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Unperturbed Dimensions of Poly-*o*-chlorostyrene

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In a previous paper,[1] one of the present authors reported that the K_θ value of the butanone solution of poly-*o*-chlorostyrene (the theta solution at 25°C) is fairly small compared with that found from the viscosity plot for the toluene solutions; the solvent effect is considered to be the cause of the difference between these K_θ values.

In this paper, in order to examine the effect of the solvent on the K_θ value and to find the temperature dependence of the K_θ values, the viscosity measurements of poly-*o*-chlorostyrene in critical consolute solvents, which were mixtures of benzene (solvent)-cyclohexane (nonsolvent) at three ratios of mixing, were made.

Experimental

Material. The preparation and fractionation of poly-*o*-chlorostyrene were done according to the method described in a previous paper.[1] The molecular weights of the polymer fractions were determined by viscosity measurements of the toluene solutions at 25°C, with an intrinsic viscosity-molecular weight relationship of $[\eta]=1.15\times10^{-4}\cdot M^{0.66}$.[1] The molecular weights of the fractions used for the determination of the theta temperature were 141.7×10^4, 89.0×10^4, 52.5×10^4, and 23.3×10^4, while those of the fractions used for the viscosity measurements were 72.0×10^4, 59.9×10^4, 47.6×10^4, 35.8×10^4, 25.9×10^4, and 14.3×10^4.

The benzene and cyclohexane used as the solvents were purified by the methods described in a previous paper.[2] The critical consolute solvent mixtures were prepared by mixing benzene and cyclohexane by volume at 25°C; the ratios of benzene *vs.* cyclohexane were (A) 1/2.2, (B) 1/2.4,

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[1] K. Matsumura, *Polymer J.*, **1**, 322 (1970).

[2] K. Matsumura, M. Fukaya, and K. Mizuno, This Bulletin, **43**, 1881 (1970).

and (C) 1/2.6.

Measurements. The methods used for the determination of the temperature and for the measurements of the viscosities of the solutions were the same as those in a previous paper.[2]

Results and Discussion

The Determination of the Theta Temperatures. An example of the measurements of the precipitation temperatures, T_p, and the determination of the theta temperature for poly-*o*-chlorostyrene in one critical consolute solvent mixture (A) is shown in Fig. 1. After the same procedures as that shown in Fig. 1, the theta temperatures were determined to be as follows: 31±2°C in solvent (A), 38±2°C in (B), and 45±3°C in (C).

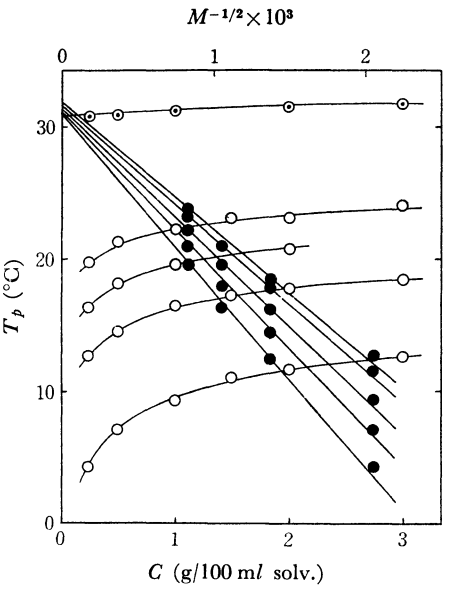

Fig. 1. The determination of the theta temperature for poly-*o*-chlorostyrene in solvent (A): ○, T_p-C for each fraction; ⊙, T_p-C for $M=\infty$; ●, T_p-$M^{-1/2}$ for several concentrations corresponding to those of ⊙.

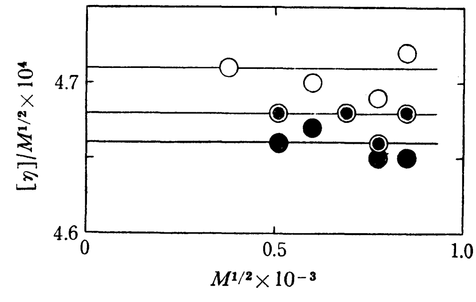

Fig. 2. Viscosity plots for poly-*o*-chlorostyrene in the critical consolute solvents: ○ (31°C), ⊙ (38°C), ● (45°C).

Viscosity. The intrinsic viscosity, $[\eta]$, and the Huggins constant, k', of poly-*o*-chlorostyrene in the critical consolute solvents are summarized in Table 1.

Discussion. As is shown in Fig. 2, the values of $[\eta]/M^{1/2}$, $(=K_\theta)$, were independent of $M^{1/2}$, as is known to be generally true for a theta solution. The K_θ values of the critical consolute solution found from Fig. 2 are shown in Table 2, together with the values of $\{\langle L^2\rangle_0/M\}^{1/2}$, $(=\{K_\theta/\Phi_0\}^{1/3})$, and σ, $(=\{\langle L^2\rangle_0/\langle L^2\rangle_{0f}\}^{1/2})$, calculated from the K_θ values, in which the value of Φ_0, the Flory parameter, was assumed to be 2.55×10^{21}, the same as that found in a previous paper.[1]

The K_θ values are in fair agreement with that of the butanone solution at 25°C (the theta solution), 4.60×10^{-4};[1] they are smaller the higher the temperature, much as with the temperature dependencies of K_θ for polystyrene and for poly-*p*-chlorostyrene.[2,3]

It was previously reported that the K_θ value of poly-*o*-chlorostyrene in butanone at 25°C is fairly small compared with that found from the viscosity plot of the toluene solution, and that this difference in K_θ values proves that the solvent effect may depend on the fact that the butanone solution gives a lower consolute temperature.

However, the results in this paper show no difference between the K_θ value of poly-*o*-chlorostyrene in a theta

TABLE 1. THE EXPERIMENTAL RESULTS OF THE VISCOSITY MEASUREMENTS FOR POLY-*o*-CHLOROSTYRENE IN THE CRITICAL CONSOLUTE SOLVENT MIXTURES

Fraction	$M\times 10^{-4}$	$[\eta]$ (dl/g), solvent			k', solvent		
		(A) 31°C	(B) 38°C	(C) 45°C	(A) 31°C	(B) 38°C	(C) 45°C
2	72.0	0.401	0.397	0.395	0.45	0.46	0.42
3	59.9	0.363	0.361	0.360	0.45	0.45	0.42
4	47.6	—	0.323	—	—	0.46	—
5	35.8	0.281	—	0.279	0.53	—	0.51
6	25.9	—	0.238	0.237	—	0.47	0.50
7	14.3	0.178	—	—	0.56	—	—

TABLE 2. THE K_θ VALUES AND THE σ VALUES OF POLY-*o*-CHLOROSTYRENE

Solvent	Temp. (°C)	$K_\theta\times 10^4$	$\{\langle L^2\rangle_0/M\}^{1/2}$ (Å)	σ
(A)	31	4.71	0.569	2.17
(B)	38	4.68	0.568	2.17
(C)	45	4.66	0.567	2.16

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3) K. Kubo, K. Ogino, and T. Nakagawa, *Nippon Kagaku Zasshi*, **88**, 1254 (1967).

solvent, which gives a lower consolute temperature, and that in a solvent, which gives a higher one. This suggests that the large value of K_θ in the toluene solution may not be caused by the solvent effect but, rather, by the downwards curvature of the viscosity plot, as was shown in a previous paper.[1] Therefore, there is difficulty in finding the value of K_θ from the viscosity plot of poly-*o*-chlorostyrene in toluene (a good solvent).