A SANS Study of the Dimensions of Polystyrene Formed by Freeze-Drying from Dilute Solution

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Introduction

Polymer molecules in the undiluted state or in concentrated solution are highly interpenetrating and hence show considerable entanglement. In dilute solutions, at concentrations below c^*, there is little or no interpenetration. It seems reasonable therefore that a noninterpenetrating polymer solid may be made from a dilute solution by rapid drying or quenching techniques. This has been done by Siegel et al.[1] and Richardson[2] who sprayed a very dilute solution of a polymer from an "atomizer" and picked up the monomolecular particles on an electron microscope substrate. More recently Kumaki[3,4] has spread dilute solutions of polystyrene in benzene on a water surface and shown, again using transmission electron microscopy, that monomolecular particles were formed. Neither of these techniques are very suitable for forming a large amount of material.

Morawetz and co-workers[5-8] have suggested that a polymer solid consisting of nonoverlapping collapsed coils can also be made by freeze-drying a solution of the polymer whose concentration is below c^*. They used donor–acceptor fluorescence techniques to study both PMMA and polystyrene that had been prepared in this way. Evidence was presented that the material does indeed consist of noninterpenetrating molecules. The technique was used to study both the degree of interpenetration of molecules in solution and the interdiffusion of polymers in the bulk.

The original aim of the work described in this note was to characterize the interpenetration of the molecules and hence their entanglement by using small angle neutron scattering (SANS). This was to be prior to a study of the reentanglement process and the effects of entanglement on mechanical properties. The SANS technique was chosen because it permits a direct measurement of the size of a polymer coil so the degree of collapse of the coils should be very clear. However no coil collapse was observed.

Experimental Techniques

The polystyrenes used in this study were a hydrogenated material of M_w = 51 000 and M_w/M_n = 1.07 and a deuterated material of M_w = 49 000 and M_w/M_n = 1.08 (polystyrene-H equivalent). Both materials were obtained from Polymer Laboratories who supplied the molecular weight data. Two 50/50 H/D solutions were made, one by dissolving 0.5 g of each material into 30 mL of benzene and the other by using 0.125 g of each polystyrene in 10 mL of benzene. The solutions were frozen by pouring them into a round-bottomed flask that was cooled in a mixture of dry ice and acetone. The flask was swirled to ensure rapid freezing. The solid benzene was sublimed off under vacuum with the solution cooled in iced water. The powder produced by this technique was very light and fluffy.

Samples suitable for SANS were made by compacting this powder under vacuum at a pressure of 700 MPa (7 kbar), first at room temperature and then at a temperature of 89 °C. The 0.75 mm thick samples produced were just transparent after pressing at room temperature and still a little cloudy after pressing at high temperature. The SANS experiments were performed on the 30-m instrument at Oak Ridge National Laboratory. The incident beam was transported to a distance of 5.5 m from the sample by means of movable beam guides and collimated by source and sample slits of 3.5 and 1.0 cm diameter, respectively. Measurements were made with the area detector (64 × 64 cm^2), with 1 cm^2 element size, positioned at sample–detector distances (SDD) of 2.66 and 7.51 m to give effective Q ranges of $0.025 < Q < 0.22$ Å^{-1} and $0.009 < Q < 0.075$ Å^{-1}. In both Q ranges the scattering patterns were corrected on a cell by cell basis for instrumental backgrounds, detector efficiency variation, divided by the transmission (T) and thickness (t), and normalized to a constant incident flux.[9] All the scattering patterns studied exhibited azimuthal symmetry and were radially averaged. The intensity data were converted to an absolute differential scattering cross section $d\Sigma/d\Omega$ per unit sample volume (in units of cm^{-1}) by means of precalibrated secondary standards.[10]

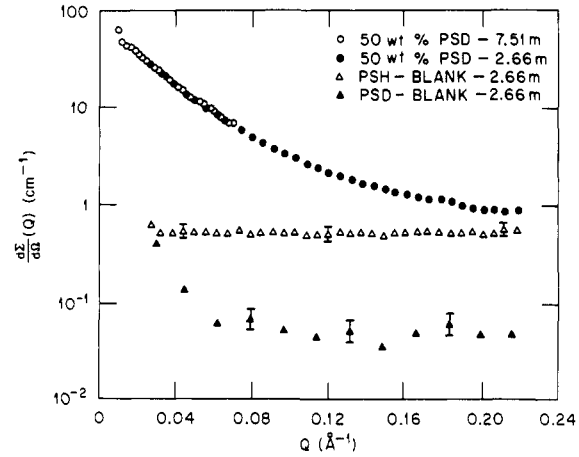

Figure 1. $d\Sigma / d\Omega(Q)$ vs Q for 50:50 wt % PSD in PSH and H and D blanks measured in two Q ranges.

Results

Figure 1 shows the cross sections of a 50/50 partially labeled sample made from the 2.5 g/dL solution in benzene, together with results for an undeuterated blank (PSH) and a fully deuterated (labeled) blank (PSH). The data sets from the 50/50 samples were independently calibrated in the two different Q ranges, without any adjustable scale factor, and show excellent agreement in the overlap range. A small upturn in the signal of the PSD blank is probably due to residual void scattering, though this is not observed in the PSH blank due to the lower scattering contrast of voids in the hydrogenous material. The contrast of voids in the 50/50 sample is intermediate between the PSH and PSD blanks and a slight upturn is just visible in the first point of the data run at 7.51 m (Figure 1). A minor correction for this effect was made as described by Hayashi et al.[11] The scattering from PSH is due largely to the angle independent incoherent scattering from the H^1 nuclei. Because it contains an appreciable fraction of multiple scattering, this background does not scale with T and t and methods for subtracting this component have been discussed by O'Reilly et al.[12] A small correction (~0.3 cm^{-1}) was made to all samples, and Figure 2 shows a typical fit of the corrected data to a Debye Gaussian coil scattering function.[13] Table I summarizes the fitting results for various samples made from solutions with concentrations of 2.5 and 3.3 g/dL in benzene. The different values represent different samples prepared from the same solution and also slight differences in the fitting methods. For example some data sets

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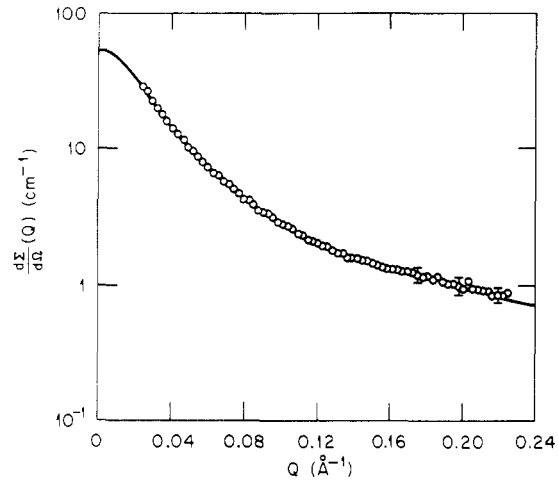

Figure 2. Least-squares fit to a Debye Gaussian coil for freeze-dried polystyrene.

Table I
Results from Fitting Data to a Debye Gaussian Coil Scattering Function

initial soln concn, g/dL	SDD, m	$d\Sigma(0)/d\Omega$, cm^{-1}	R_g, Å
2.50	2.66	56.3,57.1	62.1,60.6
		50.6,53.6	63.4,63.4
	7.51	52.0,53.6	60.2,61.3
3.33	2.66	58.8,52.7	62.2,63.5
	7.51	50.2,51.4	62.8,63.4

were fitted after subtracting off incoherent backgrounds and also by fitting the original data with a flat incoherent background as a fitting parameter. The measured (z-average) radii of gyration all lie in the range 62.2 ± 2 Å, and after corrections for polydispersity[14] and slight mismatches of the polymerization indices of the labeled and unlabeled molecules,[15] we calculate a (weight-averaged) radius of gyration for the deuterated molecules R_{gw} = 59.7 ± 2 Å. This leads to a value of $R_{gw}/M_w^{1/2}$ = 0.27 ± 0.01 Å which is characteristic of values measured in bulk polystyrene[16-18] and Θ solvents. The average value of $d\Sigma(0)/d\Omega$ = 53.6 ± 4 cm^{-1} which may be compared to a value of 52.4 cm^{-1} calculated from the nominal polymerization indices. Thus these results show that the freeze-dried material was not in the form of collapsed coils but had the normal Θ-coil dimensions.

Discussion

The system used here was not the same as those studied by Morawetz and co-workers.[5-8] This is because the original aim of the work was to characterize the reentanglement of freeze-dried material on the assumption that freeze-drying would produce collapsed coils. Also the experiments described here were done before Morawetz and co-workers published their work on polystyrenes. For their experiments on acrylic polymers Morawetz and co-workers used similar or larger quantities of solution and froze the solutions in a similar way by pouring them into a round-bottom flask that was swirled in a dry ice–acetone mixture. Their polystyrene solutions were frozen by immersing a round-bottom flask into liquid nitrogen, but they do not comment on the quantity of solution used. Morawetz and co-workers found that the degree of chain interpenetration was very low for solution concentrations c low enough that $c[\eta] < 1$. The interpenetration was found to increase until it reached a constant value for $c[\eta] > 3$. It is worth noting that $c = 3/[\eta]$ is one estimate of the overlap concentration c^*. The parameter $[\eta]$ is the intrinsic viscosity. The values of $c[\eta]$ obtained from literature values[19] of the Mark–Houwink constants for the two solutions used in this work are 0.75 and 1.0 so from Chang and Morawetz[7] little or no overlap would be expected.

The mean radius of a collapsed coil of polystyrene of molecular weight 51 000, assuming a mass density of 1.05 g/cm^3, is 27 Å. Spheres of this radius have a radius of gyration of 17 Å which is much lower than the 60 Å we observed. In addition one would expect the scattering function from collapsed coils to be similar to that for spheres rather than the Debye Gaussian coil function observed here. The arguments used for the analysis of scattering from concentrated solutions of labeled polymer chains in unlabeled chains[20] are as applicable to collapsed coils as they are to interpenetrating coils so even a small decrease in coil interpenetration should have been detectable by using the SANS technique.

To obtain separate molecules by freezing a dilute solution, it would seem likely that the cooling has to be done fast enough to quench the solvent to a glass. If the material crystallizes, then a concentrated polymer solution will form and freeze last. To suppress this solution concentration process, it is necessary either to vitrify the solvent or to crystallize so fast that the polymer molecules cannot stay clear of the crystal growth front. The terminal Rouse relaxation time for the solution concentrations used here is less than 1 μs[21] at room temperature so it is clear that very rapid crystal growth would be required. This might have happened in Morawetz et al.'s work but not in the current work as the acrylates they used had relatively high molecular weights and the polystyrenes of molecular weight 100 000 were quenched by immersing the flask in liquid nitrogen rather than the dry ice/acetone mixture used here.

It could be argued that the temperature (89 °C) used in this work to aid compaction and produce relatively void-free samples permitted diffusion and reinterpenetration of the molecules. This does not seem likely as this temperature is at least 10 °C below the T_g of the polymer and there is little evidence of diffusion on the scale of a coil below T_g. In addition, if the results of Liu and Morawetz are correct, collapsed coil expansion is about 4 decades slower than may be expected from diffusion coefficients of normal coils.[8]

The results presented here should not be considered as evidence that freeze-drying cannot produce collapsed coils or that Morawetz and co-workers did not obtain collapsed coils. Such information could only be obtained by measurements of coil sizes in samples produced by using similar molecular weights and freeze-drying procedures to those used by Morawetz and co-workers. Such experiments are currently in progress. However the lack of evidence of any coil contraction found here does suggest that collapsed coils are perhaps hard to obtain. As the fluorescence evidence for collapsed coils comes from an assumption that the energy transfer between donors and acceptors was mainly nonradiative (NET), it is worth noting that in a recent publication Horsky and Morawetz[22] have found that, in solutions, radiative energy transfer can be important.

Also Jerome and co-workers[23] have found that the ratio of donor to acceptor fluorescence did not change during phase separation of an initially phase mixed blend of two polymers, one labeled with a donor and the other with an acceptor. The phase separation was clear from DSC results. This result is hard to understand if the energy transfer is purely by NET processes.

Conclusion

Polystyrene that was freeze-dried from solutions of concentration below c^* was not in the form of collapsed coils. The chain dimensions were the same as those observed in normal bulk material.

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Communications to the Editor

Adsorption Isotope Effect for Protio- and Deuteropolystyrene at a Single Solid Surface

Many analytical methods rely on isotopic labeling. At the same time, isotopic isomers often have subtle differences in a wide range of physical properties.[1] Recently, we undertook measurements of adsorption exchange kinetics from liquid solution to a single solid surface.[2,3] It was possible to measure directly the replacement of deuteropoly(methyl methacrylate) (PMMA) by the protio species of similar degree of polymerization.[3] The time constant for this exchange is a measure of the surface residence time, provided that the segmental sticking energy of the two isotopic species is the same. Since PMMA is believed to adsorb at the carbonyl group, no protio–deutero isotope effect was expected and none was detected experimentally.[4] For polystyrene (PS) adsorbed onto a single surface of silicon oxide from cyclohexane, however, we find that the deutero isotope appears to adsorb preferentially.

Infrared spectroscopy was employed, in the mode of attenuated total reflection (ATR), to measure PS adsorption to the native surface of a silicon infrared prism.[2,3] Infrared spectra were collected, and the silicon ATR prism was prepared using methods described previously.[2] Under ambient conditions, such as we used, it is well-known that silicon is covered by a native oxide layer.[5]

The temperature of measurement was 30.0 °C, which is the Θ temperature, T_Θ, for deuteropolystyrene (PS-*d*) in cyclohexane.[6] For protiopolystyrene (PS-*h*) in cyclohexane, T_Θ = 34.5 °C,[6] so that PS-*d* at 30 °C finds itself in a slightly better solvent than does PS-*h*. Calibrations showed that Beer's law held to a good approximation for these films of low adsorbance, as expected,[7] and that the PS free in solution (0.2 mg·mL^{-1}) contributed only approximately 1% to the measured PS absorption peaks. At this solution concentration, PS-*d* and PS-*h* are completely miscible.[6,8]

In Figure 1, integrated intensities of the C–H and C–D infrared peaks, proportional to the surface excess, are plotted against elapsed time. Calibration shows that the intensity 0.10 absorbance unit·cm^{-1} is approximately a surface coverage of 2.7 mg·m^{-2}. The data for PS-*d* have been scaled by the calibrated fraction, 0.832, so that PS-*h* and PS-*d* intensities are proportional by the same constant to the surface excess. Three experiments are shown; comparison of (a) the adsorption of the pure deuteropolystyrene, (b) the adsorption of the pure protiopolystyrene, and (c) the adsorption of a mixture of PS-*d* and PS-*h* (48:52 parts by weight, respectively). The linear samples (from Pressure Chemical, reported to be methyl-terminated) had weight-average degrees of polymerization stated by the manufacturer to be N_w = 5000 (PS-*d*) and N_w = 5500 (PS-*h*), with ratios N_w/N_n (N_n, the number-average degree of polymerization) of 1.15 and 1.06, respectively. The nonideal mixing of undiluted binary mixtures of these same samples was studied previously by Bates and Wignall.[8]

In all three instances, the surface excess appeared to equilibrate within 1 h, and the ultimate levels adsorbed were the same within experimental uncertainty. For the mixture, at times less than 1 h the surface excess of PS-*d* rose while that of PS-*h* fell slightly. It appears that the adsorbed amounts of the two species may have taken similar values at early times, which is expected because of their similar concentrations in solution. At times greater

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