

Solution Behaviour of Poly(*o*-Chlorostyrene)

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ABSTRACT: Butanone was used as a theta solvent for poly(*o*-chlorostyrene) at 25°C as determined by the measurements of the precipitation temperatures of solutions. Based on lightscattering and viscosity measurements, the molecular weight dependencies of the intrinsic viscosity, the second virial coefficient and the end-to-end distance of the polymer were determined as follows: $[\eta]$, $4.60 \times 10^{-4} M_w^{0.50}$ (dl/g) in butanone, $[\eta]$, $1.15 \times 10^{-4} M_w^{0.66}$ in toluene; A_2 , $25.1 \times 10^{-4} M_w^{-0.19}$ (mol-cc/g²) in toluene; $\langle L^2 \rangle^{1/2}$, $0.56_8 \times M_w^{0.50}$ (Å) in butanone, $\langle L^2 \rangle^{1/2}$, $0.30_1 \times M_w^{0.58}$ in toluene.

The K_θ value for the butanone solution is smaller than that previously obtained for the toluene solution with the aid of the Stockmayer-Fixman relation. This difference is considered to be the effect of the solvent on the polymer dimension.

A viscosity plot of the Stockmayer-Fixman type in toluene solutions gives a downwards curvature instead of a straight line over the whole range of the polymer molecular weight.

The σ value, 2.15, found from the unperturbed dimension of poly(*o*-chlorostyrene) in butanone is comparable to that of poly(*p*-chlorostyrene).

KEY WORDS Poly(*o*-Chlorostyrene) / Butanone / Theta Solution / Toluene / Viscosity Plot / Unperturbed Dimension /

The unperturbed dimension of a polymer is obtained sometimes from the viscosity plots of the polymer in a good solvent by the Kurata-Stockmayer¹ or by the Stockmayer-Fixman² equation. But the measurements for the solution under theta conditions are also necessary, because the obtained results give a direct conclusion without any hypothesis.

In this paper, the solution properties, especially on the unperturbed dimension, of poly(*o*-chlorostyrene) in butanone (a theta solvent at 25°C) were investigated by light-scattering and viscosity measurements and were compared with the results obtained in a toluene solution.

EXPERIMENTAL

Material

The methods used for the synthesis of *o*-chlorostyrene and the preparation of poly(*o*-chlorostyrene) are the same as in a previous paper.³ The fractionation of polymer in a benzene-methanol mixture produces ten fractions from 19 g of polymer.

Butanone and toluene, used as solvents, were

purified by the methods described in a previous paper.⁴

Determination of the Precipitation Temperature

For the measurements of the precipitation temperatures, T_p , six fractions of poly(*o*-chlorostyrene) were used. The molecular weights of these fractions, determined by the light-scattering measurements at 30°C, were 100.4×10^4 , 84.2×10^4 , 61.6×10^4 , 48.4×10^4 , 40.6×10^4 , and 22.5×10^4 . T_p were determined for these fractions in butanone by the observation of the temperatures at which the solution became turbid (that is, when phase separation occurred) on slow heating, and also of the temperatures at which the turbidity of the solutions vanished (that is, when phase coalescence occurred) on slow cooling. The difference between these two temperatures was about 0.1-0.2°C.

Measurements

To measure the light-scattering of the solutions a Shimadzu photometer was used. The increment of the refractive index of the solution with concentration, dn/dc , was measured with a Shimadzu interferometer. The measurements were performed at 25°C with the wavelength 436 m μ

and 546 m μ .

For viscosity measurements of the solutions a modified Ubbelohde viscometer was used. At 25°C the flow time of toluene was 287.6 sec in this viscometer.

RESULTS

Determination of the Theta Temperature

The relation between the observed precipitation temperature, T_p , and the concentration, c , of each fraction of poly(*o*-chlorostyrene) in butanone is shown in Figure 1. The concentration of polymer was indicated by the gram per 100 ml of butanone at 25°C. For the determination of theta temperature, θ , from the critical consolute temperatures, T_c , the equation, $T_c^{-1} = \theta^{-1} (1 - bM^{-1/2})$, was used. Figure 2 shows the relation T_c^{-1} vs. $M^{-1/2}$. From the intercept of the curve in Figure 2, $\theta = 298 \pm 2^\circ\text{K}$ is obtained.

Light-Scattering and Viscosity Measurements

From the result of the light-scattering measurements for each fraction, the weight-average molecular weight, M_w , the second virial coefficient, A_2 , and the root-mean-square end-to-end distance of the polymer chain, $\langle L^2 \rangle^{1/2}$, were obtained according to a Zimm plot. The observed values of dn/dc (ml/g) at 25°C were as follows: butanone solution, 0.204 (436 m μ) and 0.191 (546 m μ); toluene solution, 0.110 (436 m μ) and 0.106

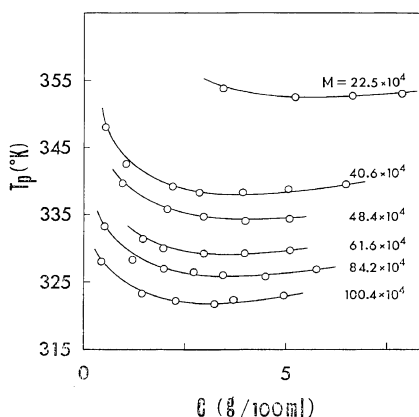


Figure 1. The phase diagram for poly(*o*-chlorostyrene) in butanone. The weight-average molecular weights of fractions are 100.4×10^4 , 84.2×10^4 , 61.6×10^4 , 48.4×10^4 , 40.6×10^4 , and 22.5×10^4 .

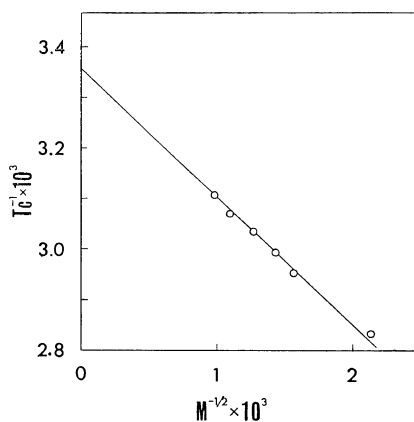


Figure 2. A plot of $T_c^{-1} - M^{-1/2}$ for poly(*o*-chlorostyrene) in butanone).

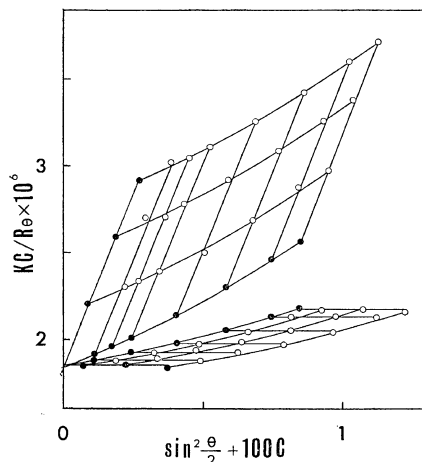


Figure 3. Zimm plot for poly(*o*-chlorostyrene) fractions 2-1 in butanone and in toluene, for the wavelength 436 m μ .

(546 m μ). The Zimm plot for the fraction 2-1 of poly(*o*-chlorostyrene) is shown in Figure 3.

The results of the light-scattering measurements are shown in Tables I and II, together with the results of the viscosity measurements (intrinsic viscosity, $[\eta]$, and Huggins constant, k').

The molecular-weight dependencies of A_2 , $\langle L^2 \rangle^{1/2}$ and $[\eta]$ respectively, are examined by the log-log plots shown in Figures 4, 5 and 6. The relations found by the least-squares method are as follows:

$$A_2, 25.1 \times 10^{-4} \times M_w^{-0.19} \text{ (mol}\cdot\text{cc/g}^2\text{)} \quad \text{in toluene,}$$

$\langle L^2 \rangle^{1/2}$, $0.56_3 \times M_w^{0.50}$ (Å) in butanone;
 $\langle L^2 \rangle^{1/2}$, $0.30_1 \times M_w^{0.58}$ in toluene;
 $[\eta]$, $4.60 \times 10^{-4} \times M_w^{0.50}$ (dl/g) in butanone;
 $[\eta]$, $1.15 \times 10^{-4} \times M_w^{0.66}$ in toluene.

Table I. The experimental results of light-scattering and viscosity measurements at 25°C for poly(*o*-chlorostyrene) in butanone

Fraction	$M_w \times 10^{-4}$	$\langle L^2 \rangle_0^{1/2}$ Å	$[\eta]$ (dl/g)	k'	$\phi_0 \times 10^{-21}$
1-1	100.0	563	0.447	0.55	2.50
1-2	83.0	516	0.417	0.51	2.52
2-1	53.5	410	0.335	0.50	2.60
2-2	40.4	360	0.291	0.50	2.52
3	21.9	263	0.215	0.53	2.59

Table II. The experimental results of light-scattering and viscosity measurements at 25°C poly(*o*-chlorostyrene) in toluene

Fraction	$M_w \times 10^{-4}$	$\langle L^2 \rangle^{1/2}$ (Å)	$A_2 \times 10^4$ ($\frac{\text{mol} \cdot \text{cc}}{\text{g}^2}$)	$[\eta]$ (dl/g)	k'	$\phi \times 10^{-21}$
1-1	100.5	912	1.78	1.038	0.33	1.38
1-2	84.0	824	1.90	0.930	0.34	1.40
2-1	54.9	640	2.05	0.709	0.34	1.48
2-2	40.5	540	2.17	0.580	0.32	1.49
3	21.7	375	2.33	0.379	0.33	1.56
5	14.2	294	2.70	0.288	0.30	1.61

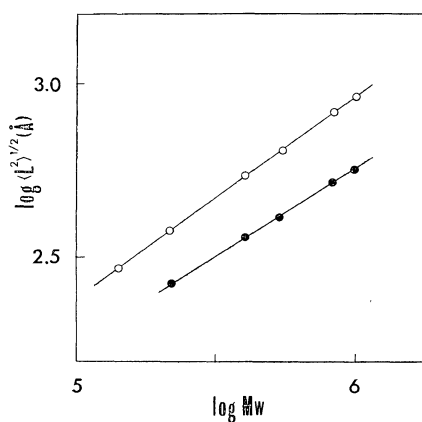


Figure 4. Molecular weight dependencies of the end-to-end distances for poly(*o*-chlorostyrene) at 25°C: open circle, toluene solution; closed circle, butanone solution.

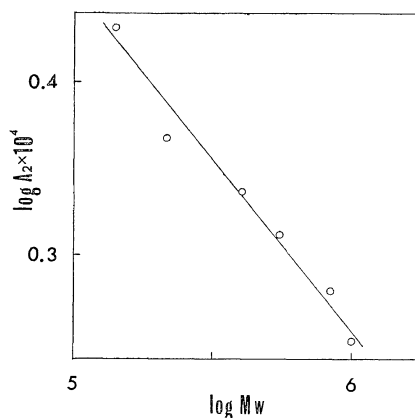


Figure 5. Molecular weight dependence of the second virial coefficient for poly(*o*-chlorostyrene) in toluene at 25°C.

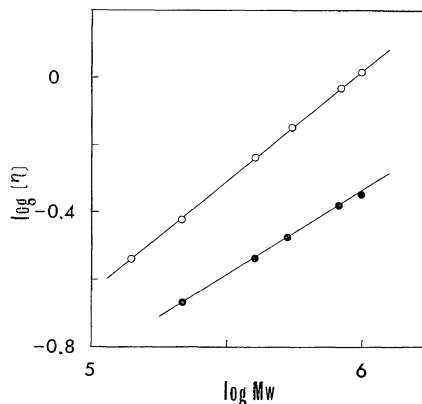


Figure 6. Molecular weight dependencies of the intrinsic viscosities for poly(*o*-chlorostyrene) at 25°C: open circle, toluene solution; closed circle, butanone solution.

DISCUSSION

The relations of M_w vs. $\langle L^2 \rangle^{1/2}$, A_2 and $[\eta]$ respectively for poly(*o*-chlorostyrene) in toluene at 25°C are not so different from the relations of other polystyrene derivatives. If the values of $\langle L^2 \rangle^{1/2}$, A_2 and $[\eta]$ for the toluene solution of poly(*o*-chlorostyrene) in this paper are compared with those in a previous paper at 35°C and 30°, the former values are found to be smaller than those of the latter.

For poly(*o*-chlorostyrene) in butanone at 25°C, the results that $\langle L^2 \rangle^{1/2}$ and $[\eta]$ are proportional

to $M^{1/2}$, and that the A_2 values are zero, show that the solution is a theta solution.

As shown in Figure 1, the butanone solution of poly(*o*-chlorostyrene) exhibits a lower consolute temperature, that is, the solubility of polymer in solvent increases at lower temperatures. Such behaviour of the solution is generally ascribed to some interactions between polymer and solvent that are more effective at lower temperatures than at higher temperatures. However, at present, the author cannot precisely explain the nature of the above interactions.

The value of K_θ , namely $[\eta]_\theta/M^{1/2}$, of poly(*o*-chlorostyrene) was found with the aid of the Stockmayer-Fixman relation, where $[\eta]_\theta$ is the intrinsic viscosity at the theta state. Figure 7

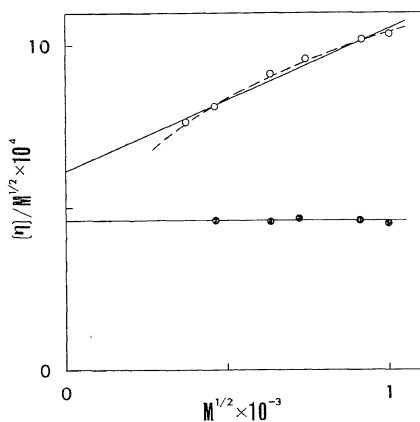


Figure 7. The viscosity plots for poly(*o*-chlorostyrene) at 25°C: open circle, toluene solution; closed circle, butanone solution; broken curve, the calculated result from the viscosity-molecular weight relationship of toluene solution.

shows the relations of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ of poly(*o*-chlorostyrene) in toluene and in butanone at 25°C. For the butanone solution, the $[\eta]/M^{1/2}$ values are independent of $M^{1/2}$, as known in general. The K_θ values obtained were 6.14×10^{-4} in toluene and 4.60×10^{-4} in butanone, respectively; the least-squares method was used for the extrapolation of the viscosity plot by a straight line to obtain the K_θ value. These K_θ values are fairly different from each other.

Many reports show that the K_θ values obtained from the viscosity plots for a polymer in good solvents are not so different from those obtained

in theta solvents. On the other hand, it has been reported that the K_θ values in theta solutions are sometimes different from each other at about the same temperature. Therefore, it is considered that the difference between the K_θ value found in the toluene solution and that found in the butanone solution of poly(*o*-chlorostyrene) demonstrates the above-mentioned solvent effect. However, most of the theta solvent experiments in literature show the upper consolute temperatures in phase diagrams, but the case of butanone as indicated in this paper has not been reported. Accordingly, the cause of the difference in K_θ values for poly(*o*-chlorostyrene) seems obscure, since the mechanism of the interaction among the components in the solution at theta state is not clear.

The K_θ value found in the toluene solution, 6.14×10^{-4} , of poly(*o*-chlorostyrene) in this paper is smaller than that shown in a previous paper, 7.25×10^{-4} .³ The fact that the K_θ values in toluene solutions are different from each other, may be explained in terms of the result that the viscosity data in the previous paper scatter, while those in this paper show a curve over the whole range of molecular weights of polymer fractions.

The relation of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ derived from the Mark-Houwink-Sakurada equation $[\eta] = KM^\alpha$ is a parabola which passes the origin of coordinates mathematically. A broken curve in Figure 7 shows the parabola derived from the observed relation ($[\eta] = 1.15 \times 10^{-4} M^{0.66}$) for poly(*o*-chlorostyrene) in toluene at 25°C. The viscosity plot for toluene solutions is consistent with this broken curve. In this case, it may be expected that the K_θ value found from the viscosity plot differs when the range of molecular weights of polymer fractions used for the experiments changes. For example, the extrapolation by a straight line on the four points at a higher molecular weight range in Figure 7 gives the K_θ value of 7.02×10^{-4} . This value fairly agrees with that in a previous paper. From this fact, it is suggested that the measurements for polymer fractions of lower molecular weight are important.

Based on light-scattering measurements for the butanone solution of poly(*o*-chlorostyrene) at 25°C, we find that the value of $\sigma (= \{\langle L^2 \rangle_0 / \langle L^2 \rangle_{or}\}^{1/2})$

equals 2.15, where $\langle L^2 \rangle_{of}$ is the mean-square end-to-end distance of a polymer chain corresponding to the fixed valence angle (109.5° for carbon atoms) and to the completely free internal rotation; $\{\langle L^2 \rangle_{of}/M\}^{1/2}$ is calculated to be 0.262 (Å) for poly-chlorostyrene. This σ value, 2.15, is about the same as those of poly(*p*-chlorostyrene), $\sigma = 2.15$,⁶ poly(*o*-methylstyrene), 2.27,⁷ and polystyrene, 2.22.¹

The author reported in a preceding paper⁷ that the difference between the σ value for poly(*o*-chlorostyrene) as reported in a former paper, 2.42,³ and the σ value for poly(*o*-methylstyrene), 2.27, suggests that the electrostatic repulsion between polar side groups of poly(*o*-chlorostyrene) affects the σ value.

But, from the findings in this paper on the unperturbed dimension of poly(*o*-chlorostyrene), it is concluded that the steric repulsion between side groups is more important than the electrostatic repulsion between polar side groups. This conclusion is similar to that for the unperturbed chain of poly(*p*-chlorostyrene).^{1,6}

As for the unperturbed dimension of poly(*o*-chlorostyrene), further discussion should be avoided

because few examples are known, in which the values of K_θ for a polymer in various theta solvents at the same temperature are different from each other. It is considered that for polymer in other theta solvents more experiments are needed.

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