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Unperturbed Dimensions of Poly-*p*-chlorostyrene

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The unperturbed dimensions of various polymers have been studied by light-scattering measurements of polymers in a theta solvent, or from results of viscosity measurements in a good solvent by the use of the Kurata-Stockmayer[1] or the Stockmayer-Fixman[2] relation.

In this paper, the temperature dependence of the unperturbed dimensions of poly-*p*-chlorostyrene was obtained by the viscosity measurements of poly-*p*-chlorostyrene in critical consolute solvents, which were mixtures of benzene (solvent) - cyclohexane (nonsolvent) at various ratios of mixing.

Experimental

Polymer. Poly-*p*-chlorostyrene was prepared by heating *p*-chlorostyrene in a sealed tube at 95°C without any initiator. A benzene solution of the polymer was fractionated at 30°C by successive precipitation with methanol. The obtained fractions were redissolved in benzene, reprecipitated with methanol, and dried under reduced pressure. Five fractions were used for the measurements.

The molecular weights of these fractions were determined by viscosity measurements of the toluene solutions at 30°C with an intrinsic viscosity - molecular weight relationship of $[\eta]=1.28\times10^{-4}\cdot M^{0.64}$.[3] The molecular weights were 100.9×10^4 (fraction 1-1), 76.8×10^4 (1-3), 49.9×10^4 (2-2), 41.2×10^4 (3), and 26.7×10^4 (4) respectively.

Solvent. The benzene and the toluene was washed successively with sulfuric acid, water, a solution of sodium hydroxide, and water, and refluxed with metallic sodium and distilled. Cyclohexane was washed with a mixture of sulfuric acid and nitric acid, and then treated in the same way as benzene.

The critical consolute solvent mixtures were prepared by mixing benzene and cyclohexane by volumes at 25°C.

Measurements. For the determination of the theta temperature, the method of Mandelkern and Flory[4] was used.

For the measurements of the viscosity of the solutions, the viscometer described in a preceding paper[5] was used.

Results and Discussion

The Determination of the Theta Temperature. The ratios of benzene *vs.* cyclohexane used for the measurements were (A) 1.8/1, (B) 1.4/1, and (C) 1.1/1 at 25°C. By the method of Mandelkern and Flory, the theta temperatures for poly-*p*-chlorostyrene in the above critical consolute solvent mixtures, (A), (B), and (C), were determined to be 28±2°C, 43±2°C, and 60±3°C respectively. An example of the measurements of the precipitation temperature and the determination of the theta temperature for poly-*p*-chlorostyrene in one critical consolute solvent mixture, (A), is shown in Fig. 1.

Viscosity. The results of the viscosity measurements of poly-*p*-chlorostyrene in the critical consolute solvents and in toluene are shown in Table 1. As is shown in Fig. 2, from the data of the toluene solutions the following relations were obtained: $[\eta]=1.72\times10^{-4}\cdot M^{0.62}$ (d*l*/g) (28°C), $[\eta]=1.35\times10^{-4}\cdot M^{0.64}$ (43°C), and $[\eta]=1.07\times10^{-4}\cdot M^{0.66}$ (60°C).

Discussion. The relations between $[\eta]/M^{1/2}$ and $M^{1/2}$ at each temperature, as obtained by the

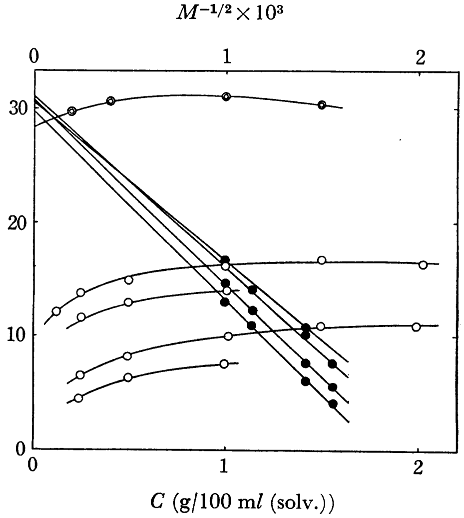

Fig. 1. The determination of the theta temperature for poly-*p*-chlorostyrene in solvent (A): open circle, T_p-C for each fraction; double circle, T_p-C for $M=\infty$; closed circle, T_p-$M^{-1/2}$ for several concentrations.

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Table 1. The experimental results of the viscosity measurements for poly-*p*-chlorostyrene in the critical consolute solvent mixtures and in toluene

Fraction	$M\times 10^{-4}$	$[\eta]_\theta$(d*l*/g) solvent (A) 28°C	(B) 43°C	(C) 60°C	$[\eta]$ (d*l*/g) solvent (toluene) 28°C	43°C	60°C
1-1	100.9	0.649	0.640	0.629	0.915	0.951	0.986
1-3	76.8	0.565	0.555	0.530	0.760	0.782	0.808
2-2	49.9	0.461	0.448	—	0.584	0.597	0.612
3	41.2	—	—	0.398	—	—	—
4	26.7	0.334	0.332	0.325	0.398	0.404	0.409

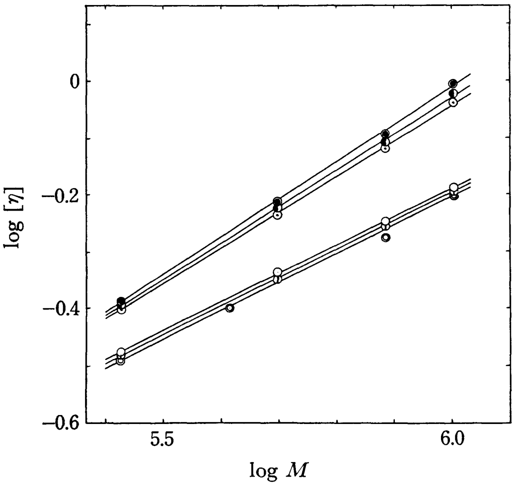

Fig. 2. Molecular weight dependencies of the intrinsic viscosities for poly-*p*-chlorostyrene: critical consolute solution, ○ (28°C), ⦶ (43°C), ◎ (60°C); toluene solution, ⊙ (28°C), ◐ (43°C), ◉ (60°C).

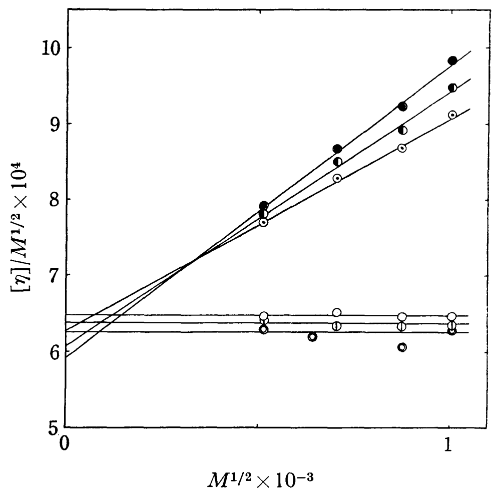

Fig. 3. Viscosity plots for poly-*p*-chlorostyrene: critical consolute solution, ○ (28°C), ⦶ (43°C), ◎ (60°C); toluene solution, ⊙ (28°C), ◐ (43°C), ◉ (60°C).

Table 2. The K_θ values and the σ values of poly-*p*- chlorostyrene: the results in this paper (upper table), and in the reference (lower table)

Solvent	Temp. (°C)	$K_\theta\times 10^4$	$\left\{\frac{\langle L^2\rangle_0}{M}\right\}^{1/2}$ (Å)	σ	Ref.
(A) (θ)	28	6.48	0.609	2.32	
(B) (θ)	43	6.37	0.605	2.31	
(C) (θ)	60	6.25	0.602	2.30	
Toluene	28	6.26	0.602	2.30	
	43	6.09	0.596	2.28	
	60	5.93	0.591	2.26	
(θ)	13.4	5.88	0.590	2.26	6)
(θ)	58.9	5.44	0.574	2.20	
	30	5.67	0.585	2.23	3)
	30	5.2	0.565	2.16	7)
	30	6.1	0.600	2.30	8)

Stockmayer-Fixman equation,[2] are shown in Fig. 3. The determined K_θ values are shown in Table 2. Here $K_\theta=[\eta]_\theta/M^{1/2}$ and $[\eta]_\theta$ is the intrinsic viscosity in the theta state. The K_θ values of the toluene solutions are in fairly good agreement with those of the critical consolute solutions at each temperature. The temperature dependence of the K_θ values of poly-*p*-chlorostyrene in the critical consolute solvents gives a linear relation, in which the K_θ values is smaller the higher the temperature, similar as with the temperature dependence of K_θ for polystyrene and for poly-*p*-chlorostyrene.[6]

The K_θ values obtained from the viscosity measurements for the critical consolute solutions are slightly larger than those values by many authors.[3,6-8] From the results for polystyrene in the theta solvents, cyclohexane and diethylmalonate, at about 35°C, it can be seen that the K_θ values of a polymer in different solvents show a fairly large disagreement at the same temperature.[9] Therefore, it can be considered that the difference between the K_θ values of poly-*p*-chlorostyrene in the theta solvents in this paper and those in the previous paper[6] is a result of the solvent effect.

On the basis of the K_θ values, the values of $\{<L^2>_0/M\}^{1/2}=(K_\theta/\Phi_0)^{1/3}$ ($\Phi_0=2.87\times10^{21}$) and $\sigma=\{<L^2>_0/<L^2>_{of}\}^{1/2}$, were found; here $<L^2>_0$ is the unperturbed dimension, and $<L^2>_{of}$ is the mean-square end-to-end distance of the polymer chain for the free rotation model. The results are shown in Table 2. The obtained σ values are slightly larger than those obtained by other authors. However, as the difference is very small, it is considered our results confirm the conclusion by many authors,[8,10] that the effect of the chlorine atom on the unperturbed dimension of poly-*p*-chlorostyrene is not very large.

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