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4. Light scattering studies of some dilute solutions of PEO-PSt-PEO triblock polymers

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SUMMARY

Three PEO-PSt-PEO triblock polymers and their parent homopolystyrene have been studied by means of light scattering technique in chloroform, toluene and ethyl acetate. It has been found that the weight average molecular weights calculated by using the equation $Mapp = Mw + 2P(\upsilon_A - \upsilon_B)/\upsilon + Q[(\upsilon_A - \upsilon_B)/\upsilon]^2$ were unbelievable negative values; and the largest deviation appeared for the sample with PEO mole content of about 50% . Data of PSt-PEO-PSt triblock polymers in literature have been quoted and discussed.

INTRODUCTION

The solution properties of block polymers have attracted great attention of a number of workers in recent years (1-10). Although osmometry and viscosity measurements may be used to get information on the second virial coefficient and the radius of gyration, respectively (6, 11-13), light scattering technique has been employed to determine both the radius of gyration and the second virial coefficient, even to provide important information about the conformation of block polymers in dilute solutions (2-8, 10).

However, light scattering studies have been restricted so far to some classical di- or triblock polymers of polystyrene-poly(methyl methacrylate), polystyrene-polyisoprene or polystyrene-polybutadiene. Kisakürek and Saysal (10) reported some results of light scattering on polystyrene-poly(ethylene oxide)-polystyrene (PSt-PEO-PSt) triblock polymers, but the range of composition of the samples was narrow, with polystyrene weight content of about 90% .

In the work reported here three poly (ethylene oxide) -polystyrene-poly(ethylene oxide) (PEO-PSt-PEO) triblock polymers (with PEO mole content ranging from 18.7% to 61.0%) and the parent polystyrene homopolymer were studied by light scattering

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in chloroform, toluene and ethyl acetate.

EXPERIMENTAL

Polymer samples - PEO-PSt-PEO triblock polymers were synthesized via sequential anionic polymerization by using sodium naphthalene as initiator (14). The main characterization results of these polymers and their parent homopolystyrene are given in Table 1.

Measurements - The specific refractive index increments (υ - dn/dc) were determined with DR-1 refractometer at a light wavelength of 436 nm and 25℃. Light scattering studies were carried out in PG-21 light scattering photometer over the angular range 45-135°, at the same light wavelength and temperature as used in dn/dc measurements. All solvents were dried and distilled before use. Polymer solutions were filtered through G5 sintered glass funnel and centrifuged at 1.2×10^4 rpm for 2 hours before being introduced into the cell.

RESULTS AND DISCUSSION

In this study, we chose chloroform, toluene and ethyl acetate as solvents which have quite different refractive index increments and solubility for PSt and PEO. Warming was necessary for dissolving block polymers 302 and 303 in toluene and ethyl acetate. The refractive index increments of the PEO-PSt-PEO triblock polymers and their parent homopolystyrene are given in Table 1, and show good linear relations with their composition in the three solvents, as pointed out previously (14).

The typical Zimm plots obtained are shown in Figures 1-3. Upon plotting the scattering data in the usual manner with a

TABLE 1 Characteristics of PEO-PSt-PEO Triblock Polymers and Their Parent Polystyrene

Code of Sample	Structure	PEO Content [b] (mole %)	υ (ml.g^{-1})		
			Chloroform	Toluene	Ethyl Acetate
300[a]	PSt	0	0.168	0.112	0.229
301	PEO-PSt-PEO	18.7	0.156	0.0975	0.216
302	PEO-PSt-PEO	51.0	0.133	0.0715	0.189
303	PEO-PST-PEO	61.0	0.121	0.0620	0.177

a) The molecular weight and molecular weight distribution of the parent homopolystyrene were determined by GPC in THF, Mw- 6.92×10^4, Mn- 3.57×10^4, Mw/Mn- 1.94

b) According to the results of ^{1}H-NMR.

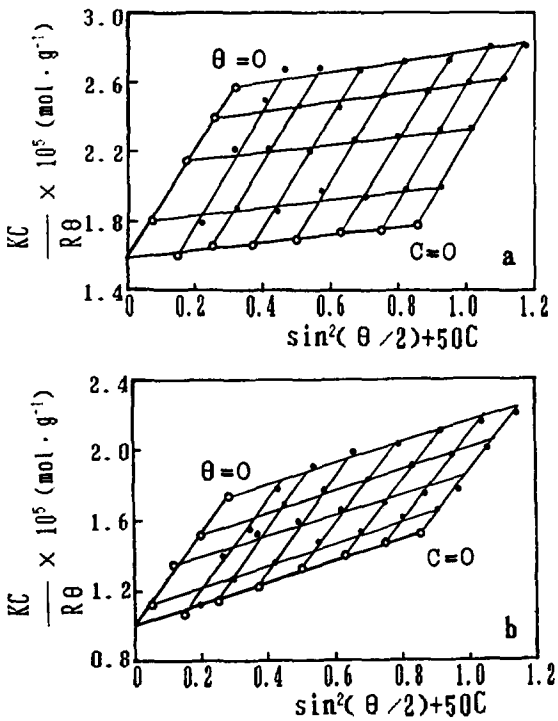

Fig.1 Zimm plots for block polymer 301 (a) and 302 (b) in chloroform

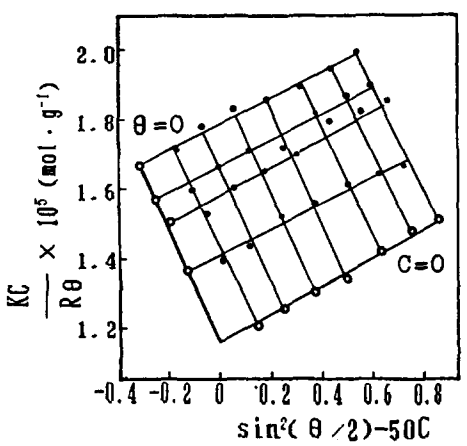

Fig.2 Zimm plot for sample 303 in chloroform

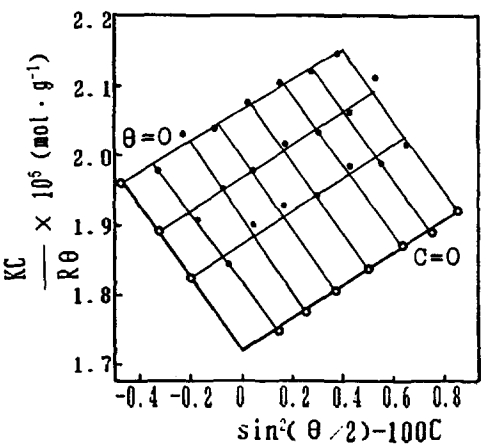

Fig.3 Zimm plot for sample 303 in ethy acetate

positive arbitrary constant k on the abscissa of the Zimm plot, we got somewhat overlappd lines in some cases, especially when ethyl acetate was employed as solvent. According to Van Wijk and Staverman (15), it is desirable to use a negative constant k in order to unravel the plots and to obtain more accurate extrapolation, as shown in Figures 2 and 3.

The light scattering data were evaluated by utilizing the standard procedures for homopolymer solutions,

$$\left(\frac{KC}{R_\theta}\right)_{\theta=0} = \frac{1}{M} + 2A_2C \qquad (1)$$

$$\left(\frac{KC}{R_\theta}\right)_{C=0} = \frac{1}{M} + \frac{16\pi^2}{3\lambda^2}\frac{1}{M}\langle Rg^2\rangle \sin^2\frac{\theta}{2} \qquad (2)$$

where C denotes the concentration, θ the scattering angle, R_θ Rayleigh's ratio, and λ the wavelength of light in the medium, M the molecular weight, $\langle Rg^2\rangle$ the mean square radius of gyration, and A_2 the second virial coefficient. The results are given in Table 2. In the case of block polymers, however, the molecular weight and radius of gyration so obtained are apparent values.

The dependence of A_2 values on the solvent for a homopolymer or a copolymer is a very good guide to the extent of interaction between solvent and polymer molecules. The calculated values of A_2 given in Table 2 show that, for PEO-PSt-PEO triblock polymers, chloroform is a good solvent, but toluene and ethyl acetate are relatively poor solvents. This conclusion is in accordance with solubility of the block polymers.

According to Bushuk and Benoit (16), the real molecular weight of a block or random copolymer (Mw) is related to the apparent molecular weight (Mapp) by the expression,

$$Mapp = Mw + 2P(\upsilon_A - \upsilon_B)/\upsilon + Q[(\upsilon_A - \upsilon_B)/\upsilon]^2 \qquad (3)$$

Where υ, υ_A, υ_B are the refractive index increments of the block polymer, homopolymer A and B, respectively. The quantity P describes the variation in chemical composition as a function of molecular weight, whereas Q is a measure of the total compositional heterogeneity in the polymer system. In principle, the real weight average molecular weight Mw, and the heterogeneity parameters, P and Q, of a block polymer could be obtained by carrying out light scattering measurements in three solvents with different refractive index increments and solving three simultaneous equations. The values of Mw, P, Q of the PEO-PSt-PEO

TABLE 2 A Summary of Light Scattering Data

Sample	$M\times10^{-4}$ (g/mol)			$A_2\times10^4$(cm^3 · mol · g^{-2})			$\langle Rg^2\rangle^{1/2}$(nm)		
	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3
300	6.67	6.87	5.97	6.3	5.3	1.3	20.8	18.9	13.6
301	6.33	8.20	5.39	7.8	6.3	6.2	15.8	14.8	15.5
302	10.0	11.4	5.80	6.5	2.9	2.6	29.5	17.2	16.1
303	8.62	13.7	5.71	4.0	1.8	0.8	24.3	10.4	17.6

* S_1= Chloroform; S_2= Toluene; S_3= Ethyl Acetae

TABLE 3 Mw, P and Q of PEO-PSt-PEO Triblock Polymers

Sample	$Mw\times10^{-4}$ (g · mol^{-1})	$P\times10^{-4}$	$Q\times10^{-4}$
301	-1.9	7.8	-6.1
302	-25.5	29.9	-21.6
303	-9.9	13.2	-7.2

triblock polymers are presented in Table 3. Surprisingly, the real molecular weights so calculated are unbelievable negative values. It is worthy of note that the largest deviation appears for the sample with PEO mole content of about 50% .

Here, it is necessary to reexamine the data in literature. The results of light scattering studies of PSt-PEO-PSt triblock polymers in reference (10) are quoted in Table 4. For comparison, the number average molecular weights have been calculated based on the composition and the molecular weight of middle PEO segment, and listed in the last column. For sample 1, which has lower molecular weight of PEO segment, the weight average molecular weight from light scattering is in good agreement with the calculated number average molecular weight. However, the light scattering studies give much lower weight average molecular weights for sample 2—5 than expected. The higher the Mn of middle PEO segment, the bigger the deviation of light scattering result is.

It is propably reasonable to suppose that the unreliable Mw data obtained from light scattering for PEO-PSt-PEO or PSt-PEO-PSt triblock polymers did not come from the accumulation of experimental error in calculation, but from the fact that equation (3) did not take into account the conformation of a block polymer in solutions which might change with the structure, composition and molecular weight of the block polymer and the

TABLE 4 Data of PSt-PEO-PSt Tribloek Polymers (10)

Sample Number	PSt content (Wt %)	Mn of PEO segment $\times 10^{-4}$	Mapp $\times 10^{-5}$			Mw $\times 10^{-5}$	Mn $\times 10^{-5}$
			S_1 *)	S_2 *)	S_3 *)		
1	94.1	0.55	1.2	1.3	1.0	1.45	0.93
2	94.3	4.0	0.4	0.5	0.4	0.62	7.0
3	93.0	4.0	0.4	0.4	0.3	0.23	5.7
4	87.9	4.0	0.4	0.4	0.5	0.36	3.3
5	92.5	4.0	0.4	0.4	0.3	0.49	5.3
6	90.0	2.0	4.2	3.3	10.1	11.1	2.0
7	93.1	2.0	5.3	2.3	16.7	13.5	1.4

*) S_1 - Benzene ; S_2 - Carbon Tetrachloride ; S_3 - Cyclohexane

solvent used, especially for amphiphilic polymers containing two segments with quite different solution properties.

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