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The Solution Properties of Poly-*o*-methylstyrene

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The solution properties of poly-*o*-methylstyrene in toluene were measured by the light-scattering and viscosity methods, and the results were compared with those obtained from poly-*o*-chlorostyrene and other polystyrene derivatives. The dependencies of the intrinsic viscosity, the second virial coefficient, and the end-to-end distance of the polymer chain on the molecular weight are as follows:

$$[\eta] = 9.22 \times 10^{-5}\cdot M_w^{0.72}\ (\mathrm{d}l/\mathrm{g}),\quad A_2 = 3.89 \times 10^{-2}\cdot M_w^{-0.38}\ (\mathrm{mol\cdot cc/g^2})$$
$$\text{and } \langle L^2\rangle^{1/2} = 0.197 \times M_w^{0.62}\ (\text{Å}).$$

It was made clear that the unperturbed dimension of poly-*o*-methylstyrene was larger than that of poly-*p*-methylstyrene, and that the cause of this difference is the large steric repulsion between the side groups of the former. Moreover, the unperturbed dimension of poly-*o*-methylstyrene was smaller than that of poly-*o*-chlorostyrene. From these results, it is considered that the large extension of poly-*o*-chlorostyrene was affected by the electrostatic repulsion between the side groups.

Many authors have reported on the solution properties of polystyrene and its derivatives. These polystyrene derivatives are mainly *p*-substituted polymers, and the results of the experiments show that the unperturbed dimension of the polymer-chain skeleton is affected not by the electrostatic interaction between the substituents placed on the *p*-position of polystyrene, but by the volume of the side group, the *p*-substituted phenyl group, of the polymer.

In a preceeding paper[1] the present author reported his experimental results on poly-*o*-chlorostyrene, which showed that the unperturbed dimension is larger than that of poly-*p*-chlorostyrene. However, the reason for the difference between these two polymers was not made clear.

In this report, by means of light-scattering and viscosity measurements of the poly-*o*-methylstyrene solution, the effect of the substituent on the polymer-chain dimensions are compared with the findings for poly-*o*-chlorostyrene.

Experimental

Sample. The poly-*o*-methylstyrene was prepared from *o*-tolylmethylcarbinol, which had itself been obtained by the Grignard reaction of *o*-bromotoluene and acetaldehyde, by dehydration with potassium bisulfate; bp 34—36°C/4 mmHg.

The monomer was polymerized by heating it in a sealed tube at 90°C for 150 hr without any initiator. The conversion rate was about 60%. The polymer was a jelly-like substance. The polymer was dissolved in hot benzene (*ca.* 20 g/*l*), and the solution was fractionated at 30°C by subsequent precipitation with methanol. Twenty fractions were obtained. They were redissolved in benzene, reprecipitated with methanol, and dried under reduced pressure.

The toluene, used as the solvent, was purified by the method described in a previous paper.[1]

It seemed that poly-*o*-methylstyrene would dissolve in toluene at room temperature. However, the flow time of the solution in the viscometer decreased with the time of heating at 30°C, showing a constant value only after about 18 hr, as is shown in Fig. 1, in which the sample used for the test of the flow time was the fraction 1-1 and the concentration of the solution was about 0.5 g/d*l*. Therefore, the toluene solution used for the measurements were prepared by heating it at 35—40°C for about 20 hr.

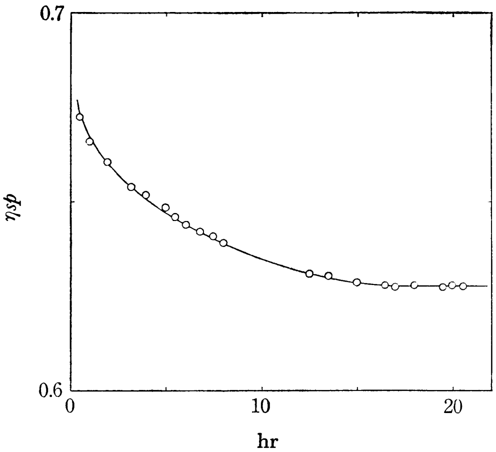

Fig. 1. Relation between the specific viscosity and time of heating at 30°C, for poly-*o*-methylstyrene (Frac. 1-1) in toluene (0.5 g/d*l*).

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[1] K. Matsumura, *Makromol. Chem.*, **124**, 204 (1969).

TABLE 1. THE EXPERIMENTAL RESULTS OF THE LIGHT-SCATTERING AND VISCOSITY MEASUREMENTS FOR POLY-*o*-METHYLSTYRENE IN TOLUENE AT 30°C

Fraction	$M_w \times 10^{-4}$	$A_2 \times 10^{-4}$ $\left(\frac{\text{mol ml}}{g^2}\right)$	$\langle L^2\rangle^{1/2}$ (Å)	$[\eta]$ $\left(\frac{\text{d}l}{\text{g}}\right)$	k'	$\phi \times 10^{-21}$
1-2	43.0	2.64	616	1.047	0.31	1.9
1-3	42.2	2.90	613	1.023	0.32	1.9
2-1	32.0	3.17	494	0.867	0.34	2.3
2-2	22.2	3.85	416	0.651	0.31	2.0
3-2	17.6	3.86	355	0.564	0.36	2.2
4	14.6	4.25	311	0.476	0.38	2.3
5	10.2	4.80	251	0.368	0.38	2.4

Measurements. A Shimadzu photometer was used for the measurement of the light-scattering of the solutions. The measurements were carried out at 30°C by the use of the 436 mμ and 546 mμ of wavelengths and covering the angular range 40—140°. The increments of the refractive index of the solution with the concentration, dn/dc, were measured at 30°C with the wavelengths of 436 mμ and 546 mμ.

For the viscosity measurements of the solutions at 30°C, a modified Ubbelohde viscometer was used. At 30°C the flow time of toluene was 270.1 sec in this viscometer.

Results and Discussion

Results. By means of the light-scattering measurements, 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 the ordinary method by means of a Zimm plot for each fraction. The observed values of dn/dc were 0.120 ml/g for the 436 mμ wavelength and 0.116 ml/g for 546 mμ. An example of the Zimm plot, that for the fraction 1—3 of poly-*o*-methylstyrene in toluene at 30°C for 436 mμ, is shown in Fig. 2.

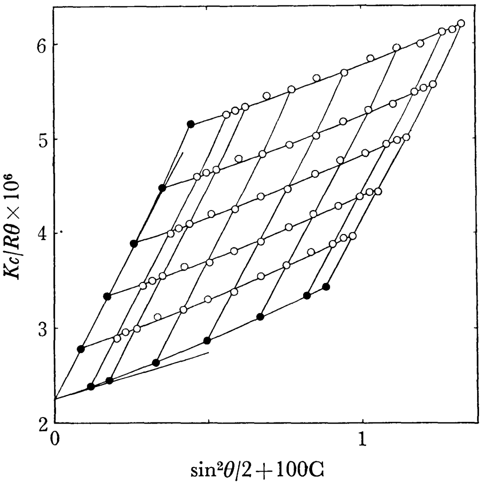

Fig. 2. Zimm plot for poly-*o*-methylstyrene 1—3 in toluene at 30°C for 436 mμ.

Through the viscosity measurements, the intrinsic viscosity, $[\eta]$, and the Huggins constant, k', shown in Fig. 3 are obtained.

These results are shown in Table 1.

The molecular-weight dependencies of $[\eta]$, A_2, and $\langle L^2\rangle^{1/2}$ are obtained by means of the log-log relations between M_w and these values; they are shown in Figs. 4, 5, and 6 respectively. By the least-squares method, these relations are found to be as follows:

$$[\eta] = 9.22 \times 10^{-5} \cdot M_w^{0.72} \ (\text{d}l/\text{g}),$$
$$A_2 = 3.89 \times 10^{-2} \cdot M_w^{-0.38} \ (\text{mol} \cdot \text{cc}/\text{g}^2),$$
$$\langle L^2\rangle^{1/2} = 0.197 \times M_w^{0.62} \ (\text{Å}).$$

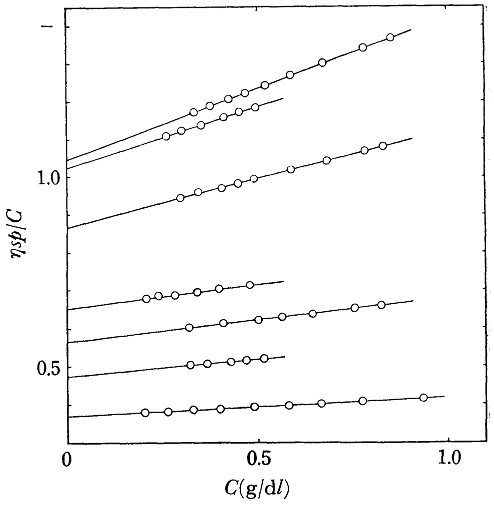

Fig. 3. Relation between reduced viscosity and concentration of poly-*o*-methylstyrene in toluene at 30°C.

TABLE 2. THE EFFECT OF TOLUENE ON THE EXPANSION OF POLY-*o*-METHYLSTYRENE AND POLYCHLOROSTYRENES P_w =4240

Polymer	Temp(°C)	$\{\langle L^2\rangle/\langle L^2\rangle_0\}^{1/2}$
Poly-*o*-methylstyrene	30	1.47
Poly-*o*-chlorostyrene	35	1.41
Poly-*m*-chlorostyrene	35	1.57
Poly-*p*-chlorostyrene	room temp.	1.48

Discussion. The dotted lines in Figs. 4—6 show the relations between M_w and $[\eta]$, A_2, and $\langle L^2\rangle^{1/2}$ of poly-*o*-chlorostyrene, in toluene at 30°C.[1] For the same molecular weight, these poly-*o*-methylstyrene values are larger than those of poly-*o*-chlorostyrene, as the figures show.

To ascertain the effect of the side group of poly-*o*-methylstyrene on the unperturbed dimension of the polymer-chain skeleton, the K_θ value was calculated by the Stockmayer-Fixman relation,[2] where $K_\theta = [\eta]_\theta/M^{1/2} = \Phi_0(\langle L^2\rangle_0/M)^{3/2}$, where $[\eta]_\theta$ is the intrinsic viscosity at the theta state, where $\langle L^2\rangle_0$ is the unperturbed dimension, and where Φ_0 is the Flory parameter at the theta state, for which the value of 2.87×10^{21} is assumed in this paper.

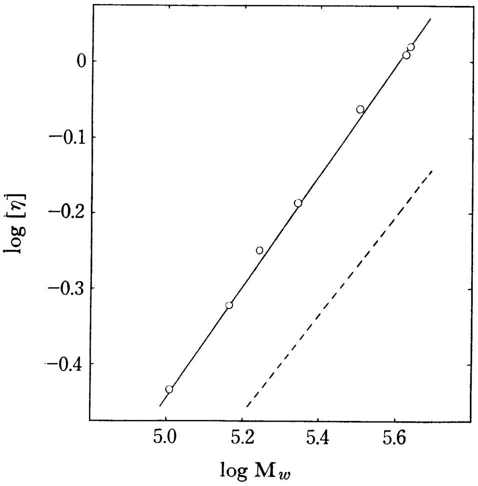

Fig. 4. Molecular weight dependencies of the intrinsic viscosities for poly-*o*-methylstyrene in toluene at 30°C. A dotted line is corresponding to poly-*o*-chlorostyrene.

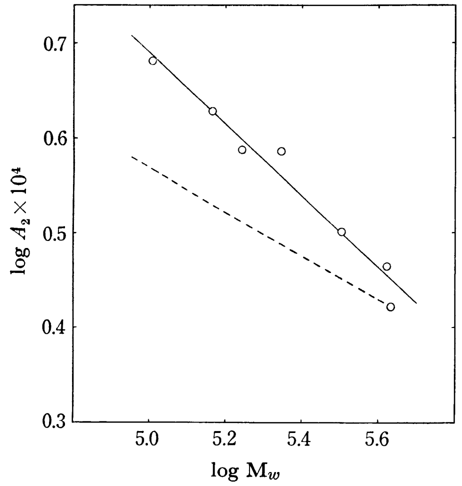

Fig. 5. Molecular weight dependencies of the second virial coefficients for poly-*o*-methylstyrene in toluene at 30°C.

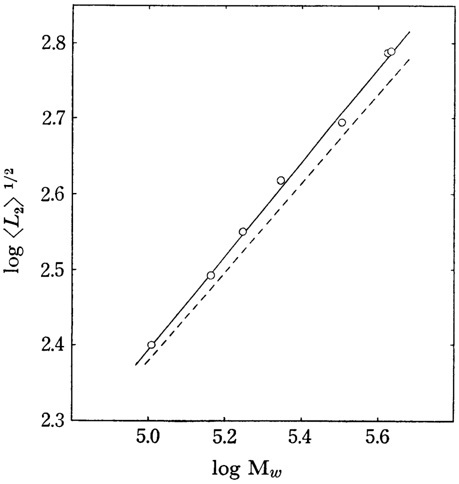

Fig. 6. Molecular weight dependencies of the end-to-end distances for poly-*o*-methylstyrene in toluene at 30°C.

As is shown in Fig. 7, K_θ was found as 7.75×10^{-4} by the least-squares method. By the use of this K_θ value, the value of $\{\langle L^2\rangle_0/M\}^{1/2}$ was calculated as 0.646 (Å), and the value of σ, $\{\langle L^2\rangle_0/\langle L^2\rangle_{0f}\}^{1/2}$, was obtained as 2.27, where $\langle L^2\rangle_{0f}$ is the mean-square end-to-end distance with the fixed valence angle of 109.5° for the carbon atom, but where there is a completely free internal rotation of the polymer-chain skeleton.

This σ value, 2.27, is slightly larger than that of poly-*p*-methylstyrene obtained by osmotic-pressure measurements at 30°C, 2.17.[3] It can, therefore,

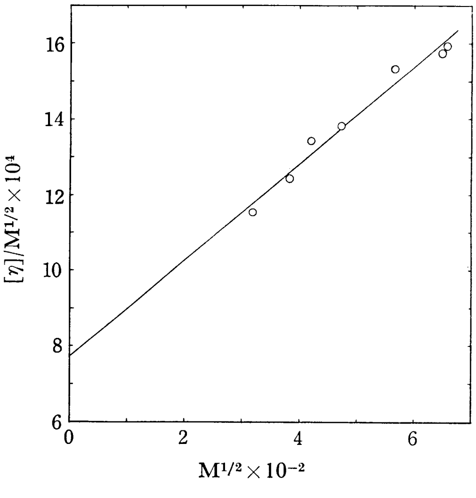

Fig. 7. Viscosity plots for poly-*o*-methylstyrene in toluene at 30°C.

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[2] W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, **1**, 137 (1963).

[3] N. Kuwahara, K. Ogino, A. Kasai, S. Ueno and M. Kaneko, *J. Polym. Sci., Part A*, **3**, 985 (1965).

be considered that the chain of poly-*o*-methylstyrene extends further than that of poly-*p*-methylstyrene. The difference between the σ values of these two polymers is caused by the steric repulsion between the neighboring side groups resulting from the difference in the substituted position of the methyl group on the phenyl group, as the strong electrostatic repulsions between the side groups for these polymers can not be considered.

The σ value, 2.27, for poly-*o*-methylstyrene is smaller than that for poly-*o*-chlorostyrene, 2.42.[1] Therefore, it can be considered that the extension of the poly-*o*-methylstyrene chain is smaller than that of the poly-*o*-chlorostyrene chain.

Kuwahara *et al.* concluded, from a comparison with the σ values for *p*-substituted polystyrene ($\sigma=2.15$ for poly-*p*-chlorostyrene, $\sigma=2.17$ for poly-*p*-methylstyrene, *etc.*) found by osmotic-pressure and viscosity measurements, that the chain conformations of these polymers are not so much affected by the electrostatic interaction between the polar side groups as by the molar volumes of the side groups, the effect of these on the polymer chain being the steric one.[3]

The molar volume of the side group of poly-*p*-methylstyrene and that of the side group of poly-*o*-methylstyrene are equal to that of toluene, 107.3 cc, and the molar volume of the side group of poly-*p*-chlorostyrene and that of the side group of poly-*o*-chlorostyrene are the same as that of chlorobenzene, 102.7 cc. Therefore, according to the findings for poly-*p*-substituted styrene, it can be considered that the difference between the σ value of poly-*o*-methylstyrene and that of poly-*o*-chlorostyrene must be a fairly small one as long as the steric effect of the side group on the chain conformation of these polymers is preferred to the electrostatic repulsion between the side groups. However, when we compare the findings for these polymers the difference between the σ values is fairly large.

From these considerations, it can be considered that the contribution of the electrostatic repulsion between the polar side groups, *o*-$Cl\cdot C_6H_4$, to the extension of the poly-*o*-chlorostyrene chain is fairly large.

The author wishes to thank Professor Akira Kotera for his kindly advice.