopy and mechanical studies, have supported this hypothesis (17,18). However, quantitative verification has never been made.

While the exact "aggregation" mechanism is unknown, some speculation is warranted. After initial network formation, the density of polymer chains and/or crosslinks varies statistically from region to region. Those sub-microscopic volumes with lower average polymer density will have, at any instant of time, a higher monomer concentration. Hence, these regions will have a higher than average rate of polymerization, leading to a form of aggregation.

The situation is aggravated if the mechanism of Bobalek, et al. (16) applies during the actual formation of the gel. This mechanism, which postulates the early formation of microgels floating in a soluble monomer-polymer mix, leads to a decidedly non-random distribution of polymer at the point of gelation.

Hence, the remaining monomer will be non-randomly distributed, and will polymerize in a non-random mode.

Alternately, a non-random distribution of crosslinks may introduce a local variation in the activity of the network with respect to the monomer, leading to local pockets high or low in monomer. Further experiments are in progress.

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Table I. Polystyrene Molecular Weight, gms/mole (Linear Polymer).

<u>Material</u>	<u>GPC</u>		<u>Intrinsic Viscosity, M_v</u>	
	<u>M_n</u>	<u>M_w</u>	<u>Cumulative</u>	<u>Delta Fraction</u>
After 10% conversion*	0.34×10^5	0.96×10^5	—	—
After 61% conversion	—	—	0.50×10^5	0.50×10^5
After 74% conversion	—	—	0.54×10^5	0.72×10^5
After 100% conversion	0.62×10^5	3.6×10^5	2.0×10^5	6.1×10^5

*Separate synthesis

Table II. Characterization of Polystyrene Networks via SANS Measurements.

Sample No.	D-PS mole %	Conversion Position of Delta Fraction	R_g Å	M_w gms/mole	Method
1	2.0	Initial	120	0.70×10^5	B(a)
2	20.1	Final	350	8.0×10^5	A(a)
3	5.38	After 75%	406	2.35×10^6	A(b)
4	10.2	After 75%	352	1.18×10^6	A(b)
5	13.9	After 75%	337	0.85×10^6	A(b)
6	10.0	After 60%	378	1.05×10^6	A(b)
7	13.9	After 60%	393	0.80×10^6	A(b)

(a) measured at SDD 16.02 meters

(b) measured at SDD 18.5 meters

Figure 1. Polystyrene Sample 1, prepared by method B, to a concentration of 2%. Small-angle neutron scattering studies yielded both the molecular weight and radius of gyration.

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