Small-angle X-ray scattering study on polymer chain dimensions in concentrated solutions in a θ-solvent

As has been reported in previous papers[1–3], the conformations of polymer chains in concentrated solutions and in bulk polymers can be estimated from the small-angle X-ray scattering of randomly tagged polymers mixed in the systems. The randomly tagged polymer is the polymer having heavy atoms with high scattering power for X-ray in some positions randomly selected along the molecule. The excess scattering from the tagged polymer is obtained by subtracting the scattering of an untagged polymer solution from that of an equimolar solution containing a small amount of the tagged polymer as well as the untagged polymer. The application of the randomly tagged polymer enables us to obtain a sufficient scattering contrast and also avoid the risk of the incompatibility and conformational change between the tagged and untagged polymers, which may arise from an excess of the tags.

The results reported in previous papers[1–3], together with those obtained by small-angle neutron scattering[4–6], revealed that the polymer chain dimensions in good solvents decrease rapidly first and then gradually with increasing polymer concentration, and that, in the bulk state, they become in accord with the unperturbed chain dimensions. Various theories[7–11] predict such decrease of the chain dimensions in good solvents. These theories for concentrated polymer solutions in good solvents also imply that the polymer chain dimensions in θ-solvents are independent of the polymer concentration. However, no theory as yet has been presented dealing explicitly with the chain dimensions in concentrated solutions in θ-solvents. Also the experimental investigation concerning this problem has not yet been reported. As cited above, the application of the tagged polymer to the neutron scattering method has succeeded in measuring the chain dimensions in concentrated solutions in good solvents and bulk polymers. However, measurements in θ-solvents have not been reported as yet, probably because the difference in thermodynamic property between the polymer tagged with deuterium and the untagged polymer becomes noticeable in θ-solvents[12]. This difficulty can be overcome by means of the randomly tagged polymers. The purpose of this Letter is to estimate the polymer chain dimensions in concentrated solutions in a θ-solvent by use of the small-angle X-ray scattering from the randomly tagged polymers.

A narrow distribution polystyrene ($M = 110\,000, M_w/M_n < 1.06$, Pressure Chemical Co., batch No. 4b) was used as the polymer sample. The tagged polymers were the copolymers of styrene and *p*-iodostyrene with two different compositions prepared by partial iodination of the polystyrene according to the method of Braun[13]. The solvent was *trans*-decalin (purity 99.8%). The temperature of the samples was kept at 21.2 ± 0.01°C, which is the θ-temperature for polystyrene[14]. The concentration of the tagged polystyrene in the mixture solutions was 0.4 g/dl, which is expressed by the weight of an equimolar amount of the polystyrene per deciliter of solution. The small-angle X-ray scattering was measured with a Kratky camera equipped with a Cu anode X-ray tube. The detail of the experimental procedure was described elsewhere[15]. The collimation error was corrected according to the procedures of Lake[16] and Schmidt[17]. The radius of gyration $\langle S^2\rangle^{1/2}$ of the polymer chain was determined from the excess scattering at small angles according to the following equation:

$$[I(h)/I(0)]^{-1/2} = 1 + \langle S^2\rangle h^2/6 + \ldots$$

with $h = (4\pi/\lambda)\sin\theta$

where $I(h)$ and $I(0)$ are the excess scattering in an arbitary unit at h and $h = 0$, respectively. The latter was estimated by extrapolation. λ is the wavelength, and θ half of the scattering angle.

Table 1 shows the radii of gyration $\langle S^2\rangle^{1/2}$ of the tagged and untagged polystyrenes at infinite dilution, obtained by the extrapolation of the concentration to zero. Also shown in the Table are the values of $\langle S^2\rangle^{1/2}$ observed at the concentration of 0.4 g/dl. As is shown in *Table 1*, the radii of gyration of the tagged polystyrenes agree with one another and also with that of the untagged polystyrene within an experimental error of 5%, and the values obtained in 0.4 g/dl solutions agree with those obtained at infinite dilution. Accordingly it is reasonably considered that the radii of gyration of the tagged polystyrenes observed at 0.4 g/dl represent that of the untagged polystyrene.

Table 1 Radii of gyration $\langle S^2\rangle^{1/2}$ of the tagged and untagged polystyrene observed at infinite dilution and 0.4 g/dl

p-Iodostyrene[a] (mol %)	$\langle S^2\rangle^{1/2}$ (Å) Infinite dilution	0.4 g/dl
0	89	89
2.3	92	94
3.5	87	90

[a] Determined by argentometry

The radii of gyration $\langle S^2\rangle^{1/2}$ of the tagged polystyrenes in concentrated solutions were determined at 5 concentrations from the excess scattering of the tagged polystyrenes in the mixture solutions. No systematic variations of $\langle S^2\rangle^{1/2}$ with the composition of the tagged polystyrene was observed within an experimental error of 8%, similarly to the case of the dilute solutions. Hence the average value was regarded as $\langle S^2\rangle^{1/2}$ of the untagged polystyrene at the corresponding concentration. The expansion factor α of the polymer chain at each concentration, which is defined by the ratio of $\langle S^2\rangle^{1/2}$ to the unperturbed radius of gyration, is then calculated. In *Figure 1*, the values of α, together with that obtained in the bulk state[2], are plotted against the volume fraction of the polymer. As is shown in the Figure, the expansion factor α of the polystyrene in the θ-solvent is almost unity in the observed concentration range.

The detailed interpretation of this result requires the advanced theoretical studies, which we expect to be developed. Then we will confine our discussion to the virial coefficients. If the second virial coefficient A_2 has a non-zero value in concentrated solutions, the polymer chain dimension must expand or contract according to the sign of A_2, probably in a similar manner to dilute

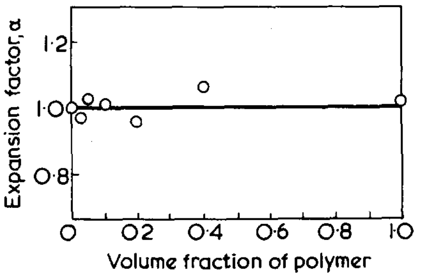

Figure 1 Concentration dependence of polystyrene chain dimension in *trans*-decalin at 21.2°C

solutions. Therefore it may be concluded that A_2 is equal to zero independently of the polymer concentration. It has almost been established that A_2 equals zero in the bulk polymer[4,5]. From the data of the osmotic pressure[14], the third virial coefficient A_3 is estimated to be 3.5×10^{-4} cm^6g^{-3}mol, despite the prediction by the two parameter theory[18] that $A_3 \rightarrow 0$ as $A_2 \rightarrow 0$. On the other hand, no effect of A_3 on the chain dimensions in θ-solvents at infinite dilution has been found, because the frequency of three-body contacts among the polymer segments is negligibly small. In concentrated solutions, however, the three-body contacts become frequent, which may affect the polymer chain dimension. Nevertheless, the result obtained in this work indicates that the chain dimension remains unchanged in concentrated solutions. From this fact, it may be suggested that A_3 diminishes with increasing polymer concentration, and that the effect of increasing frequency of the three-body contacts is compensated by the decrease of A_3 with increasing concentration.

Acknowledgement

We wish to express our thanks to Professor S. Kuwahara, Hokkaido University, for sending us the numerical data of the osmotic pressure measurements for polystyrene–*trans*-decalin system.

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(Received 4 February 1977;
revised 4 March 1977)

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Chain flexibility of poly(phenyl thiolmethacrylate)

In spite of the abundant literature published in recent years on the solution properties of polyacrylates and polymethacrylates, the corresponding sulphur containing polymers (thiolacrylates and thiolmethacrylates) have received no attention, although acrylic polymers with sulphur in the side chain possess very good physical properties, e.g. elasticity, stability towards heat and solvents and low degree of swelling[1,2].

Six fractions of poly(phenyl thiolmethacrylate) (PTPH) of M_w from 4.11×10^4 to 25.2×10^4 were prepared and characterized by light scattering(benzene), viscosity(benzene, methyl ethyl ketone) and gel permeation chromatography (toluene) at 25°C.

The values of K_Θ and of the chain flexibility factor σ are given in *Table 1*. The K_Θ value corrected for polydispersity was obtained as previously[3] using the weight-average molecular weights and the intrinsic viscosities. The value of σ was calculated by taking for Φ the theoretical value of 2.87×10^{21}. In the same Table are given the corresponding values found for poly(phenyl methacrylate) (PPH)[4,5].

Table 1 K_Θ value and chain flexibility factor σ for poly(phenyl thiolmethacrylate) and poly(phenyl methacrylate) at 25° C

Polymer–solvent	$K_\Theta \times 10^3$ (cm^3/g)	σ
Poly(phenyl thiol-methacrylate)		
Benzene		
Methyl ethyl ketone	39.5	2.26
Poly(phenyl methacrylate)[3,4]		
Benzene		
Methyl ethyl ketone	59	2.46

It is clear that the flexibility of PTPH ($\sigma = 2.26$) is much higher than that of PPH ($\sigma = 2.46$). This difference mainly arises from the change in the local intramolecular interactions caused by the substitution of the oxygen atom in PPH by a sulphur atom; the higher flexibility of the sulphur containing side group of PTPH, due to the decrease in the energy barrier around C–S bond[6], seems to contribute also to it.

It is interesting to note, that the difference in the flexibility factors between PTPH and PPH is of the same order as in the case of poly(propylene oxide) ($\sigma = 1.62$) and poly(propylene sulphide) ($\sigma = 1.49$)[7], where the substitution of oxygen by sulphur is in the main chain.

Further investigations on the influence of sulphur-containing side groups on the chain flexibility are in progress.

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