The Solution Behavior of Polystyrene Derivatives: Poly-p-chlorostyrene

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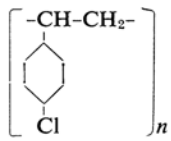
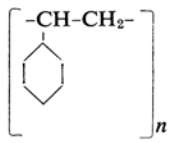
It has been revealed by the studies of the viscosity and light-scattering characteristics of polymers that the solution behavior of polymers is, in general, affected by the polarity of the solvent, the branching of the polymer, the structure and the configuration of the monomer unit, etc. Therefore, it has been interesting for the present author to study the solution properties of polystyrene derivatives, especially the effects of the variation in monomer structure on their solution behavior.

In this paper the viscosity and light-scattering characteristics of poly-*p*-chlorostyrene in butanone and in toluene have been compared with those of polystyrene.



Poly-*p*-chlorostyrene



Polystyrene

Experimental

Materials. — *p*-Chlorostyrene[1],* was redistilled under reduced pressure (b. p., 69.0°C/20 mmHg) before use. The monomer (ca. 70 g.) was sealed in a glass tube and polymerized without an initiator for 48 hr. at 100°C. Then the polymerization product was dissolved in butanone, and the polymer was precipitated with methanol. Reprecipitation was carried out twice, and, after being washed with methanol, the polymer was dried under reduced pressure. The conversion rate was about 87%.

Butanone was refluxed with potassium permanganate for one day in order to oxidize some organic impurities. The butanone distilled from this mixture was dried with potassium carbonate for a week and then redistilled. The fraction (b. p., 79.5~80.0°C) was used. Toluene was washed successively with sulfuric acid, water, a dilute solution of sodium hydroxide, and finally again with water until it was neutralized. It was then dried with metallic sodium and distilled. The fraction which distilled at 110.0~110.5°C was used.

The sample of poly-*p*-chlorostyrene was divided into two parts; each part was independently fractionated as follows: About 20 g. of polymer was dissolved in one liter of butanone. Ten fractions were fractionally precipitated with methanol by the successive precipitation method at 35°C. Each fraction was redissolved in butanone and was precipitated to eliminate the part with a lower molecular weight. Seven fractions were used for the measurements in butanone, and six in toluene.

Measurements.—The solutions for the light-scattering and viscosity studies were rendered free from dust by centrifuging for one hour at 20000 g., using a "Spinco Ultra Centrifuge, Type E" and were filtered into the light-scattering cell or into the reservoir of the viscometer, through a sintered glass filter No. 5, just before the measurements. The viscosity measurements were carried out on the butanone solutions at 25°C and on the toluene solutions at 30°C. A conventional Ubbelohde viscometer was modified so that successive dilution could be performed. The intrinsic viscosity, $[\eta]$, and the Huggins constant, k', were obtained according to the equation:

$$\eta_{sp}/C=[\eta]+k'[\eta]^2C$$

where η_{sp} is the specific viscosity and C is the concentration of polymer in g./100 ml.

An Aminco photometer[2] was used for the measurements of the light scattering. Measurements covering the angular range of 30~140° were performed at room temperature; the wavelengths used for the measurements were 436 mμ and 546 mμ. The weight-average molecular weight, M_w, the second virial coefficient, A_2, and the z-average-root-mean-square-end-to-end distance, $<D^2>_z^{1/2}$, were calculated, using the Zimm plot, according to the equations:

$$KC/R_\theta=1/M_wP(\theta)+2A_2CP(\theta)$$

$$K=2\pi^2n_0^2(dn/dc)^2/N_A\lambda^4$$

where

$P(\theta)$: the factor expressing the reduction in scattered intensity at angle θ
λ : the wavelength of light in vacuum
N_A : Avogadro's number
R_θ : Rayleigh ratio at angle θ

R_θ is calculated according to the equation[3]:

$$R_\theta=(n_0^2/\pi h)Y(G_\theta/G_0^p)S_dXV$$

where

G_θ: the galvanometer reading at angle θ
G_0^p: the galvanometer reading at angle 0° when the incident beam falls to photo tube through the opal-glass standard diffuser located at the center of the cell holder
S_d: the transmittance of the opal-glass standard diffuser,
T : the total transmittance of the neutral filters used in measuring G_0^p

* The monomer used was synthetized by the author of Ref. 1.

1) A. Kotera, *Chem. High Polymer*, **1**, 1 (1944).

2) G. Oster, *Anal. Chem.*, **25**, 1165 (1953).

3) D. K. Carpenter and W. R. Krigbaum, *J. Chem. Phys.*, **24**, 1041 (1956).

h : the width of the slit of the receiver
n_0 : the refractive index of pure solvent
X : a calculation constant determined by the Rayleigh ratio of benzene, 48.5×10^{-6}
V : the volume correction approximated by $1/\sin\theta$

The values of dn/dc, the increments of the refractive index of the solution with concentration, were determined by a Zeiss interferometer to be 0.212 ml./g. in butanone and 0.106 ml./g. in toluene at room temperature.

Results and Discussion

Results.—The plots of the reduced viscosity, η_{sp}/C, vs. the concentration, C, in butanone and in toluene are shown in Figs. 1 and 2 respectively, and the intrinsic viscosity, $[\eta]$, and the Huggins constant, k', are determined from these plots. The Zimm plots for A-6 in butanone and B 2-2 in toluene are shown in Figs. 3 and 4 as examples of the light-scattering measurements. The weight-average molecular weight, M_w, the second virial coefficient, A_2, and the z-average-root-mean-square-end-to-end distance, $\langle D^2\rangle_z^{1/2}$, for each fraction are determined from these figures.

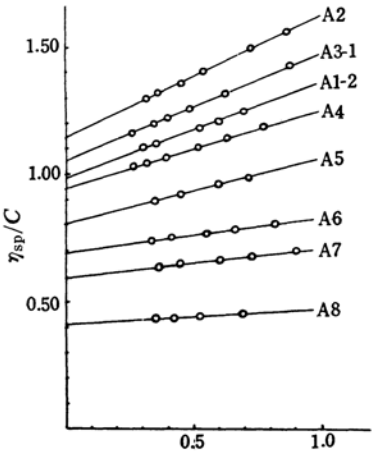


Fig. 1. Relation between reduced viscosity and concentration of poly-*p*-chlorostyrene in butanone at 25°C.

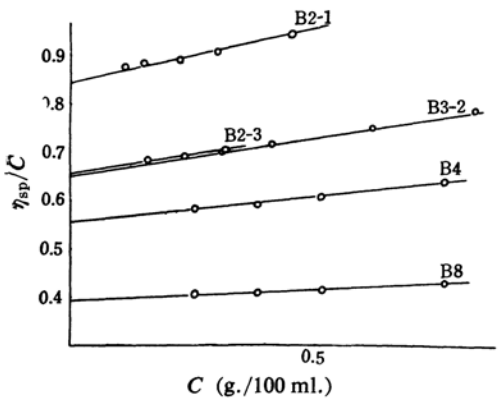


Fig. 2. Relation between reduced viscosity and concentration of poly-*p*-chlorostyrene in toluene at 30°C.

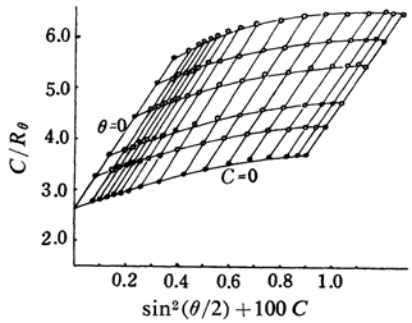


Fig. 3. Zimm plot of poly-*p*-chlorostyrene fraction A 6 in butanone for $\lambda=436$ mμ.

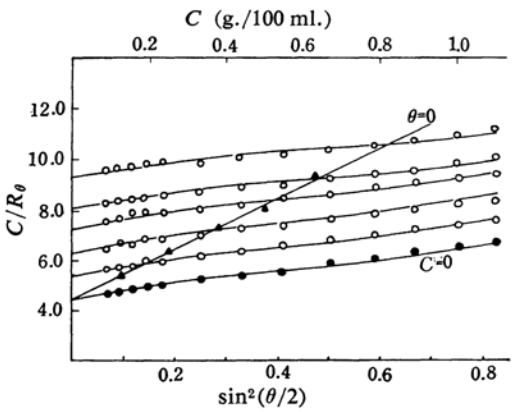


Fig. 4. Incomplete Zimm plot of poly-*p*-chlorostyrene fraction B 2-2 in toluene for $\lambda=436$ mμ. Upper abscissa shows concentration and lower abscissa shows $\sin^2(\theta/2)$. Plots of C/R_θ vs. concentration for each angle except a line for $\theta=0°$ are not shown in this figure.

The results of the viscosity and light-scattering measurements in butanone and in toluene are summarized in Tables I and II respectively.

The molecular weight (degree of polymerization) dependences of the intrinsic viscosity, $[\eta]$, the z-average-root-mean-square-end-to-end distance, $\langle D^2\rangle_z^{1/2}$, and the second virial coefficient, A_2, are usually represented by the equations:

$$[\eta]=KM_w^{\alpha} \tag{1}$$

$$\langle D^2\rangle_z^{1/2}\sim M_w^{\beta} \tag{2}$$

$$A_2\sim M_w^{\gamma} \tag{3}$$

where the constants, K, α, β and γ, are experimentally determined from a plot of $\log X$ against $\log M_w$ (or $\log P$), where X is $[\eta]$, A_2,

TABLE I. THE EXPERIMENTAL RESULTS OF POLY-*p*-CHLOROSTYRENE IN BUTANONE. THE VALUES OF M_w, A_2 AND $<D^2>_z^{1/2}$ ARE DETERMINED BY THE LIGHT SCATTERING MEASUREMENTS AND ARE AVERAGE ON THE RESULTS AT TWO WAVELENGTHS, 436 AND 546 mμ

Fraction	$[\eta]$	k'	$M_w\times10^{-4}$	$A_2\times10^4$	$<D^2>_z^{1/2}$ mμ	$\Phi\times10^{-21}$
A 1-2	0.986	0.38	110	1.5_0	130	1.6
A 2	1.114	0.40	115	1.3_0	127	1.6
A 3-1	1.051	0.39	101	1.4_0	114	1.5
A 4	0.940	0.36	76	1.7_0	101	1.4
A 6	0.688	0.33	49	2.5_7	78	1.4
A 7	0.592	0.32	36	1.7_7	68	1.5
A 8	0.410	0.36	31	2.1_8	63	2.0

Notation; M_w : Weight average molecular weight
A_2 : Second virial coefficient
$<D^2>_z^{1/2}$: Root-mean-square-end-to-end distance
k' : Huggins constant
Φ : Flory parameter
$[\eta]$: Intrinsic viscosity

TABLE II. THE EXPERIMENTAL RESULTS OF POLY-*p*-CHLOROSTYRENE IN TOLUENE. THE VALUES OF M_w, A_2 AND $<D^2>_z^{1/2}$ ARE DETERMINED BY THE LIGHT SCATTERING MEASUREMENTS FOR 436 mμ

Fraction	$[\eta]$	k'	$M_w\times10^{-4}$	$A_2\times10^4$	$<D^2>_z^{1/2}$ mμ	$\Phi\times10^{-21}$
B 2-1	0.847	0.31	102	0.7_0	95	1.0
B 2-2	0.850		99	0.7_0	93	
B 2-3	0.658	0.37	75	0.8_9	78	1.0
B 3-2	0.652	0.38	66	0.9_0	75	1.0
B 3-4	0.556	0.34	47	1.1_0	57	1.4
B 8	0.395	0.29	33		49	1.1

The notations used in this table are the same as those used in Table I.

or $<D^2>_z^{1/2}$ *. The log-log plots of the intrinsic viscosity, the second virial coefficient and the end-to-end distance against the molecular weight are shown in Figs. 5, 6 and 7 respectively.

Equations 1, 2 and 3 for poly-*p*-chlorostyrene are

$[\eta]=2.9_4\times10^{-4}M_w^{0.59}$ in butanone at 25°C
$[\eta]=1.2_8\times10^{-4}M_w^{0.64}$ in toluene at 30°C
$<D^2>_z^{1/2}\sim M_w^{0.55}$ in butanone
$<D^2>_z^{1/2}\sim M_w^{0.60}$ in toluene
$A_2\sim M_w^{-0.17}$ in butanone
$A_2\sim M_w^{-0.40}$ in toluene

Discussion.—A solvent, the polymer solution of which shows a higher value of A_2, $<D^2>_z^{1/2}$ or $[\eta]$, is called a "*good*" solvent. In the case of poly-*p*-chlorostyrene, butanone is considered to be a better solvent than toluene according to this definition, because poly-*p*-chlorostyrene in the former solvent shows higher values of A_2 and of $<D^2>_z^{1/2}$ than in the latter.

To discuss the influence of the substituent in the para position of the benzene ring on the solution behavior, the constants, K, α, β and γ, for poly-*p*-chlorostyrene and polystyrene

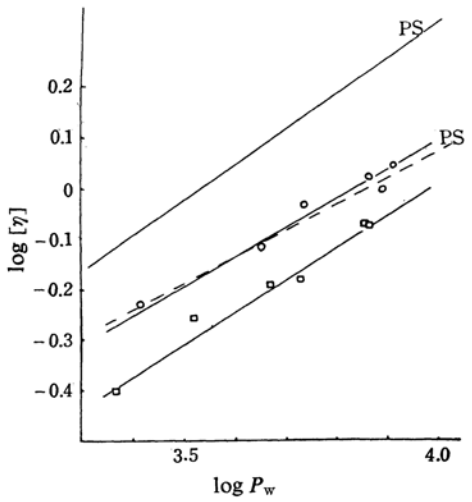


Fig. 5. Plot between intrinsic viscosity and degree of polymerization.
—PS : Polystyrene-toluene
- - -PS : Polystyrene-butanone
-□- : Poly-*p*-chlorostyrene-toluene
-○- : Poly-*p*-chlorostyrene-butanone

* The value shown as $<D^2>z^{1/2}$ gives the length $\sqrt{6}$ times as long as the root-mean-square radius of gyration, and it gives the end-to-end distance only in the case of the Gaussian chain. For convenience, however, the value is used as a relative measure of chain extension in the case of the non-Gaussian chain also.

TABLE III. COMPARISON OF THE DEPENDENCES OF SOLUTION BEHAVIORS ON MOLECULAR WEIGHT FOR POLYSTYRENE AND POLY-*p*-CHLOROSTYRENE IN BUTANONE AND TOLUENE

Solvent	Polymer	$K\times10^4$	α	β	γ
Butanone 25°C	Poly-*p*-chlorostyrene	2.9	0.59	0.55	−0.17
	Polystyrene	3.9	0.58	0.58	−0.23
Toluene 30°C	Poly-*p*-chlorostyrene	1.2	0.64	0.60	−0.40
	Polystyrene	1.3	0.70	0.68	−0.33

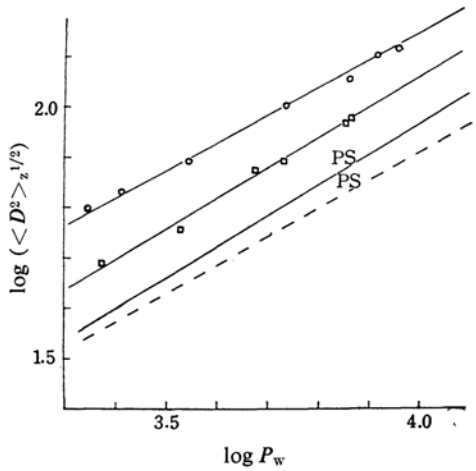


Fig. 6. Comparison of extensions of chain for poly-*p*-chlorostyrene in toluene and butanone with those of polystyrene at the same degree of polymerization.

-□-: Poly-*p*-chlorostyrene-toluene
-○-: Poly-*p*-chlorostyrene-butanone
—PS: Polystyrene-toluene
---PS: Polystyrene-butanone

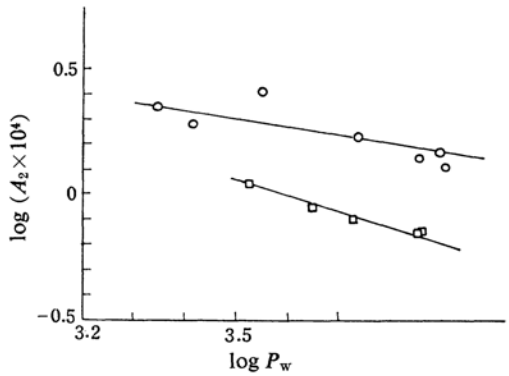


Fig. 7. Relation between second virial coefficient and degree of polymerization of poly-*p*-chloro-styrene.

-□-: Poly-*p*-chlorostyrene-toluene
-○-: Poly-*p*-chlorostyrene-butanone

are summarized and compared in Table III **.

The values of the K, α, β and γ of poly-*p*-chlorostyrene are nearly the same as those of polystyrene.

Moreover, some interesting results in their solution behavior may be deduced from a detailed comparison. (1) The value of the $[\eta]$ of poly-*p*-chlorostyrene in toluene is smaller than that of polystyrene. (2) The $[\eta]$ of polystyrene in butanone is nearly the same as that of poly-*p*-chlorostyrene. (3) The values of the $<D^2>_z^{1/2}$ of polystyrene in butanone and toluene are all smaller than those of poly-*p*-chlorostyrene. (4) The values of $[\eta]$ and $<D^2>_z^{1/2}$ for poly-*p*-chlorostyrene in toluene are smaller than those in butanone.

Generally speaking, it is not exact to define a solvent as a "*good*" or "*bad*" solvent only on the basis of a comparison of the chain extensions of various polymers in a solvent regardless of differences in their structures. However, when the basic structures of the chain molecules are similar to one another, a comparison of the chain extensions in a solvent may be used as a relative measure of the effects of solvent on polymer configurations.

On the basis of the third result described above, it may be said that both butanone and toluene act as better solvents for poly-*p*-chlorostyrene than polystyrene.

To show this result more clearly, the ratio for polystyrene and poly-*p*-chlorostyrene of $<D^2>_z^{1/2}$ to D_f, where D_f is the end-to-end distance, assuming a free rotation model for the chain configuration, are compared in Table IV at the weight-average degree of polymerization of $p_w=10^4$. To obtain quantitative information on the effect of the solvent on chain extension, it is necessary to take, as a parameter to be used for comparison, a ratio of $<D^2>_z^{1/2}/<D_0^2>_z^{1/2}$ instead of $<D^2>_z^{1/2}/D_f$,

** The formulas which have been reported for the dependence of the intrinsic viscosity of polystyrene are;

$[\eta]=1.7\times10^{-4}M_w^{0.69}$ in toluene at 25°C[4]
$[\eta]=1.2\times10^{-4}M_w^{0.71}$ in toluene at 30°C[5]
$[\eta]=0.92\times10^{-4}M_w^{0.74}$ in toluene at 30°C[6]
$[\eta]=3.9\times10^{-4}M_w^{0.58}$ in butanone at 25°C[4]
$[\eta]=2.3\times10^{-4}M_w^{0.62}$ in butanone at 30°C[7]

The equation quoted in Table III seems to be appropriate with regard to the temperature and to the measured range of the molecular weight.

4) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).
5) T. Oyama and K. Kawahara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **78**, 484 (1957).
6) S. N. Chinai et al., *J. Polymer Sci.*, **22**, 527 (1956).
7) T. Oyama and K. Kawahara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **79**, 727 (1958).

TABLE IV. VALUES OF $<D^2>_z^{1/2}/D_f$ FOR POLYSTYRENE AND POLY-*p*-CHLOROSTYRENE IN BUTANONE AND TOLUENE AT $P_w=10^4$. VALUES OF POLYSTYRENE ARE CALCULATED FROM THE DATA IN REFS. 4 AND 5.

Polymer	$<D^2>_z^{1/2}/D_f$ Solvent	
	Butanone	Toluene
Poly-*p*-chlorostyrene	3.23	2.65
Polystyrene	1.86	2.14

where $<D_0^2>_z^{1/2}$ is a z-average-root-mean-square-end-to-end distance of an unperturbed chain, because the unperturbed extension of polymer molecules with different structures varies according to differences in the dipole-dipole interaction and in the steric effects of the substituents. However, even though the values of $<D^2>_z^{1/2}/D_f$ are directly related to the effects of solvents on the polymer configuration in solution, it should be noted that the dimensions of poly-*p*-chlorostyrene in butanone are particularly extensive compared with the dimensions of poly-*p*-chlorostyrene in toluene and/or of polystyrene in toluene and butanone.

According to Flory and Fox, the relation between the intrinsic viscosity and the end-to-end distance for a linear polymer may be expressed as follows:

$$[\eta] = \Phi \frac{<D^2>_z^{3/2}}{M_w} \qquad (4)$$

where Φ is defined as an universal constant independent of the temperature, solvent and basic structure of the polymer[8]. Therefore, when Φ is a constant regardless of the solvent, the same tendencies must exist in the relations between $[\eta]$ and solvents as in the case of $<D^2>_z^{1/2}/D_f$. However, the experimental results with reference to the intrinsic viscosity which are summarized above as results 1 and 2 are not in accord with result 3. These conflicting results are substantially derived from the differences of the Φ of poly-*p*-chlorostyrene in the two solvents, as is shown in Tables I and II. The author can not explain at present why the values of Φ in the two solvents differ.

8) P. J. Flory and T. Fox, *J. Phys. Chem.*, 53, 197 (1957).

Summary

The polar group in the para position of the benzene ring of poly-*p*-chlorostyrene has a remarkable influence on the solution behavior and that, especially, the chain in the polar solvent is particularly extensive because of the interaction between the C–Cl group in the para position and the polar solvent.

The author is deeply grateful to Professor Akira Kotera and Professor Keizo Suzuki for their helpful suggestions and discussion. He also wants to thank Dr. Hideomi Matsuda and Dr. Yuji Miyazawa, who made some of the measurements of viscosity and light scattering, and Miss Michiko Takahashi, who made the centrifuging of the solutions, for their kindness. This research was supported in part by a Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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