Conformational behaviour of (styrene-*p*-chlorostyrene) triblock copolymers in dilute solutions.

2. Temperature dependence of conformational behaviour in a selective solvent

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Intrinsic viscosity, osmotic second virial coefficient and light scattering of the $B_mA_nB_m$ and $A_mB_nA_m$ copolymers (A, styrene monomeric unit; B, *p*-chlorostyrene monomeric unit, *m* and *n* denote the number of units) in cumene which is a good solvent for polystyrene but a θ solvent for poly(*p*-chlorostyrene) at 59.0°C, were studied over the temperature range 65° to 15°C. The results suggested that conformational transition from a random coil form to a segregated form occurs at a critical temperature which appears to be in the range 40° to 30°C, depending on the composition, molecular weight and structure of the block copolymers; the θ condition could not be attained by cooling the block copolymer solutions, and micelle formations due to intermolecular associations were found in some cases below the transition temperature.

INTRODUCTION

The molecular conformation of block copolymers in dilute solution has been the subject of intensive investigations in recent years and it has been suggested that there are two possible views, depending on the nature of the polymers, the selectivity of the solvents and temperature[1].

First, block copolymers in dilute solution could be treated as homopolymers, assuming that heterocontact interactions as well as homocontact interactions contribute to the expansion of the molecular chain, so that domains of unlike segments overlap and interpenetrate. Second, it can be assumed that intramolecular heterocontacts are few, so that intramolecular phase separation occurs giving a segregated conformation in which unlike segments occupy separate domains in dilute solution. In previous work[2,3], we have studied the conformational behaviour of the styrene(St)–*p*–chlorostyrene(ClSt) triblock copolymers in several solvents, and obtained results in favour of the first view. It was found that procedures and theories originally developed for homopolymer solutions are applicable to the St–ClSt block copolymers in non-selective solvents such as toluene and 2-butanone. However, the results obtained for the St–ClSt block copolymers in selective solvents such as cumene and CCl_4 which are good solvents for polystyrene(PSt) but poor for poly-*p*-chlorostyrene(PClSt) (θ = 59.0°C in cumene, and θ = 50.9°C in CCl_4) were less conclusive. The Stockmayer–Fixman equation was valid for both the $B_mA_nB_m$ and $A_mB_nA_m$ copolymers in cumene and CCl_4 at 40°C, giving reasonable values of the short-range interaction parameter, but the long-range interaction parameter obtained from the $[\eta]/M^{1/2}$ vs. $M^{1/2}$ relation was greater for the $A_mB_nA_m$ copolymers than that for the $B_mA_nB_m$ copolymers of the same composition, whereas it was found that in toluene and 2-butanone, the conformational behaviour of the $A_mB_nA_m$ copolymers was exactly the same as that of $B_mA_nB_m$ copolymers. Therefore, the molecular conformation of the St–ClSt triblock copolymers in the selective solvent could not strictly be a random conformation, though it may still be approximated by a model for a pseudo-random coil.

Dondos *et al.*[4] have proposed a concept of conformational transition for the (St–methyl methacrylate) triblock copolymers in dilute solution and assumed that below the transition temperature (T_c), molecules of the block copolymers will assume a segregated conformation whereas above T_c an increase in the number of heterocontacts yields more extended random conformation. Urwin *et al.*[5] have also suggested the existence of the transition temperature from the study of temperature dependence of intrinsic viscosities for the (St–isoprene) diblock copolymers in a selective solvent.

In the present investigation, we have studied the temperature effect on the conformation of the St–ClSt triblock copolymers in a selective solvent. Intrinsic viscosities and the second virial coefficient of osmotic pressures were measured over the range of temperature 60° to 15°C. Light scattering measurements were also made to provide additional information.

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Table 1 Characteristics of the block copolymer samples

Sample		x	M_n
Type	Code	(St mol fraction)	$\times 10^{-4}$
$A_mB_nA_m$	Ia-2	0.655	38.6
	Ib-1	0.493	30.9
	Ib-3	0.509	36.7
	Ib-5	0.480	58.1
	Ic-2	0.311	31.2
$B_mA_nB_m$	IIa-3	0.650	39.0
	IIb-4	0.518	30.1
	IIb-7	0.515	55.3
	PSt	1.000	37.6
	PClSt	0.000	38.0

EXPERIMENTAL

Preparation of block copolymers

Triblock copolymers of styrene and *p*-chlorostyrene were prepared by the anionic polymerization technique described before[2]. Sodium naphthalene was used as the initiator, and tetrahydrofuran as the solvent. *Table 1* shows the characteristics of the block copolymer samples used for measurements.

Viscometry

Viscosities of the block copolymer solutions were measured by Ubbelohde dilution viscometers known to have negligible kinetic energy corrections. Plots of η_{sp}/c vs. c were extrapolated to zero concentration to obtain intrinsic viscosities $[\eta]$ according to Huggins' equation[6]:

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c + --- \qquad (1)$$

in which η_{sp} is the specific viscosity and k_H is Huggins' constant. The concentration c of the solutions used for measurements was in the range of 0.15 to 0.60 g/dl and the flow times in the viscometers were more than 100 sec for each solution.

Osmometry

Osmotic pressure measurements in toluene and cumene solution were made using a Hewlett–Packard high speed membrane osmometer model 502. Number-average molecular weight, M_n, is related to the osmotic pressure π by the following equation[7]

$$\pi/c = RT(1/M_n + A_2c + ---) \qquad (2)$$

where c (g/dl) is the concentration of the solution, R is the gas constant and T is the absolute temperature. M_n and the second virial coefficient A_2 were determined from the linear plots of π/c vs. c.

Light scattering measurements

Light scattering measurements were made by a Shimazu light scattering photometer using light of wavelength 436 nm at 10 angles from 30° to 135°. The reduced scattered intensity $R(\theta,c)$ may be expressed in a general form:

$$Kc/R(\theta,c) = \frac{1}{MP(\theta)} + 2A_2c + --- \qquad (3)$$

$$K = (2\pi^2/\lambda_0^4N)n_0^2\nu^2$$

$$P(\theta)^{-1} = 1 + (16/3)(\pi^2n_0^2/\lambda_0^2)\langle S^2\rangle_Z \sin^2\theta/2 + ---$$

where $P(\theta)$ is the particle scattering function. A_2 is the second virial coefficient, n_0 is the solvent refractive index of the light of the wavelength λ_0, N is Avogardro's number, ν is the refractive index increment of the solution and S is the radius of gyration. Data were treated by the Zimm method (i.e. by carrying out a double extrapolation of the data to zero angle and zero concentration) and weight-average molecular weights were obtained. In the case of copolymers which are heterogeneous in chemical composition, equation (3) yields an apparent molecular weight rather than a true weight-average molecular weight as pointed out by Stockmayer *et al.*[8] and Bushuk and Benoit[9]. For the present study, in view of the controlled synthetic methods and fractionation procedures used to obtain the copolymer samples, application of equation (3) can be taken as providing a reliable measure of the weight-average molecular weight, regardless of the refractive index of the solvent[2].

The refractive index increments were determined using light of wavelength 436 nm with a Shimazu differential refractometer.

RESULTS AND DISCUSSION

Temperature dependence of intrinsic viscosities $[\eta]$

The intrinsic viscosities are plotted as a function of temperature in *Figures 1a* and *1b*. The measurements cover the temperature range 60° to 15°C for the $A_mB_nA_m$ copolymers and 60° to 15°C for the $B_mA_nB_m$ copolymers. Data for the parent homopolymers are also shown in these Figures for the purpose of comparison; a PSt standard sample ($M_n = 37.6 \times 10^4$) from the Pressure Chemicals Company and our sample of PClSt ($M_n = 38.0 \times 10^4$) prepared by anionic polymerization were used for measurements.

By lowering the temperature, a slight decrease in $[\eta]$ was observed for the homopolymers, whereas $[\eta]$ of the block copolymers decreased more rapidly and variation of $[\eta]$ with temperature was different according to the characteristics of the block copolymers; i.e. the composition, molecular weight and structure of the copolymers. *Figure 1a* shows the temperature dependence of $[\eta]$ for the $A_mB_nA_m$ copolymers; the decrease in $[\eta]$ with decreasing temperature for the sample Ia-2 of composition $x = 0.66$ (in mol fraction St) and the molecular weight $M_n = 38.6 \times 10^4$ is more gradual than that of Ib-1 and Ic-2 which have higher ClSt content ($x = 0.49$ and 0.31, respectively) and about the same molecular weight and the $[\eta]$ vs. temperature curve for Ib-5 of $x = 0.48$ and $M_n = 58.1 \times 10^4$ contains a very steep region. The same trend is observed in the $[\eta]$ vs. temperature curves for the $B_mA_nB_m$ copolymers in *Figure 1b*; the decrease in $[\eta]$ with decreasing temperature is marked for the sample IIb-7 of $x = 0.52$ and $M_n = 55.3 \times 10^4$, but more gradual for samples of smaller ClSt content and lower molecular weight. However, a general feature of the shape of the $[\eta]$ vs. temperature curves is common to all the block copolymers and there appears to be a transition point between 40° and 35°C in these curves; the temperature dependence of $[\eta]$ seems to differ above and below that temperature. These results are very similar to those previously obtained by Price *et al.* for (St–isoprene) diblock copolymers in n-decane[10]. The concentration of the solutions used for

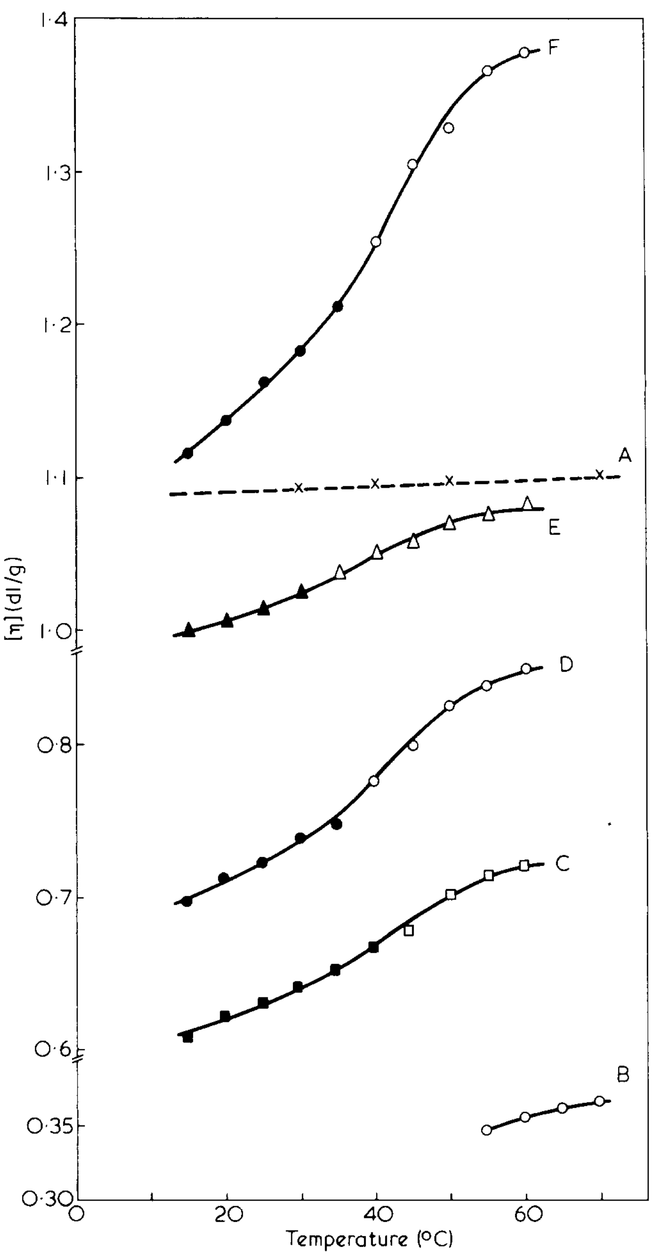

Figure 1a Temperature dependence of the intrinsic viscosities of the $A_mB_nA_m$ copolymers in cumene. A, PSt; B, PClSt; C, Ic-2; D, Ib-1; E, Ia-2; F, Ib-5

viscosity measurements were $c = 0.15 \sim 0.6$ g/dl and on lowering the temperature below 30°C, the $B_mA_nB_m$ copolymer solution of the highest concentration became somewhat turbid while the $A_mB_nA_m$ copolymer solution of the same concentration became turbid at a higher temperature, 40°C, for Ic-2, 35°C for Ib-1 and Ib-5 and 30°C for Ia-2. However, the dispersions remained quite stable down to much lower temperature and all the values of $[\eta]$ obtained under the conditions of the present experiments showed a good reproducibility. Variations of $[\eta]$ with temperature should be interpreted as a reflection of conformational change of the copolymer molecules. Cumene is a good solvent for PSt but a poor solvent for PClSt, and on lowering the temperature, PClSt becomes insoluble in cumene below 50°C. It is supposed that PClSt blocks of the copolymer molecule in cumene are in the aggregate state whereas PSt block chains should be in a more extended state. The conformation of such a molecular chain is not simple; it may still take a pseudo-random coil conformation while it is also likely that intrachain phase separation takes place leading to a segregated chain conformation for which an assumption of the statistical random coil model is not valid.

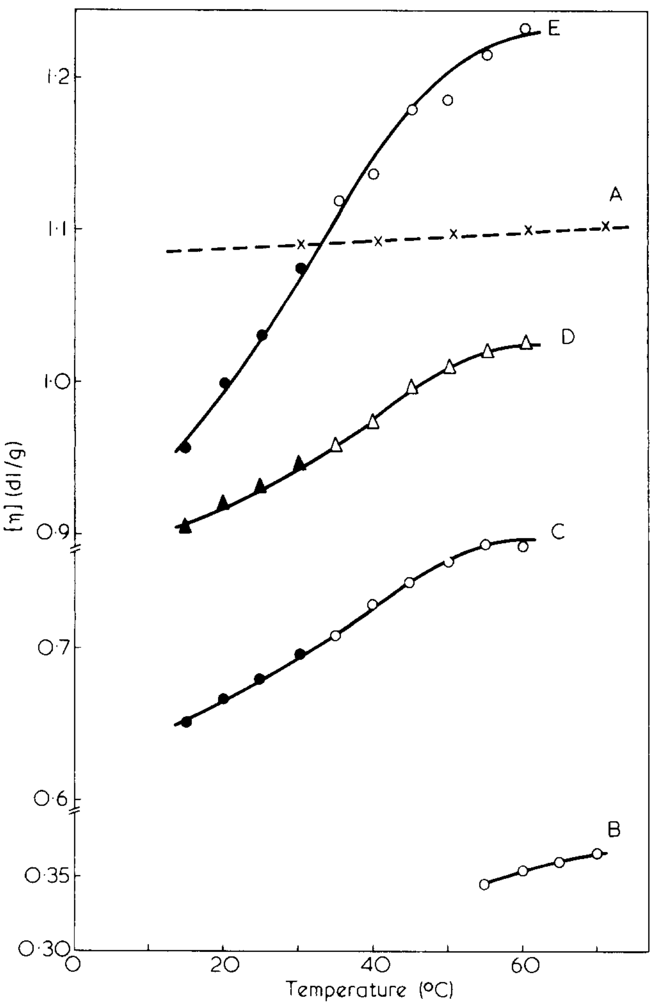

Figure 1b Temperature dependence of the intrinsic viscosities of the $B_mA_nB_m$ copolymers in cumene. A, PSt; B, PClSt; C, II b-4; D, IIa-3; E, IIb-7

In a preceeding paper[3], we have investigated the $[\eta]/M^{1/2}$ vs. $M^{1/2}$ relations in cumene at 40°C for several series of the St–ClSt triblock copolymers with different compositions and obtained results which favoured a pseudo-random coil conformation. However, it is quite likely that the conformation of the block copolymers may change from a random coil form to a segregated form with decreasing temperature and moreover, intra- and intermolecular associations may occur leading micelle formations. Dondos *et al.*[4] have previously investigated conformational behaviours of the (St–methyl methacrylate) triblock copolymers in dilute solutions and reported that the curve of $[\eta]$ vs. temperature showed rising values of $[\eta]$ with increasing temperature and a discontinuity in $[\eta]$ at a particular temperature T_c, which was followed by a sharp fall in $[\eta]$ to a minimum value, and then by a further rise after passing through minimum[4a]. Urwin *et al.* have obtained a similar result on the $[\eta]$ vs. temperature relation for the (St–isoprene) diblock copolymers in methyl cyclohexane[5c]. The marked decrease of $[\eta]$ around the region between 30° and 40°C in *Figure 1a* and *1b* may correspond to a conformational transition although a discontinuous change such as that reported by Dondos *et al.*[4a] and Urwin *et al.*[5c] was not observed in our case. In order to obtain more evidence for the conformational transition of the St–ClSt triblock copolymers in cumene, we also carried out measurements of osmotic virial coefficient and light scattering of the block copolymer solutions at various temperatures.

Temperature dependence of A_2

The osmotic pressure π of a polymer solution is developed as a function of concentration c (g/dl) of the solution as follows[11]:

$$\pi = RT(c/M_n + A_2c^2 + A_3c^3 + - - -) \qquad (4)$$

where the coefficient A_2 of c^2 is the second virial coefficient and the coefficient A_3 of c^3 is the third virial coefficient. The osmotic pressure of polymer solutions usually gives abnormally large values which markedly deviate from van't Hoff's rule for ideal solutions. Such deviation must be due to excluded volume effects of polymer molecules; the second virial coefficient A_2 relates to interactions between two molecules and the third virial coefficient A_3, interactions among three molecules. According to McMillan–Mayer's solution theory, A_2 is given as follows[12]:

$$A_2 = -\frac{N_A}{2M^2V}\int\int [F_2(1,2) - F_1(1)F_1(2)]\, d(1,2) \qquad (5)$$

where V is the volume of the solution, N_A is Avogadro's number, $F(1)$ and $F(2)$ are the distribution functions for the solute molecules 1 and 2, respectively, and $F(1,2)$ is the binary distribution function when the interaction between molecules 1 and 2 are taken into consideration. The first application of the McMillan–Mayer theory to the solutions of macromolecular chains was attempted by Zimm and it was suggested that the second virial coefficient A_2 is a decreasing function of polymer molecular weight M[13]. Since then, a number of studies have been undertaken and theories on the second virial coefficient have been developed[14,15,16]. According to them, A_2 may be expressed as:

$$A_2 = 4\pi^{3/2}N_A \frac{\langle S^2\rangle^{3/2}}{M^2}\,\phi \qquad (6)$$

$$\phi = \bar{z}h(\bar{z})$$

$$\bar{z} = (3/2\pi a^2)^{3/2}\beta n^{1/2}/\alpha_s^3$$

$$\alpha_s^2 = \frac{\langle S^2\rangle}{\langle S_0^2\rangle}$$

where n is a number of the elements, a is the diameter of a chain element sphere, β is an excluded volume for the element, α is an expansion coefficient with respect to the radius of gyration S, and $h(\bar{z})$ is the function of excluded volume which could take different formulae according to the theories developed by different researchers. The following form was given by Yamakawa *et al.*[11]:

$$h(\bar{z}) = [1 - (1 + 0.683\,\bar{z})^{-7.39}]/5.0472$$

Conformational changes of polymer molecules in dilute solution should give an effect on the A_2 values as well as $[\eta]$ values. Values of A_2 for the St–ClSt triblock copolymers in cumene were measured over the temperature range 60° to 25°C and the A_2s are presented as a function of temperature in *Figure 2a* and *2b*. Data on the homopolystyrene were also shown in these Figures. By lowering the temperature, the A_2 of PSt showed a slight decrease but remained almost constant over the temperature range 60°–30°C, whereas a more rapid decrease of A_2 was observed for the

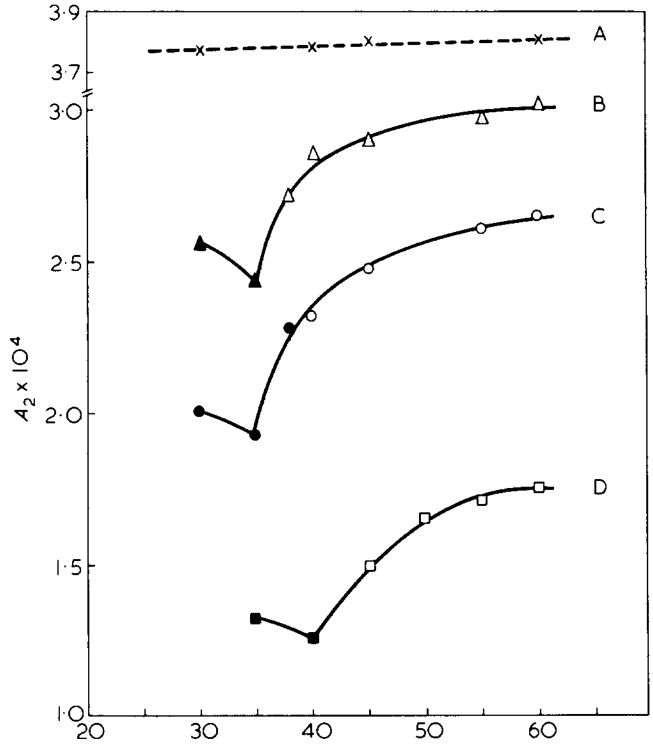

Figure 2a Temperature dependence of the second virial coefficients of the $A_mB_nA_m$ copolymers in cumene. A, PSt; B, Ia-2; C, Ib-3; D, Ic-2

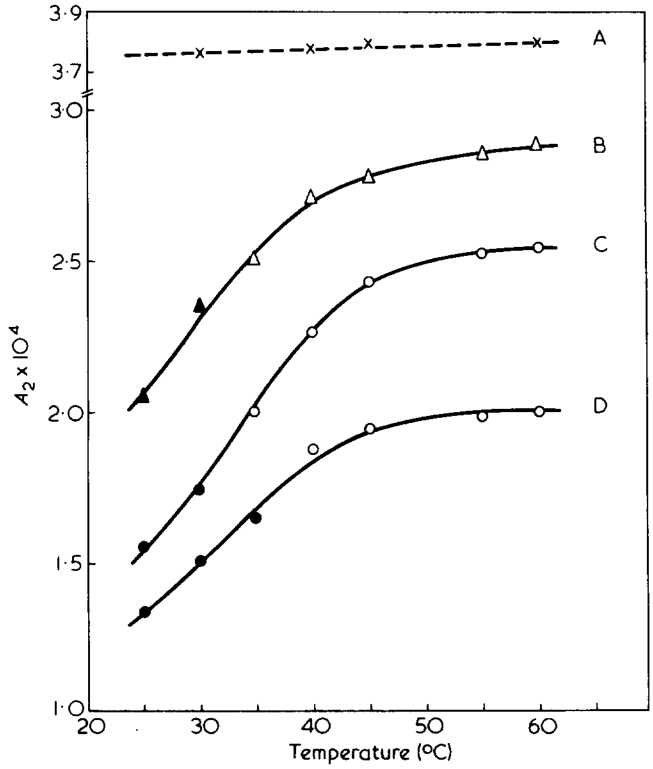

Figure 2b Temperature dependence of the second virial coefficients of the $B_mA_nB_m$ copolymers in cumene. A, PSt; B, IIa-3; C, IIb-4; D, IIb-7

Table 2 Number-average molecular weights of the St-ClSt block copolymers obtained from osmotic pressure measurements in cumene at various temperatures

Temperature (°C)	$M_n \times 10^{-4}$					
	$A_mB_nA_m$ type			$B_mA_nB_m$ type		
	Ia-2	Ib-3	Ic-2	IIa-3	IIb-4	IIb-7
25	–	–	–	38.6	30.2	56.2
30	48.7	42.4	–	38.6	29.7	57.1
	(38.6)[a]	(36.7)	(31.2)	(39.0)	(30.1)	(55.3)
35	40.2	35.9	39.2	38.3	29.9	57.0
38	39.8	35.9	–	–	–	–
40	39.8	36.1	32.8	38.8	30.2	56.9
45	39.9	36.7	31.4	38.5	30.3	56.8
50	–	–	32.6	–	–	–
55	39.4	36.9	31.8	39.1	30.1	56.4
60	39.8	36.5	32.3	38.4	30.2	56.3

[a] Values in parentheses are those determined in toluene at 30°C

block copolymers, especially below the critical temperature which appeared to be dependent on the composition, molecular weight, and structure of the block copolymers. The critical temperature of the $A_mB_nA_m$ copolymers appeared to be between 40° and 35°C for the sample Ia-2 of composition $x = 0.66$, around 40°C for Ib-3 of $x = 0.51$, and between 45°C and 40°C for Ic-2 of $x = 0.31$ whereas the $B_mA_nB_m$ copolymers showed lower critical temperatures than those for the $A_mB_nA_m$ copolymers of the same composition and molecular weight; i.e. a marked decrease of A_2 was observed between 35° and 30°C for IIa-3 of $x = 0.65$, and between 40° and 35°C for IIb-4 of $x = 0.52$. It is also noted that the variation of A_2 with temperature depends on the molecular weight of the copolymers, i.e. A_2 for IIb-7 of $x = 0.52$ and $M_n = 55.3 \times 10^4$ changed more gradually and showed lower critical temperature 35°C, comparing with that of IIb-4 which has the same composition and lower molecular weight, $M_n = 30.1 \times 10^4$. Moreover, some difference in conformational behaviours of the $A_mB_nA_m$ copolymers and the $B_mA_nB_m$ copolymers was revealed in the osmotic pressure measurements. The A_2s of the $A_mB_nA_m$ copolymers decreased very rapidly at lower temperature, showed minima and then increased again by further lowering the temperature, whereas the curves of A_2 vs. temperature for the $B_mA_nB_m$ copolymers did not show such minima. Filled circles, triangles and rectangles in *Figures 2a* and *2b* indicate that the solutions were turbid. Molecular weights of the block copolymers in cumene were examined at various temperatures and shown in *Table 2*. The molecular weights measured at the temperatures where A_2 showed an increase, which are 30°C for Ia-2 and Ib-3, and 35°C for Ic-2, gave unusual values, 20 ~ 30% larger than those obtained in toluene solution. Such results suggest that micelle formation due to intermolecular associations might occur to some extent in the block copolymer solutions, and if that is so, micelles are rather stable. Below these temperatures, the linear relations of π/c vs. c became invalid which implies that intra- and intermolecular associations proceed with decreasing temperature and cause partial precipitation of the polymers.

On the other hand, the behaviour of the $B_mA_nB_m$ copolymers differs from that of the $A_mB_nA_m$ copolymers: plots of π/c vs. c for the $B_mA_nB_m$ copolymer solutions at 25°C still showed the linearity which gave normal values of the molecular weights, though the solutions became turbid below 30°C.

From the above observations, we could derive a conclusion that the conformational change from a random coil form to a segregated form may occur at the temperature where a decrease in A_2 becomes more rapid, in both cases of the $B_mA_nB_m$ copolymers and the $A_mB_nA_m$ copolymers, but multi-molecular micelles due to intermolecular associations were not formed in the $B_mA_nB_m$ copolymer solutions. It was also noted that the condition $A_2 = 0$ could not be attained in both types of the St–ClSt block copolymer solutions by lowering the temperature; a conformational anomaly due to the transition from a random coil to a segregated form must arise before A_2 reaches zero, so that the θ state such as exists in homopolymer solutions cannot exist in the block copolymer solutions. The experimental results on temperature dependence of A_2 showed similar

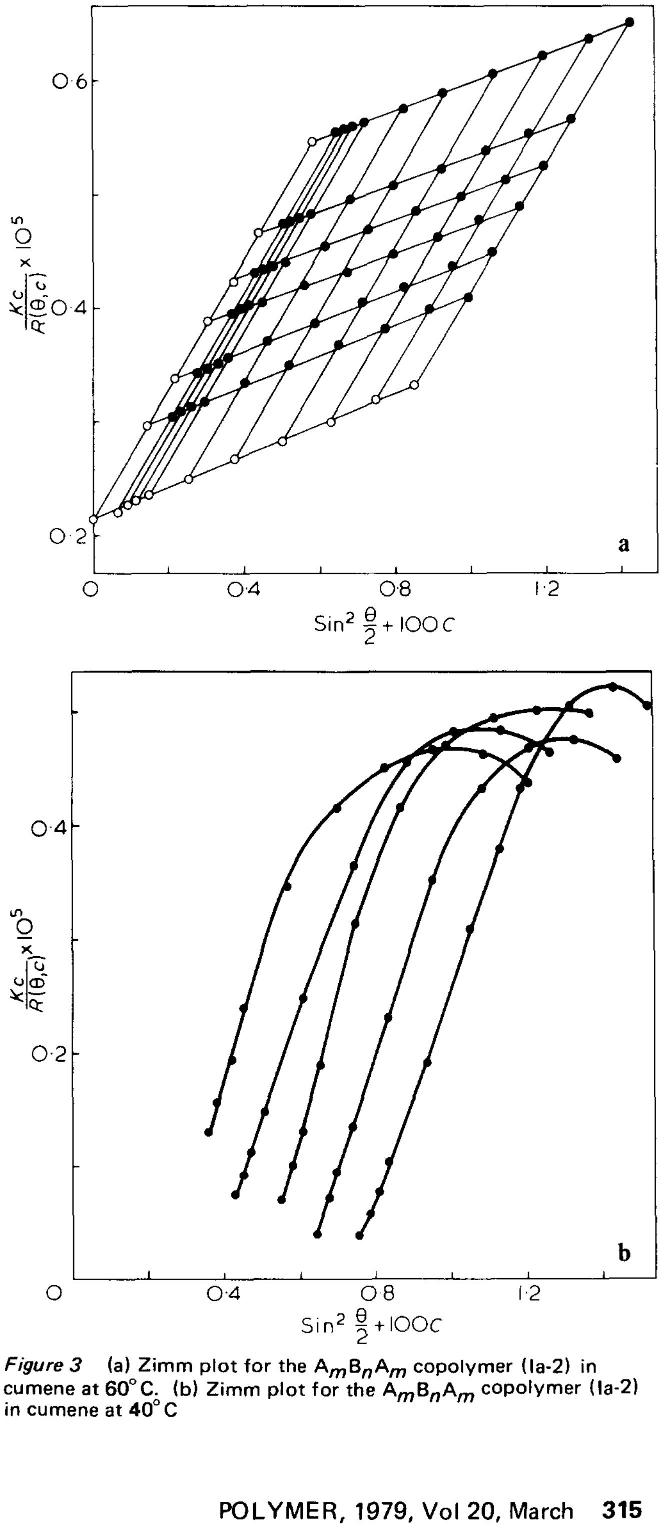

Figure 3 (a) Zimm plot for the $A_mB_nA_m$ copolymer (Ia-2) in cumene at 60°C. (b) Zimm plot for the $A_mB_nA_m$ copolymer (Ia-2) in cumene at 40°C

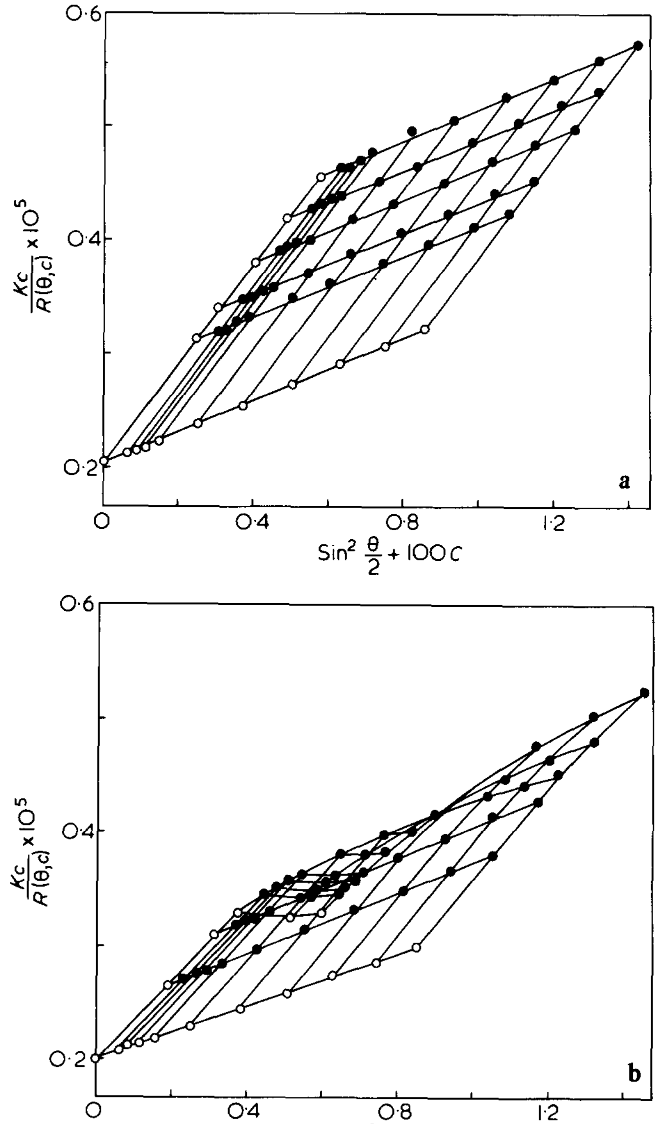

Figure 4 (a) Zimm plot for the $B_mA_nB_m$ copolymer (IIa-3) in cumene at 60°C. (b) Zimm plot for the $B_mA_nB_m$ copolymer (IIa-3) in cumene at 40°C

characteristics to those variations of $[\eta]$ with temperature, but more clearly revealing conformational change of the molecular chains. The A_2 of the St–ClSt block copolymers measured in toluene which is a good solvent for both PSt and PClSt, showed little change with decreasing temperature in the region between 60° and 25°C as well as in the case of the homopolymer solutions.

Anomalies in light scattering measurements

Typical examples of Zimm plots for the St–ClSt triblock copolymers in cumene are given in *Figures 3* and *4*. Zimm plots obtained for the $B_mA_nB_m$ copolymers in cumene were fairly normal at 60° and 40°C, yielding the same value of the molecular weight as that obtained in toluene, though values of Kc/R at lower scattering angles became somewhat smaller at 40°C, showing a deviation from linearity especially for the solutions of higher concentrations as shown in *Figure 4b*. On the other hand, Zimm plots for Ia-2 of the $A_mB_nA_m$ copolymer in cumene were perfectly normal at 60°C but distorted at 40°C. Such an anomaly in Zimm plots was previously reported for poly(vinyl alcohol) solution[18] and amylase solution[19], and interpreted as due to multi-molecular micelle formation caused by intermolecular association. Formation of multi-molecular micelles in block copolymer solutions has also been reported for (St–methyl methacrylate) diblock copolymers[20,21] (St–isoprene) diblock copolymers[10] and (St–butadiene) triblock copolymers[22,23].

The results of light scattering measurements together with those of osmotic pressure measurements support the view that by lowering temperature molecular conformations of the $A_mB_nA_m$ copolymers in cumene change from a random coil form to a segregated form; intermolecular association then takes place at least partly, giving rise to multi-molecular micelle formation. The temperature at which micelles are formed should be dependent on the composition and molecular weight of the copolymers but there appeared to be slight differences between the temperature supposed from the data on temperature dependence of A_2 and the temperature where an anomaly in the light scattering data becomes evident, which cannot be explained satisfactorily at present.

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