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# Solution Properties of Poly-*m*-chlorostyrene

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The solution properties of poly-*m*-chlorostyrene in toluene and butanone were measured by the light-scattering and viscosity methods. The dependencies of the second virial coefficients, the end-to-end distances, and the intrinsic viscosities on the molecular weights were not very different from those of the other polystyrene derivatives. It was made clear that the unperturbed dimension of poly-*m*-chlorostyrene was larger than that of poly-*p*-chlorostyrene, and similar to that of poly-*o*-chlorostyrene. The relationships between poly-*m*-chlorostyrene and solvents (toluene and butanone) were similar to those between polystyrene and poly-*o*-chlorostyrene and the solvents, but the reverse of that between poly-*p*-chlorostyrene and the latter; that is, compared with butanone, toluene was a "good" solvent for poly-*m*-chlorostyrene.

A number of reports on the solution properties of polystyrene and its derivatives, mainly *p*-substituted polymers, have been made.

In this paper, by light-scattering and viscosity measurements of poly-*m*-chlorostyrene solutions, the effects of the substituted position of the chlorine atom on the polymer chain are compared with the findings concerning poly-*o*-chlorostyrene and poly-*p*-chlorostyrene.

## Experimenta

**Sample.** *m-Chlorostyrene.* *m*-Chlorostyene was prepared from *m*-chlorophenylmethylcarbinol, which had been obtained by the Grignard reaction of *m*-chlorobenzaldehyde and methylbromide,[1] by dehydration with potassium bisulfate; bp 56—58°C/7 mmHg.

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[1] L. A. Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944).

*Polymer*. The monomer was polymerized by heating it in a sealed tube at 90°C for 60 hr without any initiator. The conversion rate was about 85%.

The polymer was dissolved in benzene (*ca*. 20 g/*l*), and the solution was fractionated at 35°C by successive precipitation with methanol. Thirteen fractions were obtained from 25 g of the polymer. Each fraction was redissolved in benzene, reprecipitated with methanol, and dried under reduced pressure.

*Solvents*. The toluene was washed successively with sulfuric acid, water, a solution of sodium hydroxide, and water. The purified toluene was refluxed with metallic sodium and distilled; bp 110.4—110.6°C.

The butanone was boiled with potassium permanganate for a day, dried with magnesium sulfate, and distilled; bp 79.2—79.5°C.

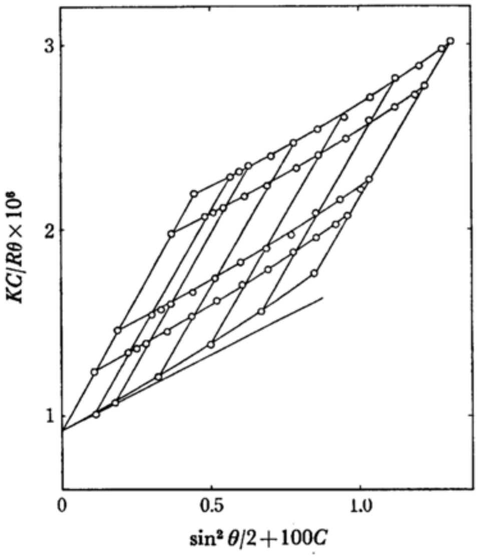
**Measurements.** For the measurements of the light-scattering of the solutions, a Shimadzu photometer was used. The measurements were performed at 35°C with toluene solutions and at 30°C with butanone solutions, by the use of the 436 m$\mu$ wavelength and the angular range covering 40—135°. The increments of the refractive index of the solution with the concentration, d*n*/d*c*, were measured at each temperature with the wavelength of 436 m$\mu$.

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

## Results and Discussion

**Results.** By 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 by the Zimm plot for each fraction according to the ordinary method. An example of the Zimm plot for Fraction 2 of poly-*m*-chlorostyrene in butanone at 30°C is shown in Fig. 1. The observed values of d*n*/d*c* were 0.118 m*l*/g in a toluene solution at 35°C and 0.211 m*l*/g in a butanone solution at 30°C for the wavelength of 436 m$\mu$.

As Figs. 2 and 3 show, the intrinsic viscosity,



Fit. 1. Zimm plot for poly-*m*-chlorostyrene fraction 2 in butanone at 30°C.

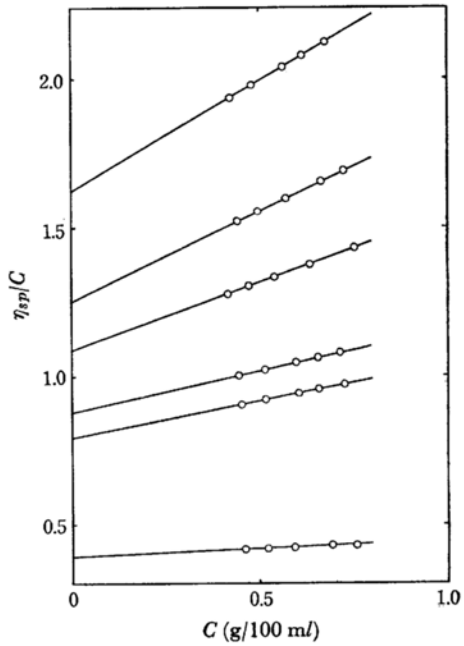


Fig. 2. Relation between reduced viscosity and concentration of poly-*m*-chlorostyrene in toluene at 30°C.

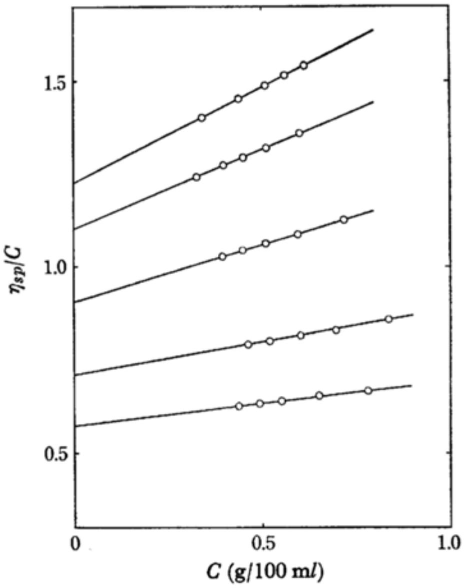


Fig. 3. Relation between reduced viscosity and concentration of poly-*m*-chlorostyrene in butanone at 30°C.

$[\eta]$, and the Huggins constant, $k'$, are obtained through the viscosity measurements.

These results are shown in Tables 1 and 2.

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

$$[\eta] = 1.19\times 10^{-4}\cdot M_w^{0.68}\ (\mathrm{d}l/\mathrm{g}) \quad \text{in toluene at 30°C,}$$

$$= 1.71 \times 10^{-4}\cdot M_w^{0.64} \quad \text{in butanone at 30°C,}$$

$$A_2 = 26.5 \times 10^{-3}\cdot M_w^{-0.33}\ (\mathrm{mol\cdot cc/g^2}) \quad \text{in toluene at 35°C,}$$

$$= 1.54 \times 10^{-3}\cdot M_w^{-0.17} \quad \text{in butanone at 30°C,}$$

$$\langle L^2\rangle^{1/2} = 0.60 \times M_w^{0.54}(\text{Å}) \quad \text{in toluene at 35°C,}$$

$$= 0.31 \times M_w^{0.58} \quad \text{in butanone at 30°C.}$$

TABLE 1. THE EXPERIMENTAL RESULTS OF THE LIGHT-SCATTERING MEASUREMENTS AT 35°C FOR THE WAVELENGTH 436 m$\mu$, AND OF THE VISCOSITY MEASUREMENTS AT 30°C, FOR POLY-*m*-CHLOROSTYRENE IN TOLUENE

| Fraction | $M_w$ $\times 10^{-4}$ | $A_2\times 10^4$ $\left(\frac{\mathrm{mol\cdot cc}}{\mathrm{g^2}}\right)$ | $\langle L^2\rangle^{1/2}$ (Å) | $[\eta]$ (d$l$/g) | $k'$ | $\Phi\times 10^{-21}$ |
|---|---|---|---|---|---|---|
| 2 | 107.5 | 2.42 | 1080 | 1.515 | 0.37 | 1.3 |
| 3-1 | 84.8 | 2.90 | 955 | 1.245 | 0.40 | 1.2 |
| 3-2 | 64.5 | 3.40 | 830 | 1.080 | 0.39 | 1.2 |
| 4-1 | 47.6 | 3.50 | 715 | 0.867 | 0.39 | 1.1 |
| 4-2 | 41.7 | 4.11 | 645 | 0.788 | 0.40 | 1.2 |
| 6 | 14.5 | 5.08 | 370 | 0.387 | 0.36 | 1.1 |

TABLE 2. THE EXPERIMENTAL RESULTS OF THE LIGHT-SCATTERING MEASUREMENTS FOR THE WAVELENGTH 436 m$\mu$, AND OF THE VISCOSITY MEASUREMENTS AT 30°C, FOR POLY-*m*-CHLOROSTYRENE IN BUTANONE

| Fraction | $M_w$ $\times 10^{-4}$ | $A_2\times 10^4$ $\left(\frac{\mathrm{mol\cdot cc}}{\mathrm{g^2}}\right)$ | $\langle L^2\rangle^{1/2}$ (Å) | $[\eta]$ (d$l$/g) | $k'$ | $\Phi\times 10^{-21}$ |
|---|---|---|---|---|---|---|
| 2 | 106.4 | 1.44 | 992 | 1.224 | 0.35 | 1.4 |
| 3-1 | 87.7 | 1.52 | 876 | 1.099 | 0.36 | 1.5 |
| 3-2 | 67.3 | 1.57 | 721 | 0.904 | 0.38 | 1.6 |
| 3-3 | 44.1 | 1.68 | 592 | 0.706 | 0.35 | 1.5 |
| 4-3 | 32.2 | 1.78 | 493 | 0.571 | 0.37 | 1.5 |

**Discussion.** The relations of $M_w$ to $[\eta]$, $A_2$, and $\langle L^2\rangle^{1/2}$ for poly-*m*-chlorostyrene in toluene and butanone are not very different from those for the other polystyrene derivatives.

Stockmayer and Fixman[2] proposed the following equation, by which the unperturbed dimension of the polymer chain could be deduced from the experimental values of the intrinsic viscosities and the molecular weights of the polymer in a good solvent:

$$[\eta]/M^{1/2} = K_\theta + 0.51\mathrm{B}_0\Phi\cdot M^{1/2},$$

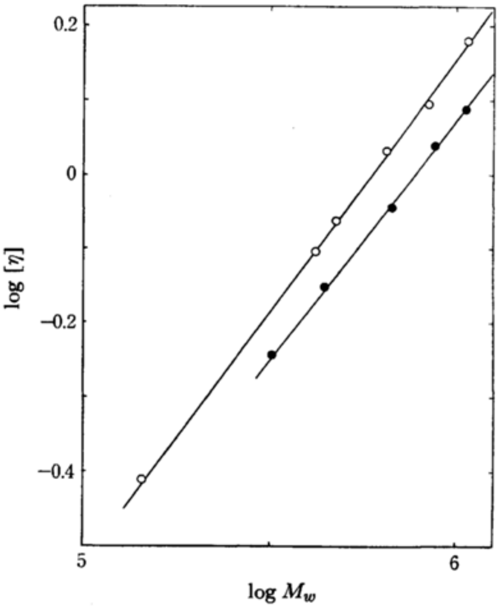


Fig. 4. Molecular weight dependencies of the intrinsic viscosities for poly-*m*-chlorostyrene at 30°C: open circle, toluene solution; colsed circle, butanone solution.

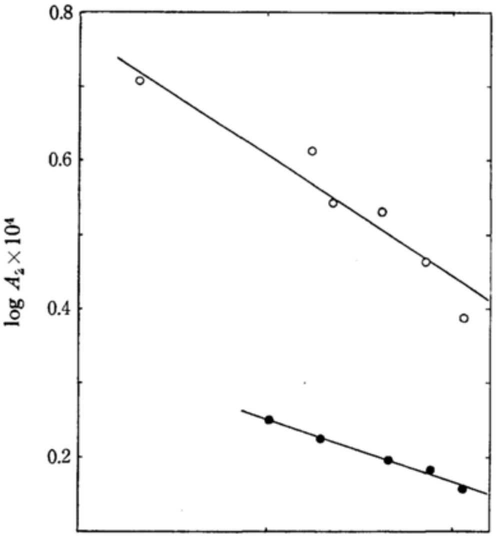


Fig. 5. Molecular weight dependencies of the second virial coefficients for poly-*m*-chlorostyrene: open circule, toluene solution at 35°C; closed circle, butanone solution at 30°C.

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[2] W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, **C1**, 137 (1963).

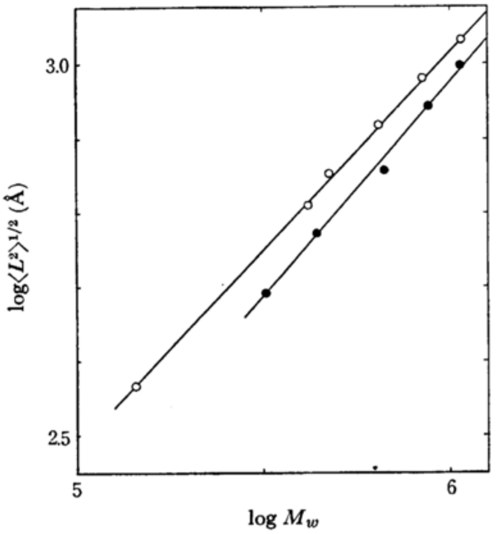

Fig. 6. Molecular weight dependencies of the end-to-end distances for poly-*m*-chlorostyrene: open circle, toluene solution at 35°C; closed circle, butanone solution at 30°C.

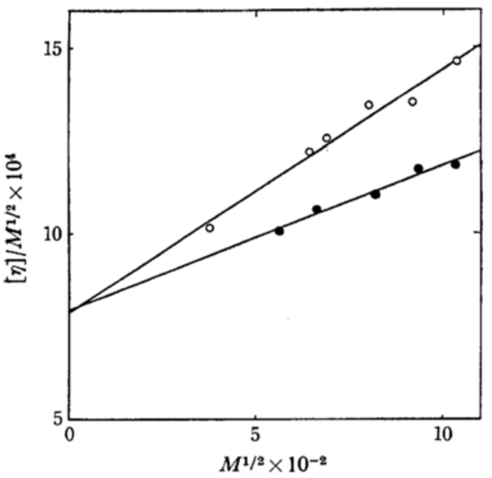

Fig. 7. Viscosity plots for poly-*m*-chlorostyrene in toluene (open circle) and in butanone (closed circle) at 30°C, by the Stockmayer-Fixman equation.

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 of the polymer chain, and where $\Phi_0$ is the Flory parameter at the theta state, for which the value of $2.87\times10^{21}$ is assumed in this paper.

As is shown in Fig. 7, the $K_\theta$ values for poly-*m*-chlorostyrene in toluene and butanone calculated by the above equation are $7.89\times10^{-4}$ and $7.93\times10^{-4}$ respectively; the least-squares method was used for the extrapolation to obtain the $K_\theta$ values. These values show an excellent agreement with each other and give $(7.91\pm0.02)\times10^{-4}$ (d*l*/g) as the average value.

On the basis of the $K_\theta$ value, the value of $(\langle L^2\rangle_0/M)^{1/2}$ was found to be 0.651 (Å), and the value of $\sigma$, $(\langle L^2\rangle_0/\langle L^2\rangle_f)^{1/2}$, in which $\langle L^2\rangle_f$ is the mean-square end-to-end distance, assuming a fixed valence angle of 109.5°, but a completely free internal rotation for the polymer chain; this value is obtained as 2.48.

The $\sigma$ value for poly-*m*-chlorostyrene, 2.48, is slightly larger than that obtained for poly-*p*-chlorostyrene by the light-scattering measurement, 2.23,[3] and by the osmotic pressure measurements, 2.15[4] and 2.30.[5] This result shows that the chain of poly-*m*-chlorostyrene is considered to be more extended than that of poly-*p*-chlorostyrene. As the $\sigma$ value for poly-*m*-chlorostyrene is also slightly larger than that for poly-*o*-chlorostyrene, 2.41,[6] the chain of the former polymer seems to be more extended than that of the latter. However, as the difference between both $\sigma$ values is exceedingly small, the extension of the poly-*m*-chlorostyrene chain may be considered to be similar to that of poly-*o*-chlorostyrene.

The large $\sigma$ value of poly-*m*-chlorostyrene shows that either the steric repulsion or the electrostatic repulsion, or both the repulsions, exist between the neighboring side groups, unlike the case of poly-*p*-chlorostyrene, for which no electrostatic repulsion is seen in the findings on various *p*-substituted polystyrenes.[7] The difference in $\sigma$ value between these two polymers is surely caused by the difference in the substituted positions of the chlorine atoms on the phenyl group. Of course, at present, it is impossible to decide which of the two types of repulsions has the more effect on the dimensions of poly-*m*-chlorostyrene. For this purpose, it becomes necessary to measure the solution properties of *m*-substituted polystyrene, in which no electrostatic interaction occurs between the substituents. In addition, experiments under the theta conditions are necessary.

The effect of the solvent on the polymer-chain dimensions is measured by the $(\langle L^2\rangle/\langle L^2\rangle_0)^{1/2}$ ratio. A solvent which has a large value of the ratio has a strong interaction with the polymer segment; as a result of this, the polymer chain is considered to be extended greatly compared with the unperturbed state. That is, such a solvent is one of the "good" solvents. Table 3 shows the $(\langle L^2\rangle/\langle L^2\rangle_0)^{1/2}$ ratios for polychlorostyrene and polystyrene with the same degree of polymerization,

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[3] T. Saito, This Bulletin, **35**, 1580 (1962).

[4] N. Kuwahara, K. Ogino, A. Kasai, S. Ueno and M. Kaneko, *J. Polymer Sci.*, **A3**, 985 (1965).

[5] K. Takamizawa, This Bulletin, **39**, 1186 (1966).

[6] K. Matsumura, *Makromol. Chem.*, in press.

[7] N. Kuwahara, K. Ogino, M. Konuma, N. Iida and M. Kaneko, *J. Polymer Sci.*, **A2**, 614 (1966).

TABLE 3. THE EFFECTS OF SOLVENTS ON THE EXPANSION OF POLYCHLOROSTYRENE AND POLYSTYRENE AT THE SAME DEGREE OF POLYMERIZATION $P_w=7220$

| Polymer | Solvent | Temp. (°C) | $\left(\frac{\langle L^2\rangle}{\langle L^2\rangle_0}\right)^{1/2}$ |
|---|---|---|---|
| Poly-*m*-chlorostyrene | Toluene | 35 | 1.61 |
| | Butanone | 30 | 1.45 |
| Poly-*o*-chlorostyrene | Toluene | 35 | 1.48 |
| Poly-*p*-chlorostyrene | Toluene | room temp. | 1.57 |
| | Butanone | room temp. | 2.05 |
| Polystyrene | Toluene | room temp. | 1.36 |
| | Butanone | room temp. | 1.04 |

$P_w=7220$, which corresponds to the molecular weight of $10^6$ for polychlorostyrene, in toluene and butanone at about 30°C. The ratio, 1.61, for poly-*m*-chlorostyrene in a toluene solution; this is similar to that of poly-*p*-chlorostyrene in toluene, but larger than that for a butanone solution, 1.45, which is itself similar to that of poly-*o*-chlorostyrene in toluene. From a comparison of these values, it is considered that toluene is a "good" solvent for poly-*m*-chlorostyrene compared with butanone. These relationships between poly-*m*-chlorostyrene and solvents (toluene and butanone) are similar to those of polystyrene and poly-*o*-chlorostyrene*[1] and the reverse to that of poly-*p*-chlorostyrene.

The relations between $M_w$ and $[\eta]$, $A_2$, and $\langle L^2\rangle^{1/2}$ also give a means by which to know whether or not a solvent is a "good" solvent for a polymer. As Figs. 3, 4, and 5 shows, the observed values of $[\eta]$, $A_2$, and $\langle L^2\rangle^{1/2}$ of the toluene solution are larger than those of a butanone solution at the same molecular weight of poly-*m*-chlorostyrene. These relationships between poly-*m*-chlorostyrene and solvents support the above conclusion when compared with the $(\langle L^2\rangle/\langle L^2\rangle_0)^{1/2}$ ratio.

The author wishes to express his thanks to Professor Akira Kotera for his helpful discussions, and to Dr. Takahide Saito for his encouragement. The author is also indebted to Professor Tomoji Inoue for the use of the instrument for the experiments.

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*[1] It has been observed by the author that butanone is a theta solvent for poly-*o*-chlorostyrene.