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The Solution Behavior of Polystyrene Derivatives: Poly-*p*-methoxystyrene

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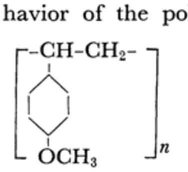
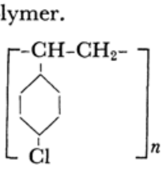
The solution behavior of poly-*p*-methoxystyrene in toluene and butanone was measured by light-scattering and viscosity methods, and the results were compared with those of polystyrene and poly-*p*-chlorostyrene in order to discuss the mutual interactions between the solvent and the substituent on the phenyl group. The results show that toluene is a good solvent and butanone a poor one for poly-*p*-methoxystyrene; these relationships between poly-*p*-methoxystyrene and solvents are inverse to those for poly-*p*-chlorostyrene and similar to those for polystyrene, although the extensions of poly-*p*-chlorostyrene and poly-*p*-methoxystyrene are much larger than that of polystyrene at the same degree of polymerization because of the strong mutual interaction between the solvent and the substituent on the phenyl group. It is clear, from the application of Kurata-Stockmayer theory to the experimental results obtained for poly-*p*-methoxystyrene, that the unperturbed dimension of poly-*p*-methoxystyrene is larger than that of polystyrene; this result may be interpreted as being due to an increase in the volume of the chain element of the polymer molecule.

In a preceding paper,⁽¹⁾ the viscosity and light-scattering characteristics of poly-*p*-chlorostyrene in butanone and toluene were compared with those of polystyrene; it was concluded that the para substituent (chlorine atom) of the phenyl group affected the dependence of the viscosity, the extension, and the second virial coefficient on the molecular weight, and that the extension of poly-*p*-chlorostyrene, as compared with that of polystyrene, is markedly influenced by the polarity of the substituent.

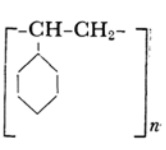
In the present paper the viscosity and light-scattering characteristics of poly-*p*-methoxystyrene in butanone and toluene are compared with those of polystyrene and poly-*p*-chlorostyrene. This comparison provides information on the effect of the para methoxy substituent on the solution behavior of the polymer.



poly-*p*-methoxystyrene



poly-*p*-chlorostyrene



polystyrene

Experimental

Materials. — *p*-Methoxystyrene was polymerized without an initiator for 24 hr. at 100°C. The polymer was dissolved in benzene and was precipitated (from this solution) with methanol. Polymerization occurred to the extent of almost 100%.

Butanone and toluene were purified by the method used in the preceding paper.⁽¹⁾

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(1) T. Saito, This Bulletin, **35**, 1580 (1962).

Fractionation.—About 14 g. of poly-*p*-methoxystyrene was dissolved in 500 ml. of butanone. Then fractions were obtained by the successive precipitation method with methanol as a precipitant at 37°C. Seven fractions were used for the measurements.

Viscosity and Light Scattering.—A conventional Ubbelohde viscometer was modified so that successive dilution could be performed. The intrinsic viscosity, $[\eta]$, and the Huggins constant, k', were obtained for the solution in toluene at 30°C and in butanone at 25°C. An Aminco photometer was used for the measurement of the light scattering. The details of the measurement have been described in the preceding paper. The values of dn/dc, the increment of the refractive index of the solution with the concentration, were determined with a Zeiss interferometer; they were 0.219 ml./g. in butanone and 0.105 ml./g. in toluene at room temperature. To remove dust, the solutions for light-scattering and viscosity studies were centrifuged for one hour at 20000 g. on a Phywe ultracentrifuge and were filtered into the light-scattering cell or the reservoir of the viscometer through a sintered glass filter (No. 6) just before the measurements.

Results and Discussions

Results.—Plots of the reduced viscosity, η_{sp}/C, vs. the concentration, C, for each fraction are shown in Figs. 1 and 2; the intrinsic viscosity, $[\eta]$, and the Huggins constant, k', were determined from these plots. The Zimm plot for Fraction 7, as an example of light-scattering measurements, is given in Fig. 3; the weight-average molecular weight, M_w, the second virial coefficient, A_2, and the z average root mean square end-to-end distance, $\langle D^2\rangle_z^{1/2}$, were determined for seven fractions from Zimm plots similar to those in Fig. 3.

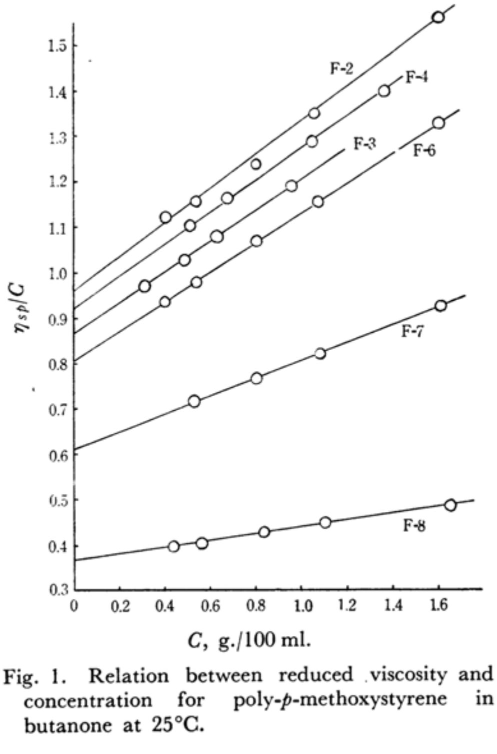

Fig. 1. Relation between reduced viscosity and concentration for poly-*p*-methoxystyrene in butanone at 25°C.

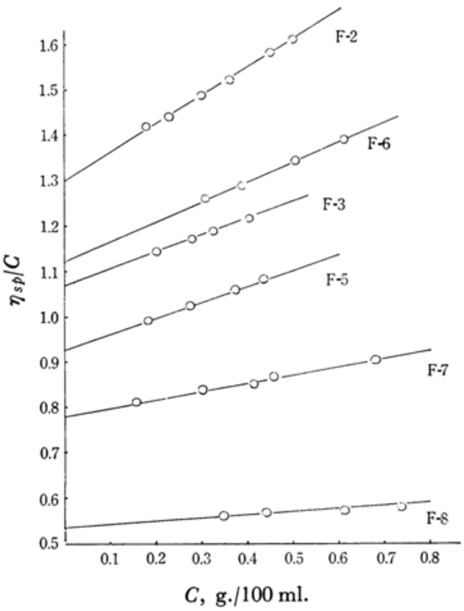

Fig. 2. Relation between reduced viscosity and concentration for poly-*p*-methoxystyrene in toluene at 30°C.

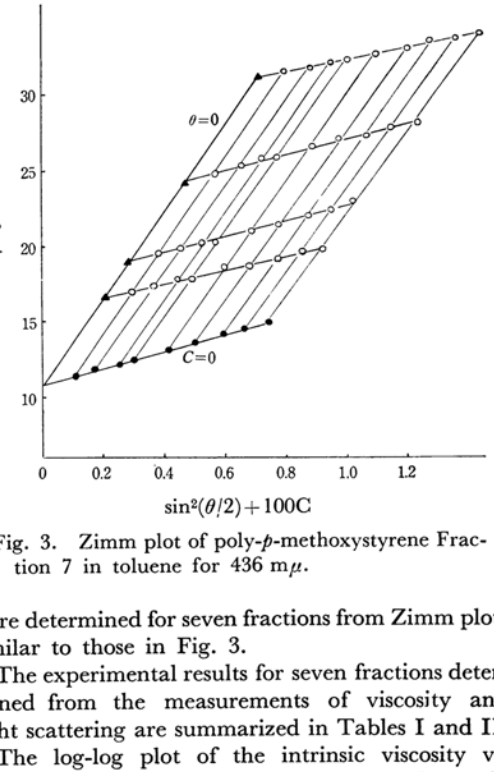

Fig. 3. Zimm plot of poly-*p*-methoxystyrene Fraction 7 in toluene for 436 mμ.

The experimental results for seven fractions determined from the measurements of viscosity and light scattering are summarized in Tables I and II.

The log-log plot of the intrinsic viscosity vs. the weight-average molecular weight is shown in Fig. 4.

The relation between the intrinsic viscosity and the molecular weight is represented by the equation:

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

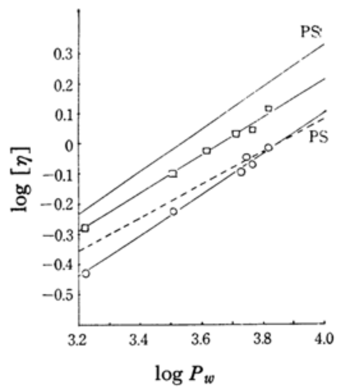

Fig. 4. Plots between intrinsic viscosity and degrees of polymerization.
—— PS: Polystyrene-toluene
---- PS: Polystyrene-butanone
-□-: Poly-*p*-methoxystyrene - toluene
-○-: Poly-*p*-methoxystyrene - butanone

TABLE I. THE EXPERIMENTAL RESULTS FOR POLY-*p*-METHOXYSTYRENE IN BUTANONE.

The values of M_w, A_2 and $\langle D^2\rangle_z^{1/2}$ are the averaged results for two wavelengths, 436 mμ and 546 mμ. Viscosity measurements were carried ou tat 25°C.

Fraction	$[\eta]$	k'	$M_w\times$ 10^{-4}	$A_2\times$ 10^4	$\langle D^2\rangle_z^{1/2}$ mμ	$\Phi\times$ 10^{-21}
2	0.957	0.39	87	1.2_5	85	1.4
3	0.864	0.44	78	1.4_0	75	1.6
4	0.907	0.44	75	1.5_0	73	1.8
6	0.800	0.50	73	1.6_0	73	1.5
7	0.617	0.48	43	1.7_2	55	1.6
8	0.364	0.54	22	1.7_8	37	1.6

Notation: M_w: weight average molecular weight, A_2: second virial coefficient, $\langle D^2\rangle_z^{1/2}$: z average root mean square end-to-end distance, $[\eta]$: intrinsic viscosity, k': Huggins constant, Φ: Flory parameter.

TABLE II. THE EXPERIMENTAL RESULTS FOR POLY-*p*-METHOXYSTYRENE IN TOLUENE

The light scattering measurements were made at 436 mμ and the viscosity measurements were carried out at 30°C.

Fracticn	$[\eta]$	k'	$M_w\times$ 10^{-4}	$A_2\times$ 10^4	$\langle D^2\rangle_z^{1/2}$ mμ	$\Phi\times$ 10^{-21}
2	1.300	0.36	85	2.1_3	92	1.4
3	1.080	0.23	70	1.8_9	83	1.3
5	0.935	0.40	56	2.1_8	71	1.5
6	1.120	0.36	78	2.0_4	87	1.3
7	0.783	0.29	43	3.1_0	66	0.9
8	0.532	0.30	22		41	1.7

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

where M_w is a weight-average molecular weight and K and α are constants determined from a plot of $\log[\eta]$ against $\log M_w$. Equation 1 for poly-*p*-methoxystyrene is as follows:

$$[\eta]=0.80\times10^{-4}M_w^{0.69} \text{ in butanone at } 25^\circ\text{C},$$

$$[\eta]=2.41\times10^{-4}M_w^{0.62} \text{ in toluene at } 30^\circ\text{C}.$$

The dependence of the root mean square end-to-end distance on the molecular weight is expressed by:

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

where β is a constant as determined from a plot of $\log(\langle D^2\rangle_z^{1/2})$ against $\log M_w$, and the relations for poly-*p*-methoxystyrene are:

$$\langle D^2\rangle_z^{1/2}\sim M_w^{0.57} \text{ in butanone}$$

$$\langle D^2\rangle_z^{1/2}\sim M_w^{0.58} \text{ in toluene}$$

The second virial coefficient of a polymer solution depends on the molecular weight:

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

and the dependences of poly-*p*-methoxystyrene are:

$$A_2\sim M_w^{-0.20} \text{ in butanone}$$

$$A_2\sim M_w^{-0.40} \text{ in toluene}$$

Discussion.—The constants, K, α, β and γ, in Eqs. 1, 2 and 3 are summarized in Table III, where the constants for polystyrene and poly-*p*-chlorostyrene are also included for the sake of comparison. The values of the constants for poly-*p*-methoxystyrene are similar to those given in the literature for various vinyl polymers, and it seems likely that there is no abnormal tendency in the solution behavior of poly-*p*-methoxystyrene. However, a detailed comparison of the data for poly-*p*-methoxystyrene with those for polystyrene and poly-*p*-chlorostyrene brings to light some interesting facts with regard to the effects of the solvent on the extension of the polymer chain. The dimensions of poly-*p*-methoxystyrene in toluene are larger than those in butanone; this relationship between the solvent and the dimension is the same as in the case of polystyrene, but it is reversed in the case of poly-*p*-chlorostyrene.

In order to clarify the effects of solvents on the dimensions of polymer chains, the $\langle D^2\rangle_z^{1/2}/D_f$ values for polystyrene derivatives in toluene and butanone are compared with one another at $P_w=10^4$; these values are shown in Table IV, where D_f is the end-to-end distance of the chain, assuming a free rotation model, and where $\langle D^2\rangle_z^{1/2}$ is obtained from a plot of $\log(\langle D^2\rangle_z^{1/2})$ vs. $\log P_w$.

Of course, a comparison of the effect of a solvent on the dimensions of the chain must be based on a value of $\langle D^2\rangle_z^{1/2}/\langle D_0^2\rangle_z^{1/2}$, where $\langle D_0^2\rangle_z^{1/2}$ is a z-average root mean square unperturbed end-to-end distance, but when the basic structures of the polymers are similar to each other, the $\langle D^2\rangle_z^{1/2}/D_f$ ratio can be considered to be a relative measure of the solvent effect.

As is shown in Table III or IV, toluene is a better solvent for poly-*p*-methoxystyrene than butanone;

TABLE III. CONSTANTS FOR THE SOLUTION BEHAVIOR OF POLYSTYRENE DERIVATIVES IN TOLUENE AND BUTANONE

Solvent	Polymer	$K\times 10^4$	α	β	γ
Butanone (25°)	Poly-*p*-chlorostyrene	2.9_4	0.59	0.55	−0.17
	Poly-*p*-methoxystyrene	0.8_0	0.69	0.57	−0.20
	Polystyrene	3.9_0	0.58	0.58	−0.23
Toluene (30°C)	Poly-*p*-chlorostyrene	1.2_8	0.64	0.60	−0.40
	Poly-*p*-methoxystyrene	2.4_1	0.62	0.58	−0.40
	Polystyrene	1.3_0	0.70	0.68	−0.33

this relationship is the same as that for polystyrene.2−4) However, the values of $\langle D^2\rangle_z^{1/2}/D_f$ obtained for poly-*p*-methoxystyrene show that the *p*-methoxy-phenyl groups are involved in greater mutual interactions than are the phenyl groups.

The finding that the extension of poly-*p*-methoxystyrene in toluene is nearly the same as, or slightly larger than, that of poly-*p*-chlorostyrene may be explained as follows: the increased stability of the extended form of the chain in the case of poly-*p*-methoxystyrene in comparison with the case of poly-*p*-chlorostyrene is to be attributed to the mutual interaction between the C_6H_5–OCH_3 group being greater than that between the C_6H_5–Cl groups.

Kotera et al.5,6) measured the dipole moments of poly-*p*-chlorostyrene and poly-*p*-methoxystyrene at different temperatures and concluded from their experimental results that the chain of poly-*p*-methoxystyrene is more extensive than that of poly-*p*-chlorostyrene. Their measurements were carried out in a non-polar solvent; hence, their results are substantially in accord with our data.

Kurata and Stockmayer have recently proposed new equations for deriving the unperturbed dimension of polymer molecule from the intrinsic viscosity data of the polymer molecule in a good solvent; they have also shown the wide applicability of their method to the correct estimation of short-range interactions of a polymer molecule.7) The new equations proposed by them are as follows:

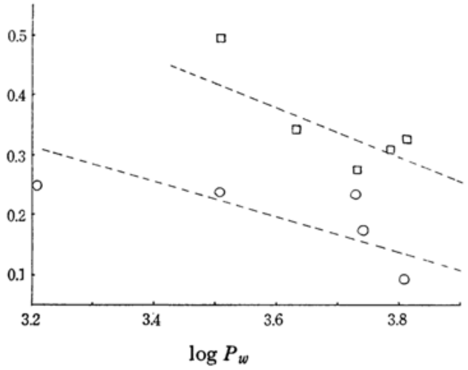

Fig. 6. Relation between second virial coefficient and degrees of polymerization of poly-*p*-methoxystyrene.

-□-: Poly-*p*-methoxystyrene - toluene

-○-: Poly-*p*-methoxystyrene - butanone

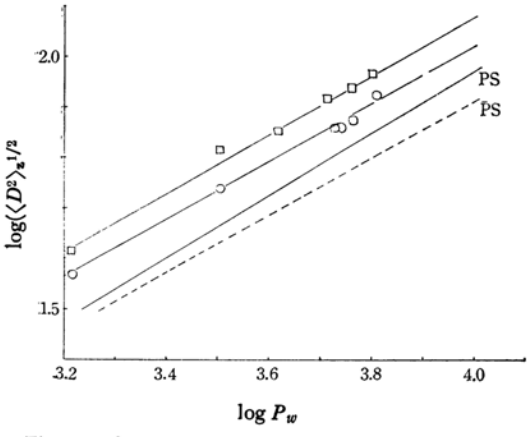

Fig. 5. Comparison of extension of chain of poly-*p*-methoxystyrene; the data for polystyrene is included.

—— PS: Polystyrene-toluene

---- PS: Polystyrene-butanone

-□-: Poly-*p*-methoxystyrene - toluene

-○-: Poly-*p*-methoxystyrene - butanone

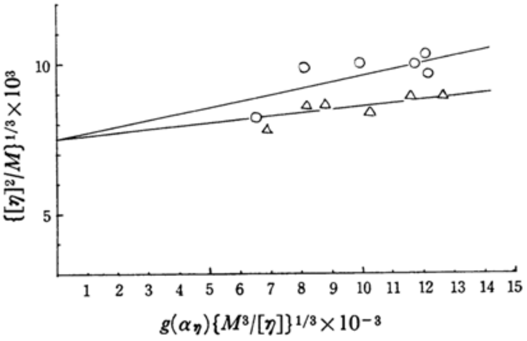

Fig. 7. The dependence of $([\eta]^2/M)^{1/3}$ on $g(\alpha_\eta)\times(M^2/[\eta])^{1/3}$ for poly-*p*-methoxystyrene.

○ Butanone at 25°C

△ Toluene at 30°C

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2) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 30 (1950).

3) T. Oyama and K. Kawahara, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zassi*), **78**, 484 (1957).

4) C. E. H. Bawn and M. A. Wajid, *J. Polymer Sci.*, **12**, 109 (1953).

5) A. Kotera, Annual Meeting of the Chemical Society of Japan, April, 1943.

6) A. Kotera, K. Matsumura, K. Fujimori and H. Yamamoto, Annual Meeting of the Society of Polymer Science, Japan, May, 1952.

7) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolymer. Forsch.*, **3**, 196 (1963).

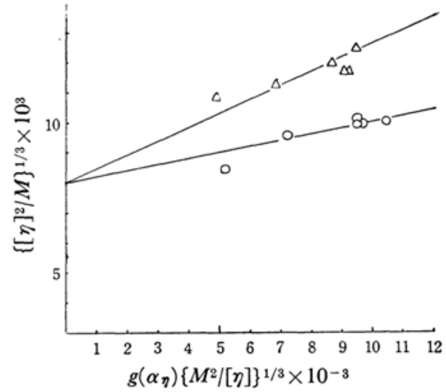

Fig. 8. The dependence of $([\eta]^2/M)^{1/3}$ on $g(\alpha_\eta)\times(M^2/[\eta])^{1/3}$ for poly-*p*-chlorostyrene.
△ Toluene at 30°C
○ Butanone at 25°C

TABLE IV. VALUES OF $\langle D^2\rangle_z^{1/2}/D_f$ FOR POLYSTYRENE DERIVATIVES IN TOLUENE AND BUTANONE AT $P_w=10^4$

The values for polystyrene were calculated from the data in Refs. 2 and 3.

Polymer	$\langle D^2\rangle_z^{1/2}/D_f$ Solvent	
	Butanone	Toluene
Poly-*p*-chlorostyrene	3.24	2.57
Poly-*p*-methoxystyrene	2.39	2.73
Polystyrene	1.86	2.14

TABLE V. THE RATIOS BETWEEN THE UNPERTURBED DIMENSIONS AND THE DIMENSION WHEN A FREE ROTATION MODEL IS ASSUMED FOR POLYSTYRENE, POLY-*p*-METHOXYSTYRENE AND POLY-*p*-CHLOROSTYRENE

Polymer	r
Poly-*p*-methoxystyrene	2.39
Poly-*p*-chlorostyrene	2.34
Polystyrene	2.30

$$([\eta]^2/M)^{1/3} = K^{2/3}+0.363B\Phi_0(g(\alpha_\eta)M^2/[\eta])^{1/3}$$
$$K^{1/3} = \Phi_0^{1/3}A$$
$$\alpha_\eta = [\eta]/[\eta]_\theta$$
$$g(\alpha_\eta) = 8\alpha_\eta^3/(3\alpha_\eta^2+1)^{2/3}$$

where α_η is an expansion parameter of the polymer molecule obtained from the intrinsic viscosity; M, the molecular weight; Φ_0, the Flory parameter (2.8×10^{21}); $g(\alpha_\eta)$, a function of the volume exclusion of the polymer, and a parameter, A, is related to the unperturbed dimension of the polymer. An approximate value of K, which permits us to obtain α_η or $g(\alpha_\eta)$, is obtained from plots of $([\eta]^2/M)^{1/3}$ against $(M^2/[\eta])^{1/3}$, ignoring $g(\alpha_\eta)$; then, using this result, an improved value of K is obtained from plots of $([\eta]^2/M)^{1/3}$ against $g(\alpha_\eta)(M^2/[\eta])^{1/3}$. The final value of K, K_θ, is obtained in the second trial.

The unperturbed dimension of the polymer molecule is calculated from the value of A and the ratio, r, between the unperturbed dimension of poly-*p*-methoxystyrene, or poly-*p*-chlorostyrene, obtained from this plot, and that obtained when a free rotation model for the polymer chain is assumed; these values of r, together with the one quoted for polystyrene in the literature, are shown in Table V. The values of r for both these para-substituted polymers (2.34 for poly-*p*-chlorostyrene and 2.39 for poly-*p*-methoxystyrene) are larger than that for polystyrene 2.30),* and the value of r for poly-*p*-methoxystyrene seems to be a little larger than that for poly-*p*-chlorostyrene; these results are in accord with that described above.

A detailed discussion of the values for the unperturbed dimension for the para-substituted polymer molecule obtained from the plots shown in Figs. 7 and 8, will be avoided here because some scatter exists in the plots of the dependences of $([\eta]^2/M)^{1/3}$ on $g(\alpha_\eta)(M^2/[\eta])^{1/3}$ and no experimental data for samples with small molecular weights are available.

Although there seems to be a little ambiguity in the values of K_θ obtained from our data for poly-*p*-methoxystyrene and poly-*p*-chlorostyrene, both r values for these polymers are larger than that for polystyrene; this result may be due to the larger molecular volumes of the monomer units for these polymers.**

The Flory parameter, Φ, is calculated by using the equation:

$$[\eta]=\Phi\langle D^2\rangle_z^{3/2}/M_w \qquad (4)$$

where $\langle D^2\rangle_z^{1/2}$ is the z-average root mean square end-to-end distance, M_w is the weight average molecular weight, and $[\eta]$ is the intrinsic viscosity. The values of Φ for poly-*p*-methoxystyrene are 1.5×10^{21} in toluene and 1.6×10^{21} in butanone; these results are similar to those for various vinyl polymers given in the literature.

Conclusion

The solution behavior of poly-*p*-methoxystyrene is similar to that of polystyrene; this may be ascribed to the comparatively similar basic structure of the two polymers. However, poly-*p*-methoxystyrene has the more extended chain, because the mutual interactions of *p*-methoxy-phenyl groups are larger than those of phenyl groups or *p*-chlorophenyl groups.

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* Obtained in our laboratory for polystyrene by measuring the light-scattering properties in cyclohexane at 35°C. The value of r for atactic polystyrene given by Kurata and Stockmayer is 2.20 ± 0.05.[7]

** The other approximation for the determination of the unperturbed dimension depending upon the same theoretical viewpoint as that by Kurata and Stockmayer was given by W. Stockmayer and M. Fixman (*J. Polymer Sci.*, **C1**, 137 (1963)). The results obtained from both approximations are the same.