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SOLUTION PROPERTIES OF STYRENE-*p*-CHLOROSTYRENE DIBLOCK COPOLYMERS—II

LIGHT SCATTERING STUDIES IN A SELECTIVE SOLVENT

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Abstract—Conformational behaviour of styrene–*p*-chlorostyrene diblock copolymers in cumene (a good solvent for polystyrene but a θ solvent for poly-*p*-chlorostyrene) was studied over the temperature range 15–60° by light scattering, osmotic pressure and intrinsic viscosity measurements. Two samples of copolymer (AB-4 and AB-2) were used. The composition of the samples was *c.* 50 mol% of styrene and the number-average molecular weights were 27.7×10^4 for the AB-4 and 19.5×10^4 for the AB-2. It was found that below 40° the number-average molecular weight of the AB-4 sample seemed to increase gradually with decreasing temperature and around 40°, marked decreases in the osmotic second virial coefficient and intrinsic viscosity were observed. The Zimm plot for the AB-2 sample was fairly normal at 40°. It seems that the temperature where an anomaly becomes evident in Zimm plots is dependent on the molecular weight of the sample. The experimental results for the diblock copolymers could be understood from the view that intermolecular association took place to some extent in the solutions on lowering the temperature giving rise to multi-molecular micelles.

INTRODUCTION

In previous work [1], the conformational behaviour of styrene (St)–*p*-chlorostyrene (ClSt) diblock copolymers in a selective solvent (cumene) was studied by viscosity measurements. At both 55° and 50°, Stockmayer–Fixman plots, $[\eta]/M^{1/2}$ vs $M^{1/2}$, showed good linear relationships and gave reasonable values of unperturbed dimensions. These results indicated that the molecular conformation of the diblock copolymers could be approximated by a model of a quasi-random coil form rather than a segregated form. However, in selective solvents, the possibility that the molecular chain takes a segregated form rather than a quasi-random coil form was pointed out [2]. Dondos *et al.* [3, 4] and Urwin *et al.* [5] reported that the transition from a random coil form to a segregated form occurs at the transition temperature for the triblock copolymers of (St–methyl methacrylate) and the diblock copolymers of (St–isoprene) respectively. It was also reported that in selective solvents intermolecular associations occured among the segregated molecules and multi-molecular micelles were formed [2]. Formation of multi-molecular micelles in block copolymer solutions has been observed in some cases, e.g. diblock copolymers of (St–methyl methacrylate) [6–8] and (St–isoprene) [9], and the diblock and triblock copolymers of (St–butadiene) [10–13].

Previously, the conformational behaviour of St–ClSt triblock copolymers of the ABA and BAB type (A:polystyrene; B:poly-*p*-chlorostyrene) in the selective solvent cumene was studied by viscosity, osmotic pressure and light-scattering measurements [14]. The results suggested that, on lowering the temperature, conformational change from a quasi-random coil form to a segregated form may occur, and multi-molecular micelle formation caused by intermolecular associations took place at least partly in the ABA type copolymer solutions. The temperature at which an anomaly due to multi-molecular micelle formation was observed was dependent on the composition and molecular weight of the copolymers.

In this paper, the temperature dependence of the conformational behaviour of St–ClSt diblock copolymers in cumene has been studied by light scattering, osmotic pressure and intrinsic viscosity measurements.

EXPERIMENTAL

Materials

The St–ClSt diblock copolymers were prepared by anionic polymerization with cumyl-potassium as initiator and tetrahydrofuran as solvent [1]. The characteristics of the copolymer samples were as follows; for AB-4, the ClSt content in mole fraction was 0.506, $\bar{M}_n \times 10^{-4}$ was 27.7 and $M_{app} \times 10^{-4}$ was 34.1; the corresponding quantities for AB-2 were 0.486, 19.5 and 22.9. The molecular weights refer to toluene solutions at 30°C.

Measurements

Light scattering measurements were made by a Shimazu light scattering photometer using 436 nm light. The concentrations of the solutions ranged from 0.07 to 0.6 g dl^{-1}. Solutions were clarified by filtration through ultrafine glass filter at about 55° and measurements were made at five temperatures (55, 50, 45, 40 and 25°). For measurements below 45°, the scattered light intensities of the solutions increased with time. Therefore, measurements were started after the solutions reached stable states where there was no time-dependent change of the scattered light intensities. The reduced light scattering intensity R_θ can be expressed thus [15]:

$$Kc/R_\theta = 1/MP(\theta) + 2A_2c + \cdots, \qquad (1)$$

where $P(\theta)$ is the particle scattering function, K is the well-known optical constant containing the refractive index increment, A_2 is the second virial coefficient and c is the concentration. Data were analysed according to Zimm's procedure [15] and molecular weight M were obtained. For the copolymers which are heterogeneous in chemical composition, Eqn (1) yields an apparent molecular weight M_{app} but not a true weight-average molecular weight, $\bar{M}_w$ [16, 17]. The refractive index increments v were determined at 436 nm with a Shimazu differential refractometer. The values v for AB-4 in cumene solution were 0.125 at 55°, 0.124 at 40° and 0.122 ml g^{-1} at 25°.

Osmotic pressure measurements in cumene solution were made using a Hewlett-Packard high-speed membrane osmometer model 502. Number-average molecular weight, $\bar{M}_n$, is related to the osmotic pressure π thus [15].

$$\pi/c = RT(1/\bar{M}_n + 2A_{2\pi}c + \cdots), \qquad (2)$$

where c is the concentration, R is the gas constant and T is the absolute temperature. $\bar{M}_n$ and second virial coefficients $A_{2\pi}$ were determined from the linear plots of π/c vs c.

Viscosities were measured with Ubbelohde dilution viscometers known to have negligible kinetic energy corrections. Intrinsic viscosities $[\eta]$ were determined according to the Huggins equation [18].

RESULTS AND DISCUSSION

$A_{2\pi}$ and $\bar{M}_n$ for the AB-4 sample of the diblock copolymer in cumene obtained from the osmotic pressure measurements are plotted as a function of temperature in Fig. 1. For comparison, the $A_{2\pi}$ for a polystyrene (PSt) standard sample ($\bar{M}_n = 37.6 \times 10^4$) from the Pressure Chemical Company is also shown. Cumene is a good solvent for PSt but a poor solvent for poly-*p*-chlorostyrene (PClSt, $\theta = 59.0°$) [19]. PClSt is insoluble in cumene below around 50°. However, the diblock copolymer samples were soluble in cumene over the range 60–15°.

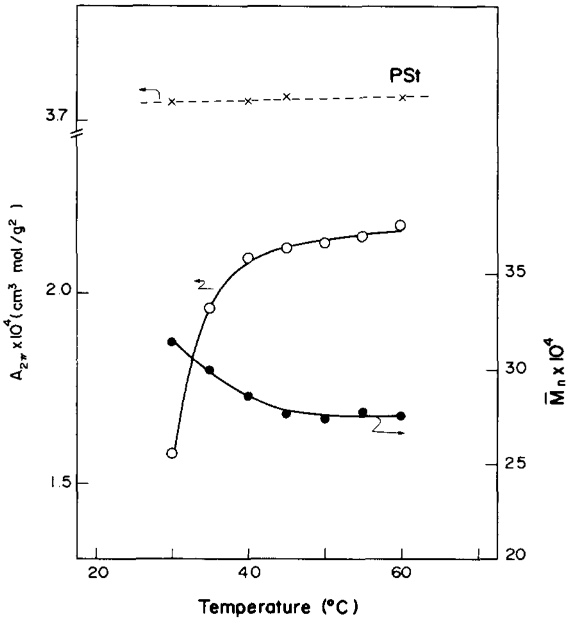

Fig. 1. Plots of $A_{2\pi}$ and $\bar{M}_n$ vs temperature for the St–ClSt diblock copolymer (AB-4) in cumene.

As shown in Fig. 1, although a slight decrease was observed, the values of $A_{2\pi}$ for PSt in cumene remained almost constant over the range 60–30° whereas a marked decrease in $A_{2\pi}$ for the diblock copolymer was observed between 40 and 30°; the temperature dependence of $A_{2\pi}$ seems to differ above and below about 40°. It was noted that the value of $A_{2\pi}$ for the diblock copolymer did not come down to zero on lowering the temperature. A variation of $A_{2\pi}$ with decreasing temperature could be interpreted as a reflection of conformational change of the diblock copolymer; a conformational change from a quasi-random coil form to a segregated form may occur in the region between 40 and 30°.

The values of $\bar{M}_n$ for the diblock copolymer in cumene above 45° were approximately equal to the value obtained in toluene solution. A gradual increase in $\bar{M}_n$ was observed below 40° where a decrease in $A_{2\pi}$ became more rapid, and the value of $\bar{M}_n$ at 30° was about 15% larger than that measured in toluene solution. An increase of $\bar{M}_n$ measured in cumene at lower temperature suggests that intermolecular associations may occur to some extent among the segregated molecules giving rise to multi-molecular micelles.

The Zimm plots for the AB-4 sample of the St–ClSt diblock copolymer in cumene are given in Fig. 2. The Zimm plot at 55° was normal, and almost so at 50° although the values of (Kc/R_θ) at lower scattering angles became somewhat smaller, showing deviation from linearity especially for the solutions of higher concentration. On the other hand, the Zimm plots below 45° were considerably distorted. Particularly at 45°, slopes of the (Kc/R_θ) vs $\sin^2\frac{\theta}{2}$ plots increased rapidly with increase in concentration, and the values of (Kc/R_θ) at the lower angles markedly decreased.

In Fig. 3, the values of (Kc/R_θ) extrapolated to zero angle at each temperature are plotted against the concentration. The values of $(Kc/R_\theta)_{\theta=0}$ below 45° were much smaller than those at 55° and 50°, and even reduced rapidly with decreasing temperature and with increasing concentration. The values of M_{app} obtained by extrapolating $(Kc/R_\theta)_{\theta=0}$ to zero concentration were 34.7×10^4 at 55° and 34.0×10^4 at 50°. These values were close to the value measured in toluene solution. It was difficult to determine the value of M_{app} at 45° because the curve was so steep at lower concentrations. At 40°, the $(Kc/R_\theta)_{\theta=0}$ vs c plots showed some curvature, but the value of M_{app} could be extrapolated as about 1.3×10^6. An extremely large value of M_{app}, c. 1×10^7, was obtained at 25°. The results of light scattering suggest that intermolecular associations occur partly in cumene solution below 45° and the extent of associations increases with decreasing temperature and with increasing concentration.

In order to examine whether the temperature (45°) where an anomaly in Zimm plots becomes evident is characteristic of the nature of the block copolymer sample, light scattering of a different diblock copolymer sample, AB-2, in cumene was measured and compared with that of the AB-4 sample. The number-

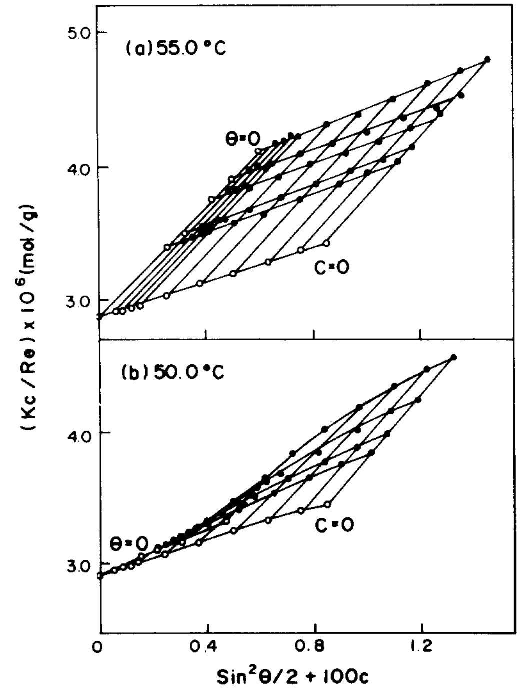

Fig. 2a. Zimm plots for the St–ClSt diblock copolymer (AB-4) in cumene: (a) at 55°; (b) at 50°.

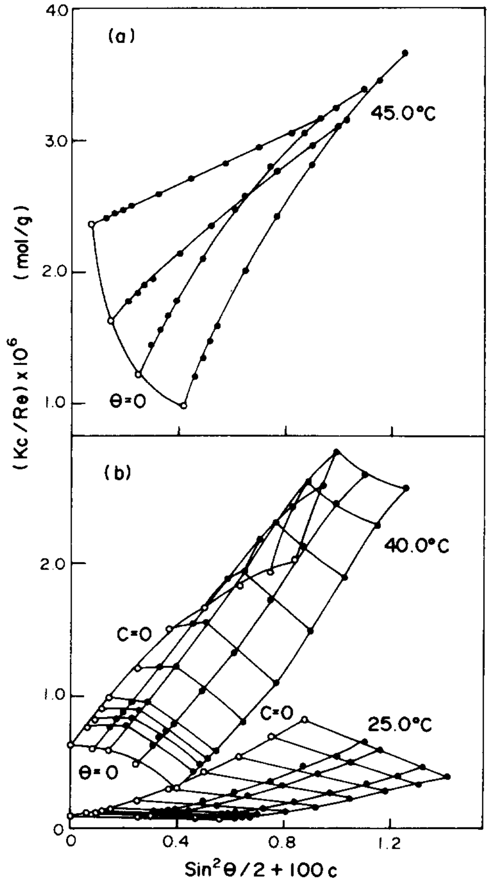

Fig. 2b. Zimm plots for the St–ClSt diblock copolymer (AB-4) in cumene: (a) at 45°; (b) at 40 and 25°.

average molecular weight and chlorostyrene content in mole fraction of the AB-2 sample were 19.5 × 10^4 and 0.486, respectively. As shown in Fig. 4, the Zimm plot for the AB-2 sample at 40° was fairly normal and the derived value of M_{app} (= 22.7 × 10^4) was close to the value obtained in toluene solution. It was observed that the temperature where an anomaly in Zimm plots became evident was higher for the AB-4 sample than for the AB-2 sample; multi-molecular micelle formation occurred at higher temperature in the AB-4 solution. It was previously reported that, for St–ClSt triblock copolymers in cumene [14], the samples with larger molecular weight and higher *p*-chlorostyrene content showed anomalies in Zimm

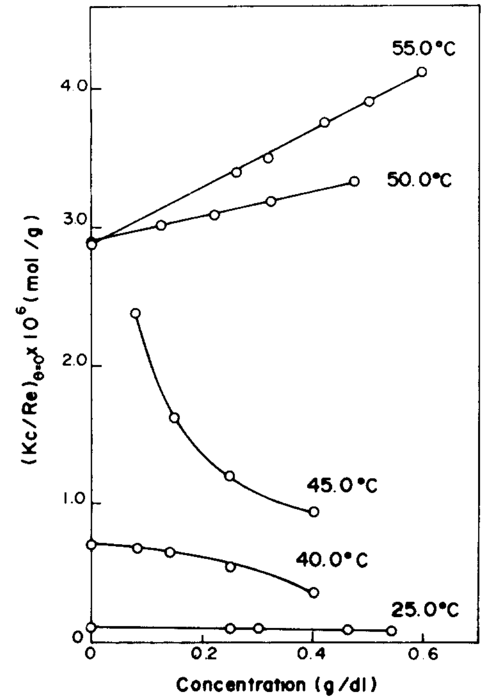

Fig. 3. Concentration dependence of $(Kc/R_\theta)_{\theta=0}$ for the St–ClSt diblock copolymer (AB-4) in cumene.

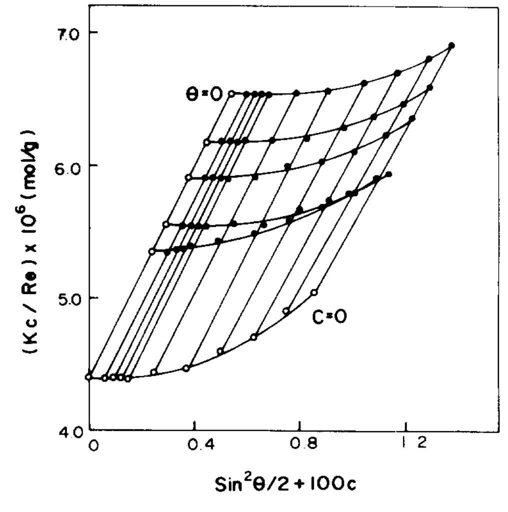

Fig. 4. Zimm plot for the St–ClSt diblock copolymer (AB-2) in cumene at 40°.

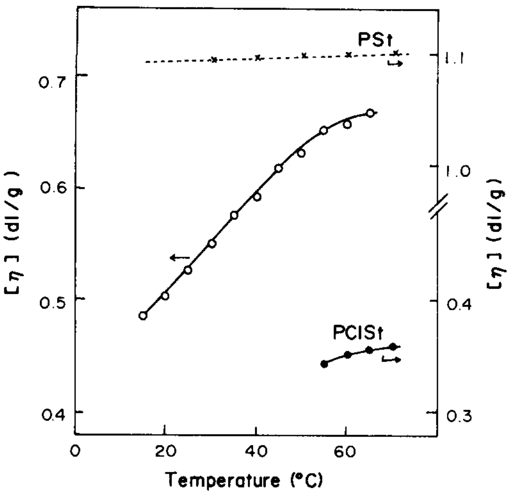

Fig. 5. Temperature dependence of the intrinsic viscosities of the St–ClSt diblock copolymer (AB-4) in cumene.

plots at higher temperature. The present results for the diblock copolymers showed trends similar to those previously obtained for the triblock copolymers. However, it should be pointed out that slight differences in molecular weight distribution and compositional distribution of the copolymer samples might be an additional cause of the discrepancy in their light scattering data. Further study on this point will be necessary.

From the results of light scattering and osmometry for the AB-4 sample in cumene, it was shown that an anomaly became evident at 45° in Zimm plots, but at 40° in the data of osmotic pressure, and the value of M_{app} obtained from light scattering data at 40° differed greatly from that of $\overline{M}_n$ obtained from osmometry at 40°. Such a big difference between the values of M_{app} and $\overline{M}_n$ at 40° suggests that the intermolecular associations took place only partly and most of the copolymers in solution remained in the state of monomolecular dispersion, but the molecular weights of the micelles formed should be very large. The formation of multi-molecular micelles could be more sensitively detected in light scattering measurements than in osmotic pressure measurements. This may be the reason why an anomaly was observed in Zimm plots at higher temperature than in the data of osmotic pressure.

In the previous work [1], we studied the molecular weight dependence of the intrinsic viscosity for the St–ClSt diblock copolymers in cumene and observed no anomalies at 40° and 55°; the $[\eta]/M^{\frac{1}{2}}$ vs $M^{\frac{1}{2}}$ plots showed good linearity at both temperatures and gave reasonable values of the unperturbed dimension. In the present study, intrinsic viscosities of the diblock copolymer in cumene were measured down to 15° and plotted as a function of temperature in Fig. 5. The $[\eta]$ data of the PSt standard sample and the PClSt sample ($\overline{M}_n = 38.0 \times 10^4$) prepared anionically are also shown in Fig. 5. A slight decrease in $[\eta]$ was observed for the PSt and PClSt with lowering temperature, whereas $[\eta]$ for the diblock copolymer decreased rapidly below about the temperature at which PClSt becomes insoluble. The rapid decrease of $[\eta]$ with decreasing temperature may be cuased by intramolecular associations. However, multi-molecular micelle formation was not revealed from the $[\eta]$ data.

In conclusion, the experimental results for the diblock copolymers in cumene could be understood in terms of the view that intermolecular associations occurred at least partly among the segregated molecules giving rise to multi-molecular micelles on lowering temperature, as previously found from study of St–ClSt triblock copolymer solutions.

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