Chain Conformation of Polystyrene in Bulk by Small-Angle X-Ray Scattering

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Synopsis

Small-angle x-ray scattering from solid solutions of different molecular weight fractions of partially brominated polystyrene in polystyrene has been studied. The results of this study indicate that polymer chains in bulk have a radius of gyration proportional to the square root of molecular weight, which is consistent with the random coil model. However, these radii are approximately 20% larger than the unperturbed radii deduced by light scattering in dilute solutions.

INTRODUCTION

Several experimental methods have been developed to study chain conformation of linear polymer molecules in dilute solution, and solution properties of the polymer have been studied extensively.[1] Few studies have been published, however, that describe the dimensions of amorphous polymer molecules in the solid state or in concentrated solution, despite their importance for the fundamental understanding of structure and properties of bulk polymers. Recently, the problem of chain conformation in bulk has been actively pursued by a neutron scattering method.[2-5] Most of the results obtained by neutron scattering imply that Gaussian conformation of polymer chains exists in the bulk state. Recently, Graessley[6] reviewed the problem of polymer chain conformations in bulk, and he concluded that the polymer chains in bulk are in a random coiled state, perhaps slightly expanded beyond θ dimensions.

In this report, we present studies on the chain conformation of polystyrene in bulk by a small-angle x-ray scattering technique. We have lightly brominated the polymer chain and investigated the chain conformation of this partially brominated polystyrene.

EXPERIMENTAL

Two samples of narrow molecular weight distribution polystyrene were obtained from Pressure Chemical Company, Pittsburgh, Pa. They will be designated as fractions I and II. Fraction III was synthesized anionically and was kindly provided by Dr. H. S. Makowski of this laboratory. The molecular weight and polydispersity of fractions I, II, and III are given in Table I. The polystyrene fractions were then brominated according to the procedure by Maura and Pochetti.[7] To a three-neck 100-ml round-bottom flask equipped with a mechanical stirrer and a reflux condenser were added 10 g powdered polystyrene, 50 ml glacial acetic acid, and 0.02 g of a powdered iron catalyst. The suspension was

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TABLE I
Polystyrene Fractions Studied and Their Molecular Weights

	Original polystyrene		Brominated polystyrene			
	M_w	M_w/M_n	M_w	M_z	M_w/M_n	Bromine content, mole-%
Fraction I	3.7×10^4	1.03	4.1×10^4	4.46×10^4	1.09	2.41
Fraction II	9.72×10^4	1.06	9.5×10^4	1.22×10^5	1.28	1.05
Fraction III	1.60×10^5	1.07	1.63×10^5	1.81×10^5	1.11	1.71

then stirred, and 10 ml bromine was added to the flask. The suspension was then heated to 100°C and was allowed to reflux for 1 hr at that temperature. The product was cooled to room temperature and filtered. It was washed once with dilute $NaHCO_3$, with distilled water three times, and with methanol. The brominated polymer was dissolved in toluene and filtered to remove trace inorganic salts. This polymer solution was precipitated in methanol and the product was dried under vacuum at 60°C for 24 hr. (Though iodinated polystyrene would provide a higher x-ray scattering power, iodinated polystyrene was unstable under x-ray irradiation and became opaque indicating some kind of phase separation.)

Infrared measurements on the brominated samples indicate that aromatic substitution of bromine atoms is primarily in the para position. The level of bromination was controlled by varying the reaction time of the bromination. The polystyrene fractions were only partially brominated, so that the resulting partially brominated polystyrene would be miscible with corresponding polystyrene fractions. The bromine content determined by the Dietert method in each fraction is given in Table I. It was also shown by GPC measurements that the bromination reaction broadened the molecular weight distribution of the polystyrene. The brominated polystyrene was fractionated, and the fraction whose molecular weight was closest to that of the original polystyrene fraction was used to make a solid solution of brominated polystyrene in the unbrominated polystyrene. The concentration of the solid solution was 0.5% for all three fractions. The molecular weight distribution of the brominated polystyrene fractions was studied by GPC analysis, and their M_w/M_n values are also given in Table I.

This solid solution was molded to a thickness of 50 mil at 140°C. A polystyrene pad of identical thickness was also prepared at the same temperature. Observation of these samples with a polarizing microscope showed no stress or orientation in the samples.

Small-angle x-ray scattering experiments were performed using a Kratky camera with a 60 μ entrance slit and a sample-to-detector distance of 210 mm. A detailed description of the camera is given elsewhere.[8] Monochromatization of the x-rays from the Cu target was achieved using a Ni filter and a pulse height analyzer. The stability of the x-ray generator was checked periodically, and very little deviation was detected beyond the probable statistical error.

The scattering experiments were first performed with dilute solid solutions of the brominated polystyrene. The scattering intensity for these materials is designated as I_{Br-PS}. Subsequently, the scattering intensity I_{PS} of the polystyrene sample of corresponding molecular weight was measured. To within experimental error, no difference in absorption was observed between the solid

solution of brominated polystyrene in polystyrene and the unbrominated polystyrene. This result is reasonable since the concentration of Br atoms in the sample is very low. In fact, the absorption can be estimated from the mass absorption coefficient for each constituent element in the sample. The 0.5% solid solution of fraction I contains 0.012 Br atoms per 100 carbon atoms. The difference in absorption between this solid solution and the corresponding polystyrene fraction would be less than 2% for a 50-mil-thick sample. This value is less than experimental uncertainties and therefore was not detected.

The net intensity $\Delta I = I_{Br-PS} - I_{PS}$ is the scattering from aggregates of bromine atoms. The statistical counting error in measuring I_{Br-PS} and I_{PS} is in the range of 0.55% in the small-angle (high count) region, and increases to 3% in the higher-angle (low count) region. This range of counting errors corresponds to an error for ΔI ranging from 6.6% to 10%. A plot of the logarithm of the net intensity results in a statistical error in the radius of gyration of less than 10%.

The Kratky small-angle x-ray camera provides an x-ray beam geometry approximating a slit of infinite height. The above net intensity ΔI was corrected for smearing effect caused by the slit according to a procedure developed by Schmidt.[9]

RESULTS AND DISCUSSION

The small-angle x-ray scattering from N noninteracting particles can be approximated by a Guinier relation[10]:

$$\lim_{h \to 0} I(h) = Nn^2 I_e(h) \exp\left(-\frac{h^2 R^2}{3}\right)$$

where $I_e(h)$ is the scattering intensity from a single electron, n is the number of electrons in a particle, $h = 4\pi/\lambda \cdot \sin\theta$, λ is the x-ray wavelength, 2θ is the scattering angle, and R is the radius of gyration of the particle. Implicit in the Guinier relation are the assumptions that interparticle scattering is negligible and that the particles are of uniform size. According to this equation, the plot of logarithm of $I(h)$ against h^2 should be a straight line whose tangent is proportional to R^2. For a particle system having a size distribution, the plot becomes concave upward.

The logarithm of intensity is plotted as a function of h^2 in Figure 1 for the three polystyrene fractions studied. At very small angles, the plots in Figure 1 rise steeply despite the fact that any effect from the primary beam or from the slit has been already subtracted. The origin of this excess small-angle x-ray scattering is not known, though similar phenomena have been frequently observed. The excess scattering may be due to association of several molecules forming an aggregate; if so, this might be substantiated by performing further work as a function of concentration. From very careful work on very dilute solutions of polystyrene, Kratky et al.[11] have observed similar phenomena, and they have interpreted this behavior as being due to the association of two or more polystyrene molecules. In our further analysis, we shall discard this excess scattering at very small angles.

The small-angle x-ray scattering throughout the small-angle region could possibly be influenced by other factors such as voids present in the samples or by impurities. It has been shown, however, by Wendorff and Fischer[12] that
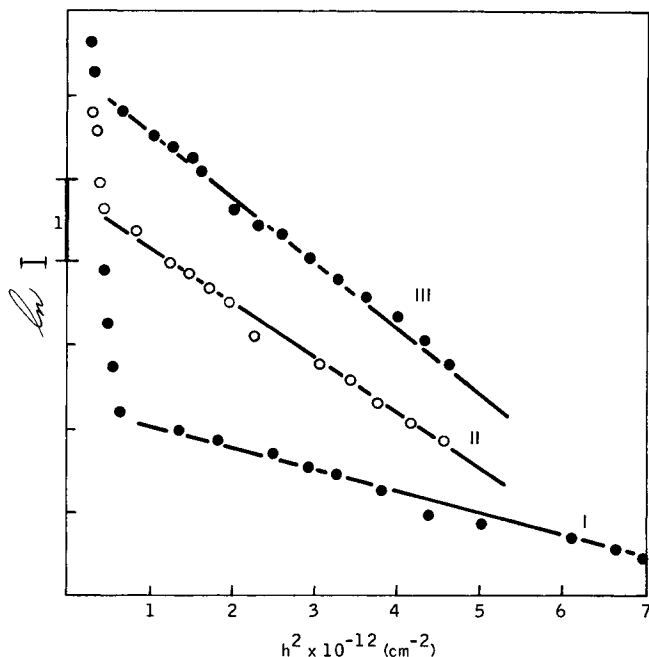
Fig. 1. Plot of logarithm of intensity vs h^2 for fractions I, II, and III.

small-angle x-ray scattering of the amorphous samples which are treated similarly to the ones of this study cannot be attributed to voids in the sample. Wendorff and Fischer further state that foreign particles, such as stabilizer, contribute to the small-angle x-ray scattering. The polystyrene samples of this study did not contain any stabilizer, and the samples were purified before the x-ray experiment. Therefore, it is concluded that SAXS in Figure 1 is caused solely by aggregates of bromine atoms.

The slope that should be used in calculating the radius of gyration is not the average slope of the plot of $\ln I$ versus h^2 but the value at $h = 0$. However, in practice, the slope at $h = 0$ cannot be obtained since the scattering intensity cannot be measured below a certain minimum angle. If the plot of $\ln I$ versus h^2 shows a small curvature over relatively large portions of the small-angle region, the measurement can be made of the slope at several values of h^2 and these values can be extrapolated to obtain a limiting value of the slope at $h = 0$. This method is not applicable in our experiment since there is a rapid increase in the intensity at the very small angles as shown in Figure 1.

There is, however, a limiting value of h, for a particle of given radius of gyration and form, above which the Guinier approximation is no longer valid. For the spherical particle, Guinier states (ref. 10, p. 128) that the Guinier approximation holds up to the limit $hR = 1.3$. This corresponds to $h^2 = 2.3 \times 10^{12}$ (cm^{-2}) for fraction I provided $R = 86$ Å, to $h^2 = 0.96 \times 10^{12}$ (cm^{-2}) for fraction II provided $R = 141$ Å, and to $h^2 = 0.68 \times 10^{12}$ (cm^{-2}) for fraction III provided $R = 157$ Å. This allows us only a small range of angles in our plots for fractions I, II, III. However, many reports also indicate that for a spherical particle system the Guinier approximation is still approximately valid in an angular region much higher than the $hR = 1.3$ limit. This wide validity occurs because for the spherical particle system, in the plot of $\ln I$ versus h^2 the curve does not deviate

considerably from the true Guinier plot in the relatively high-angular region. Pessen et al.[13] have shown, in their study of lysozyme protein, that the Guinier plot can be drawn through the angular region much above the limit of $hR = 1.3$. In this case, they have shown that the linear plot can be extended to above $hR = 1.7$. Similar data treatment was also done in SAXS studies on vacancy clusters in copper foils.[14] In this study, the Guinier relation was shown to be valid to $hR = 2.14$. Based on these considerations, tangential lines were drawn for fractions I, II, and III, as shown in Figure 1. The radii of gyration calculated from these slopes are tabulated in Table II.

It is possible that the bromination of the polystyrene may have changed the thermodynamics of the system, i.e., the chain dimensions of the polymers. In other words, brominated polystyrene may possess a molecular size different from that of polystyrene of corresponding molecular weight. Therefore, strictly speaking, one should measure the molecular size of the brominated polystyrene at the θ conditions and compare this value with the value in bulk. However, because of the very small degree of bromination, we assume here that the partial bromination has not disturbed the thermodynamics of the system and it there- fore, can be assumed that the molecular size has not changed. Similarly, we also assume that the polystyrene and the partially brominated polystyrene are completely miscible. This complete miscibility can be indirectly justified by the molecular size as measured in this experiment, which is shown in Table II.

The radius of gyration that one measures by the small-angle x-ray scattering is a z-average value, and z-average molecular weight of the brominated fractions are also given in Table I. These molecular weights were obtained by GPC measurements. The unperturbed radius of gyration from the z-average mo- lecular weight can be calculated using the formula

$$\frac{\langle r^2 \rangle_0^{1/2}}{M^{0.5}} \times 1000 = K \ (\text{Å})$$

where $\langle r^2 \rangle_0^{1/2}$ is the end-to-end distance of an unperturbed polymer chain which is related to the unperturbed radius of gyration by

$$\langle r^2 \rangle_0^{1/2}/\sqrt{6} = \langle R^2 \rangle_0^{1/2}$$

The value of K reported in the literature[15] ranges from 650 to 870. Using these upper and lower values of K, unperturbed values of the radius of gyration were calculated and are given in Table II. Also given in Table II are values of the expansion coefficient $\alpha = \langle R^2 \rangle^{1/2}/\langle R^2 \rangle_0^{1/2}$ for the three fractions, which range from 1.1 to 1.5. Interestingly, α is identical for all three molecular weight frac- tions. As discussed in the Experimental section, the error in measuring $\langle R^2 \rangle^{1/2}$

TABLE II
Radii of Gyration in Bulk Measured by Small-Angle X-Ray Scattering and Those of
Unperturbed State

	$\langle R^2 \rangle^{1/2}$ ($\pm 10\%$), Å	$\langle R^2 \rangle_0^{1/2}$, Å	α ($\pm 10\%$)
Fraction I	86	56 ~ 75	1.15 ~ 1.53
Fraction II	141	92 ~ 124	1.14 ~ 1.52
Fraction III	157	106 ~ 148	1.06 ~ 1.48

is less than 10%. Therefore, there is a definite expansion of molecular dimensions in bulk for the three fractions studied.

The identical values of α for the three fractions indirectly justify the previous assumption that the polystyrene molecular size has not changed upon bromination. That is, despite the different degree of bromination, fractions I, II, and III, which also have different molecular weight, are expanded to the same degree.

Several factors can be considered as possible reasons for this apparent expansion of the chain. First, there may exist a consistent instrumental discrepancy between the different experimental techniques. The chain dimension at the θ condition has been obtained by the light-scattering method, while the present study was performed by the small-angle x-ray scattering technique. As stated previously, this question can really be resolved if the unperturbed chain dimension at θ conditions is measured also by the small-angle x-ray scattering technique. The chain expansion by $10 \sim 20\%$ in bulk has also been observed by Kirste et al.[4] on PMMA when compared with that in θ solvent. He attributes this to the instrumental discrepancies in the scattering constants between the neutron and light scattering experiments from which the two sets of data are obtained. However, the frequent observation of the chain expansion, by Kirste and in the present work, using different techniques, may indicate that the observed expansion of the chain dimension is real. Secondly, the expansion may be due to the excluded volume effect which predicts that the radius of gyration is proportional to $M^{0.6}$ rather then to $M^{0.5}$. The value of the exponent of M can be obtained from a plot of R against M_z on a logarithmic scale. The tangent of the plot will be the exponent.

In Figure 2 this plot is given with data presently available for the three molecular weight fractions of polystyrene. The data points do not lie on a line of tangent 0.6. Instead, they are on a line of tangent 0.5. This confirms Flory's original contention[17] that the polymer chains in bulk are essentially in a conformation which can be calculated by Gaussian statistics and there is no excluded
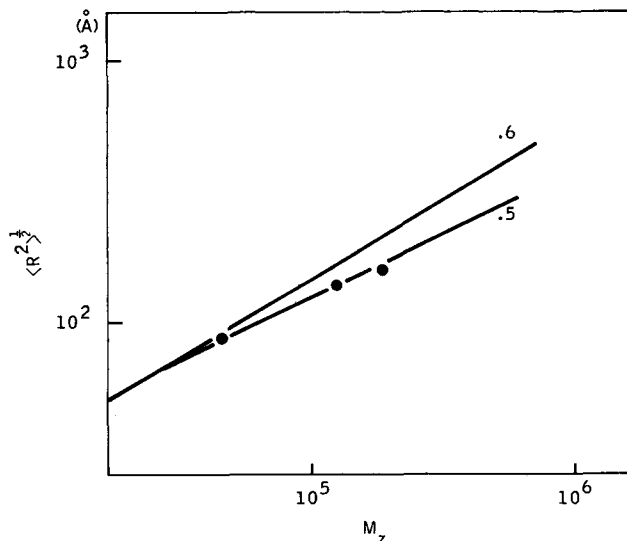

Fig. 2. Plot of radii of gyration vs z-average molecular weight on a logarithmic scale.

volume effect. A similar conclusion was drawn by Benoit[5] from his neutron scattering experiment on polystyrene in bulk.

As briefly mentioned previously, the chain conformation of amorphous polymers is being studied actively by a neutron scattering technique. Ballard et al.[2] and Cotton et al.[3] studied the chain dimensions of polystyrene in bulk and reached the conclusion that the chain dimensions are essentially identical with that of the unperturbed state, i.e., $\alpha = 1$. Kirste's work on PMAA[4] and the work of Benoit et al.[5] on polystyrene suggest that the molecular weight dependence of $\langle R^2 \rangle^{1/2}$ is $M^{1/2}$, indicating no long-range correlation, i.e., no excluded volume effect. As mentioned before, Kirste observed a $10 \sim 20\%$ expansion of the chain dimension in bulk as compared with that at θ conditions. He attributes this to the systematic discrepancy in the scattering constants between the neutron and light scattering experiments. Benoit, however, performed the measurement on radius of gyration of polystyrene fractions at θ condition using both the light scattering and neutron scattering techniques and obtained the identical results. It appears therefore that the chain expansion Kirste observed is real.

This is, of course, consistent with the findings of the present study. It may therefore be concluded that the polymer chains in bulk have a conformation consistent with that of a random coiled model, but they are somewhat expanded as compared with the conformation of the unperturbed state.

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