TABLE IV
THE γ RELAXATION. COLE–COLE PLOT DATA

Copolymer	$(1-\alpha)$	$(\Delta\epsilon')$ (area)	$(\Delta\epsilon')$ (Cole–Cole)	$(\Delta\epsilon'_{\max})$ (theory)
A	0.62	0.097	0.078	0.05
B	0.45	0.106	0.085	0.11
C	0.61	0.206	0.105	0.13
D	0.27	0.206	0.121	0.21
ET–CO	0.30			

son purposes. It is seen that the shape of the Cole–Cole plots for sample D and the ethylene–carbon monoxide polymer are quite similar but that samples A, B, and C show quite different behavior. Table IV collects the parameters derivable from the Cole–Cole plots for the γ relaxation as well as values of $\Delta\epsilon'$ estimated from eq 3. It is seen that the breadth of the relaxation time distribution as evidenced by the parameter $(1 - \alpha)$ is considerably greater for sample D than for A, B, and C, and is in fact comparable to the value obtained for the ethylene–carbon monoxide copolymer. This and the activation energy data would indicate that the γ process in sample D is of the polyethylene type perhaps rendered dielectrically active by adventitious oxidation. This is consistent with the phase separated structure believed to exist in sample D.

The same arguments indicate that phosphonic acid groups must contribute to the γ relaxation in samples A, B, and C. Assuming this contribution to arise from rotation of isolated phosphonic acid groups about the CP axis, we would expect only the perpendicular component of the dipole moment of the phosphonic acid group to be active. Using this simple model and calculating $\Delta\epsilon'$ on the basis of the Onsager equation, fairly good agreement results for A, B, and C as shown in Table IV. In general the agreement is better for values of $\Delta\epsilon'$ derived from Cole–Cole plots than from areas of plots of ϵ'' *vs.* $1/T$.

Summary

The model proposed to account for the experimental evidence is one in which, at low phosphonic acid contents (*e.g.*, copolymer A) we have essentially isolated randomly placed phosphonic acid groups throughout the polymer.

As the phosphonic acid content is increased hydrogen bonding between acid groups occurs and increases with increasing phosphonic acid content leading to dimers, trimers, etc., and ultimately (*e.g.*, copolymer D) to a two-phase structure in which we have large hydrogen-bonded aggregates embedded in a polyethylene matrix which still contains a few isolated phosphonic acid groups and oligomers.

The situation here is quite different from that reported for ethylene–carboxylic acid systems in which carboxylic acid dimers prevail due to the unusual symmetry of that dimer. There is, however, reason to believe that a similar situation to the one reported here may exist for ethylene–carboxylic acid copolymers of very high carboxylic acid content.[23]

Acknowledgments. The authors are grateful to the National Science Foundation for partial support of this research under Grant GP 8581 and to the Petroleum Research Fund of the American Chemical Society for partial support of this research under Grant 2914 A5.

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Thermodynamic and Hydrodynamic Properties of Linear Polymer Solutions. I. Light Scattering of Monodisperse Poly(α-methylstyrene)

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ABSTRACT: Second virial coefficients and expansion factors of monodisperse poly(α-methylstyrenes) covering a wide range of molecular weight are determined by light scattering measurement in Θ and non-Θ solvents and are compared with current theories of these solution properties. It is concluded that the Flory theory of α^5-type is valid when the molecular weight is high enough to permit reliable determination of the radius of gyration.

There are, roughly speaking, two groups of theories on the expansion factor of linear polymers as a function of molecular weight, temperature, solvent species, etc. One is represented by the theory of Flory (eq 1) which is usually called an equation of the α^5-type,[1-4] while the other is represented by the theory of Stockmayer and Fixman (eq 2) which is called an equation of the α^3-type.[5-8] The expansion factor α is defined by $\alpha_s^2 = \langle S^2\rangle/\langle S^2\rangle_0$, where $\langle S^2\rangle_0^{1/2}$ and $\langle S^2\rangle^{1/2}$ are the radii of gyration at the Θ and non-Θ temperatures, respectively

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Flory[1-3]

$$\alpha_s^5 - \alpha_s^3 = C_s z \quad (1)$$

Stockmayer and Fixman[7]

$$\alpha_s^3 - 1 = 1.9z \quad (2)$$

where C_s is a numerical constant, that is, $C_s = 2.60$ according to Flory or 134/105 if modified as was done by Stockmayer.[9] The z parameter is defined in the form

$$z = B(\langle S^2\rangle_0/M)^{-3/2}M^{1/2} \quad (3)$$

and

$$B = (1/4\pi)^{3/2}(1/m_s)^2\beta \quad (4)$$

where M is the molecular weight of the polymer, m_s is the molecular weight of a segment, and β is the binary cluster integral for the interaction between the nonbonded segments. There are various theories[10-12] ranging between eq 1 and eq 2 and a summary of the theories has been given by Norisuye, Kawahara, Teramoto, and Fujita.[13]

The expansion factor α can be calculated from the radius of gyration determined by light scattering and also estimated from limiting viscosity number $[\eta]$ by using Flory and Fox's relationship[2]

$$[\eta]/[\eta]_0 = \alpha_\eta^3 = \alpha_s^3 \quad (5)$$

where $[\eta]_0$ is the limiting viscosity number at the Θ temperature. Although many experimental studies of limiting viscosity number appeared to be favorable to the theory of Stockmayer and Fixman,[8,14] recent light scattering experiments show that the theory of Flory accounts well for experiments of α_s but the theory of Stockmayer and Fixman[7] is in disagreement with experimental results of α_s.[13,15-17] That is, an apparent contradiction is found between the behavior of α_s and that of α_η. Moreover, the contradiction between α_s and α_η is explained with different reasons by different authors.[16,18,19]

The difference of the reason for the contradiction is due to differences in the methods of estimating z employed by Berry[15] and by Novisuye, *et al.*[13] Berry assumed that in poor solvents B is expressed by a linear function of $(1 - \Theta/T)$ over the whole experimental range as follows

$$B = B_0(1 - \Theta/T) \quad (6)$$

and determined the value of constant B_0 from the temperature dependence of second virial coefficient.[15] Using the values of z thus determined, Berry concluded that the theory of Flory (eq 1) or, rather, the theory of Flory and Fisk[4] which is slightly modified, is valid over the whole experimental range of molecular weights. In contrast to the procedure of Berry, Norisuye, *et al.*,[13] and also Tanaka, Imai, and Yamakawa[17] emphasized that z may not necessarily be linear with respect to $(1 - \Theta/T)$ over a wide range of temperature, though it should be linear with respect to $M^{1/2}$. Using this criterion for z and also a criterion concerning the relationship between second virial coefficient and expansion factor, they examined the current theories and concluded that a theory of Yamakawa and Tanaka,[11] which is of the α^4-type, and also the theory of Flory[1-4,9] are valid over the whole experimental range of molecular weight. Then, they calculated z from the data of α_s^2 using the theory of Yamakawa and Tanaka.[11]

In spite of these important researches, a question still remains as to the reliability of the methods not only of Berry, but also of Norisuye, *et al.*, to estimate z. As indicated in the following discussion, the proportionallity of z to square root of molecular weight is not sensitive enough to distinguish among the theories *if the molecular weights are low.* If we assume that α_s over the whole range of molecular weight might be expressed by an equation in z, we would easily overlook the failure of a theory of the α^5-type in the range of low molecular weights.

It is our opinion that, at the present stage of theory, molecular weight may be the only reliable parameter in good solvents. Therefore, one of the purposes in the present work is to examine the current theories dealing with α_s using molecular weight, only, and to examine the method of determining z experimentally. To do so, it is necessary to extend our experiments to much higher molecular weights than those used in previous researches, *i.e.*, to determine the radius of gyration of high molecular weight polymers in good solvents. It is also one of the purposes in this work to study the method of determining the radius of gyration of high molecular weight polymers in good solvents. Our discussion on the difference between the behavior of α_s and that of α_η will be given in an accompanying paper.[20]

Experimental Section

Samples. The poly(α-methylstyrene) samples used in this work were prepared by the anionic polymerization method with *n*-BuLi, as reported previously.[21] The purification, fractionation, and molecular weight distribution determination of the samples were reported in previous papers.[21-24]

Recently, Cowie and Bywater[25] reported that the tacticity of poly(α-methylstyrene) depends on the polymerization method employed, and the solution properties of the samples, such as the Θ temperature and unperturbed dimensions, are affected by the tacticity. The nmr spectra of our

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poly(α-methylstyrenes) were determined with a JNMC-60 spectrometer on 10% solutions of the samples in carbon disulfide at 40°. There have been many discussions about the assignment of the peaks in the nmr spectrum of poly(α-methylstyrene).[26-31] However, because it is unnecessary in this work to determine absolute values of tacticity of the samples, we calculated the amounts of iso, syndio, and heterotactic forms using the method of Brownstein, Bywater, and Worsfold.[26] Figure 1 shows the change in the fraction of the various forms with molecular weight thus determined. Thus we may conclude that the tacticity of our samples is independent of molecular weight if the molecular weight is higher than 2×10^5.

Solvents. Benzene and toluene were purified by shaking with concentrated sulfuric acid until free from thiophene and no color remained in acid layer; then with water, dilute sodium hydroxide, and two portions of water. The benzene and the toluene were dried by shaking with calcium chloride, followed by fractional distillation over sodium metal in a stream of dried-nitrogen gas to avoid oxidation. The method of purification of cyclohexane is the same as reported previously.[23] Methylcyclohexane used for viscosity measurements was purified by the same method as for cyclohexane.

Commercially available decalin, after removing impurities by shaking with acid, was stirred with aluminium trichloride powder at room temperature for 1 week in order to isomerize the cis form to the trans form and was fractionally distilled *in vacuo* over sodium metal in a stream of nitrogen gas. The purity of *trans*-decalin thus purified was more than 99.8% by gas chromatography.

Light Scattering Measurement. The weight-average molecular weights of the samples were determined in cyclohexane, in toluene, and in *trans*-decalin at various temperature ranges using an instrument modified from a Shimadzu photoelectric light-scattering photometer, as was reported in detail previously.[23,32] Unpolarized light of 436 mμ was used as incident beam. The solvents and solutions were filtered directly into the cell through Millipore filters of 0.3 and 0.45 μ pore sizes.

The relative intensity of scattered light from polymer solutions is generally given by the following equations[33]

$$Kc/R_\theta = 1/M_wP(\theta) + 2A_2(P_2(\theta)/P(\theta)^2)c + \cdots \qquad (7)$$

where

$$K = 2\pi^2 n_0^2(\partial n/\partial c)^2/N_A\lambda_0 \qquad (8)$$

and n_0 is the refractive index of solvent, $(\partial n/\partial c)$ refractive index increment of the solution, N_A Avogadro's number, λ_0 the wavelength of the incident beam *in vacuo*, R_θ excess scattering intensity of polymer solute at scattering angle θ, c concentration of polymer solute, M_w weight-average molecular weight, A_2 second virial coefficient, $P(\theta)$ and $P_2(\theta)$ are particle scattering factors from one and two polymer molecules, respectively. We can obtain $P(\theta)$ from

$$(R_\theta)_{c=0}/(R_\theta)_{c=0,\theta=0} = P(\theta) \qquad (9)$$

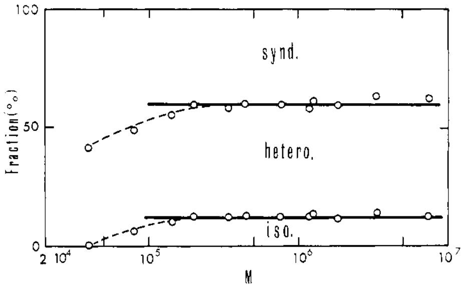

Figure 1. Relationship between the fractions of three stereoregular configuration forms (%) and molecular weights. The lower curve denotes the fraction of isotactic form and the upper curve denotes the sum of isotactic and heterotactic forms. Therefore, the fraction of syndiotactic form is given by the distance between the line of 100% and the upper curve.

Debye[34] calculated the $P(\theta)$ function for a Gaussian chain as follows

$$P(\theta) = (2/x^2)(\exp(-x) - 1 + x) \qquad (10)$$

$$x = 16\pi^2(n_0/\lambda_0)^2\langle S^2\rangle \sin^2(\theta/2) \qquad (11)$$

When $x < 1$, $P(\theta)$ is expanded into a series of x as follows

$$P(\theta)^{-1} = 1 + x/3 + x^2/36 + O(x^3) + \cdots \qquad (12a)$$

$$= (1 + x/6)^2 + \cdots \qquad (12b)$$

using which we may calculate $\langle S^2\rangle$ from the initial slope of a plot of $(Kc/R_\theta)_{c=0}{}^{1/2}$ *vs.* $\sin^2(\theta/2)$. For a molecular weight of several million however, it is difficult to estimate $\langle S^2\rangle$ from the initial slope. Then, we plot the observed $P(\theta)$ against $\sin^2(\theta/2)$ and determine $\langle S^2\rangle$ values so that the best fit may be found between the observed $P(\theta)$ and eq 10. One example is shown in Figure 2. The reason for the use of eq 10 in good solvents will be discussed below.

By extrapolating the values of (Kc/R_θ) observed at various angles to 0°, we determine $(Kc/R_\theta)_{\theta=0}$ and plot them against c. Now

$$(Kc/R_\theta)_{\theta=0} = 1/M_w + 2A_2c + 3A_3c^2 + \cdots \qquad (13)$$

In poor solvents, we estimate the second virial coefficient A_2 from the initial slope of the $(Kc/R_\theta)_{\theta=0}$ *vs.* c plot thus obtained. In good solvents, however, the third virial coefficient A_3 cannot be neglected compared with A_2. Following the method of Flory,[3] therefore, we assume

$$A_3 = gA_2{}^2M_w \qquad (14)$$

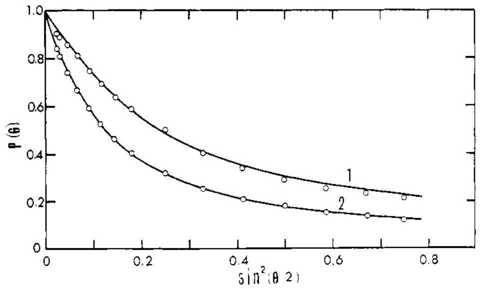

Figure 2. Examples of fitting the observed values with the particle scattering factors $P(\theta)$ of Debye.[34] The upper and lower points show the data of PαS-14 in *trans*-decalin at 10 and 50°, respectively. The solid lines are the calculated values of Debye with $\langle S^2\rangle = 59.85 \times 10^{-12}$ and $\langle S^2\rangle = 117.9 \times 10^{-12}$ cm², respectively.

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TABLE I
MOLECULAR CHARACTERISTICS OF MONODISPERSE POLY(α-METHYLSTYRENE)

Samples	$M_w \times 10^{-6}$	Solvents used in expts	$M_n \times 10^{-6}$	M_w/M_n
PαS-1			0.039_3	
PαS-2			0.080_1	
PαS-3			0.142	
PαS-4	0.20_4	T	0.204	1.00
PαS-5	0.34_2	T	0.340	1.005
PαS-6	0.44_4	T	0.438	1.014
PαS-7	0.69_4	T	0.680	1.02
PαS-8	0.768	D		
PαS-9	1.19	D	1.18	1.008
PαS-10	1.24	T		
PαS-11	1.46	T		
PαS-12	1.82	D		
PαS-13	3.30	D		
PαS-14	7.47	D		

TABLE II
MOLECULAR CHARACTERISTICS OF MONODISPERSE POLY(α-METHYLSTYRENE)

Samples	$10^4 A_2^{\mathrm{LS}\ a}$	$10^{12}\langle S^2 \rangle,^a$ cm^2	10^4 $A_2^{\mathrm{osmo}\ a}$	$10^{12}\langle S^2 \rangle_0$ (in D,Θ)	10^{12} $\langle S^2 \rangle_0$ (in C,Θ)
PαS-1			5.77		
PαS-2			4.74		
PαS-4	3.24	3.18	3.59		
PαS-5	2.80	4.98	3.13		2.81
PαS-6	2.65	7.31	2.88		
PαS-7	2.20	11.9	2.50		
PαS-8				6.15	
PαS-9	1.85	23.0	2.12	9.55	10.5
PαS-10	1.94	20.9			
PαS-11	1.82	30.7			
PαS-12	1.67	39.7		15.9_6	15.7
PαS-13	1.48	73.3		26.0_1	27.3
PαS-14	1.17	187.0		58.52	61.8

[a] In toluene, at 25°.

with $g = {}^1/_3$. That is, we have

$$(Kc/R_\theta)_{\theta=0}{}^{1/2} = (1/M_w)^{1/2}(1 + A_2M_wc) \qquad (15)$$

From the initial slope of $(M_wKc/R_\theta)_{\theta=0}{}^{1/2}$ *vs.* c plot, we can determine A_2.

Osmotic Pressure Measurements. Osmotic pressure measurements were carried out at 25.0 ± 0.01° by a high-speed membrane osmometer, type-502, of the Hewlett-Packard Co. The membranes used were S&S type-08 of Carl Schleicher and Schuell Co. for toluene solutions. The membrane conditioning was carried out by using mixtures of water–ethanol and ethanol–toluene.

The following equations are used to calculate the number-average molecular weights M_n

$$(\pi/c)^{1/2} = (\pi/c)_0{}^{1/2}(1 + (\Gamma_2/2)c) \qquad (16)$$

where $M_n = RT/(\pi/c)_0$, $A_2 = (\pi/c)_0\Gamma_2/RT$. In this case, we use the assumption, $\Gamma_3 = g\Gamma_2{}^2$ with $g = {}^1/_4$. The difference between g in light scattering and that in osmometry should be noted.

The polymer samples were dissolved in solvents and stored for several days in a thermostated box at 60°. The solutions were occasionally shaken by hand to avoid degradation by strong stirring. The dissolution states of the samples were checked by viscosity measurements at constant time intervals. If the molecular weight was higher than 3×10^6, we needed about 1 week until the viscosity became constant.

Results

M_w, M_n, and other molecular characteristics of the samples used in this work are listed in Tables I and II. Since the weight-average molecular weights of a sample, observed in cyclohexane, in *trans*-decalin, and in toluene at various temperatures, agreed with each other within experimental uncertainty (5%), we show the values determined in toluene (T) or *trans*-decalin (D) in Table I together with solvents used. The number-average molecular weights from osmotic pressure measurements, carried out in toluene at 25°, are also listed in the fourth column of the table. From the table we may conclude that the molecular weight distributions of the samples are very narrow and the ratios, M_w/M_n, are nearly unity. Θ temperatures were determined in cyclohexane and in *trans*-decalin by plotting the second virial coefficient A_2 against temperature. The Θ temperature in cyclohexane, as reported previously,[23] is 34.5 ± 0.5° over the whole range of molecular weights, while in *trans*-decalin, the Θ temperature is 9.5 ± 0.5°. The values of unperturbed dimensions $\langle S^2 \rangle_0$ were determined by interpolation in $\langle S^2 \rangle$ *vs.* $(1 - \Theta/T)$ plots at $T = \Theta$.

The observed values of $\langle S^2 \rangle_0/M$ were found to be independent of molecular weight both in cyclohexane and in *trans*-decalin, the average values of $\langle S^2 \rangle_0/M$ being 8.4 $\times 10^{-18}$ in cyclohexane and 8.0 $\times 10^{-18}$ in *trans*-decalin, respectively. The difference of the value in cyclohexane from the previously reported value ($\langle S^2 \rangle_0/M = 9.1 \times 10^{-18}$) was caused by our reevaluation of molecular weights of the samples used in the previous paper,[23] but the difference does not affect the conclusion in the previous paper at all. The value $\langle S^2 \rangle_0/M = 8.4 \times 10^{-18}$ in cyclohexane is in very good agreement with the data of Mijnlieff and Coumou.[35]

The discrepancy between the unperturbed dimensions in cyclohexane and in *trans*-decalin is significant and may be caused by either a solvent effect, due to the difference in the chemical structures of cyclohexane and *trans*-decalin, or a temperature effect. Since both solvents are nonpolar, however, it may be more reasonable to assume that the difference of chemical structure would not affect the unperturbed dimension much. Furthermore, it can be assumed that the unperturbed dimensions increase linearly from the value at 9.5° to that at 35° and become nearly constant at temperatures higher than 35°, by taking into account the change of K_θ in the viscosity equation $[\eta]_0 = K_\theta M_w{}^{1/2}$ with temperature, as shown in the accompanying paper.[20] This assumption is not important for our present purpose, since the change in $\langle S^2 \rangle_0$ with temperature can modify the calculated expansion factor only slightly.

Figure 3 shows the molecular weight dependence of the second virial coefficients observed in toluene from both light scattering and osmotic pressure measurements. In spite of the narrow molecular weight distribution of the present samples, a discrepancy is found between the second virial coefficients observed by osmotic

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pressure measurement and by light-scattering measurment, A_2^{osmo} and A_2^{LS} A_2^{osmo} is larger than A_2^{LS}. This is caused by the difference in the assumptions about g values, that is, by the fact that $g = {}^1/_4$ is assumed in eq 16 whereas $g = {}^1/_3$ in eq 15. If we assume $g = {}^1/_3$ in eq 16 the values of A_2 from osmotic pressure data become identical with the values from light-scattering data, as shown in Figure 3. Therefore, we employ A_2^{LS} calculated from eq 15 for the sake of convenience. Moreover, it is to be noted that if we determine A_3 by using a method of Stockmayer and Casassa,[36] the values of A_2 obtained from light scattering and osmotic pressure data agree with each other and are identical with the values from light-scattering data.

Discussion

Determination of $\langle S^2\rangle$ in Good Solvents. The plot of $(Kc/R_\theta)_{c=0}$ *vs.* $\sin^2(\theta/2)$ for low molecular weight samples shows a straight line both in poor solvents and in good solvents so that the radius of gyration can be estimated from the initial slope of the straight line, whereas the plot for monodisperse polymer samples with high molecular weights shows an upward curvature even in poor solvents or in the Θ solvent. In poor solvents, a plot of $(Kc/R_\theta)_{c=0}^{1/2}$ *vs.* $\sin^2(\theta/2)$, as suggested by Berry,[15] is found to be effective, but in good solvents even $(Kc/R_\theta)_{c=0}^{1/2}$ *vs.* $\sin^2(\theta/2)$ plots show remarkable deviations from straight lines if the molecular weight is higher than 10^6, as can be seen in Figure 4. The only method we have at present for estimating the radius of gyration of monodisperse polymer with high molecular weights may be to find a value giving good agreement between the observed and theoretical values of $P^{-1}(\theta)$. In practice, $\langle S^2\rangle$ in poor or Θ solvents is determined so as to give satisfactory agreement between eq 10 and the experimental data in Figure 2.

In good solvent media, however, some discussion may be necessary to determine the appropriate theory of $P(\theta)$: Debye, Chu, and Kaufmann[37] fitted the observed angular dependence of scattered light at a finite polymer concentration to eq 10 by assuming that only the variation of a constant representing the radius of gyration with concentration could be adjusted in good solvents and the contribution of the particle-scattering factor from two molecules $P_2(\theta)$ in eq 7 is negligible. They concluded that the polymer conformation obeys Gaussian statistics even in good solvents. This method of Debye, *et al.*, corresponds to Flory's assumption[3] of the uniform expansion of a polymer coil due to the excluded volume effect of segments. Although Debye, *et al.*, applied the method to the data at finite concentrations, the method may be more safely adopted for $(Kc/R_\theta)_{c=0}$ values. A solid line (D) in Figure 4 shows $P^{-1}(\theta)$ calculated from eq 10 by using the value of x or $\langle S^2\rangle$ chosen to give the best agreement between the experimental data and eq 10. The agreement between the observed and calculated values is quite good at low scattering angles and the initial slope drawn with the value of $\langle S^2\rangle$ thus determined appears to be reasonable, as shown in the figure.

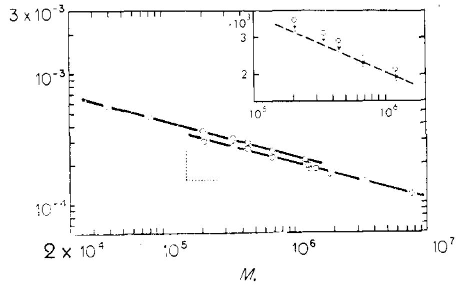

Figure 3. Plots of log A_2 *vs.* log M: O, A_2^{osmo}; ⦶, A_2^{LS}. Solid lines are drawn by the least-square method. The upper figure explains the detail of the relationship between A_2^{LS} and A_2^{osmo}. Small black points denoted by arrow show A_2^{osmo} obtained assuming $g = {}^1/_3$ in eq 16. The broken line denotes the experimental data of A_2^{LS}.

However, the application of the theory of Debye to the light scattering in good solvent has been criticized by many authors.[35,38,39] That is, Gaussian statistics should fail due to the excluded volume effect in good solvent media. Ptitsyn[38] assumed that the excluded volume effect does not alter the Gaussian character of the distribution function $W(i,j)$ for the distance between two repeating units, i and j, but influences the mean square distance $\langle r_{ij}^2\rangle$ between them, so that

$$W(i,j)\mathrm{d}r_{ij} = 4\pi(3/2\pi\langle r_{ij}^2\rangle)^{3/2}\exp(-3r_{ij}^2/2\langle r_{ij}^2\rangle)r_{ij}^2\mathrm{d}r_{ij} \tag{17}$$

where

$$\langle r_{ij}^2\rangle = \alpha_0^2(j - i)^{1+\epsilon}a^2 \tag{18}$$

and α_0, a, ϵ are constants representing the uniform expansion, the length of repeating unit, and the non-Gaussian character, respectively. If $\epsilon = 0$, the theory of Ptitsyn agrees with that of Debye, *et al.*[37] Using

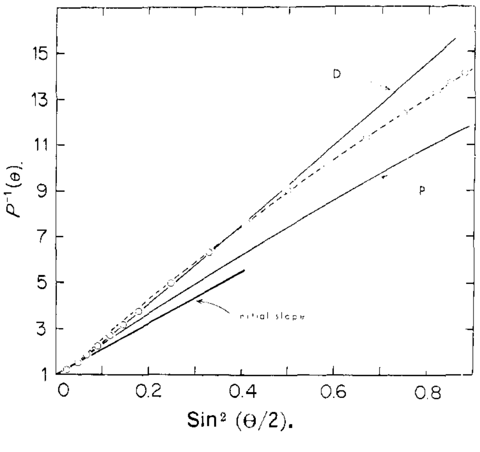

Figure 4. Plots of $P^{-1}(\theta)$ *vs.* $\sin^2(\theta/2)$ of PαS-14 in toluene at 25°: D and P show the theoretical curves of Debye[34] (eq 10) and that of Ptitsyn[38] (eq 19) by using $\epsilon = 0.15$ and $\langle S^2\rangle = 187 \times 10^{-12}$ cm², respectively. The broken line shows the theoretical curve of Ptitsyn, assuming $\epsilon = 0.15$ and $\langle S^2\rangle = 230 \times 10^{-12}$ cm².

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(36) W. H. Stockmayer and E. F. Casassa, *J. Chem. Phys.*, **20**, 1560 (1952).

(37) P. Debye, B. Chu, and H. Kaufmann, *J. Polym. Sci., Part A*, **1**, 2387 (1963).

(38) O. B. Ptitsyn, *Zh. Fiz. Khim.*, **31**, 1091 (1957).

(39) H. Benoit, *C. R. Acad. Sci., Paris*, **245**, 2244 (1957), and C. Loucheux, G. Weill, and H. Benoit, *J. Chim. Phys.*, **55**, 540 (1958).

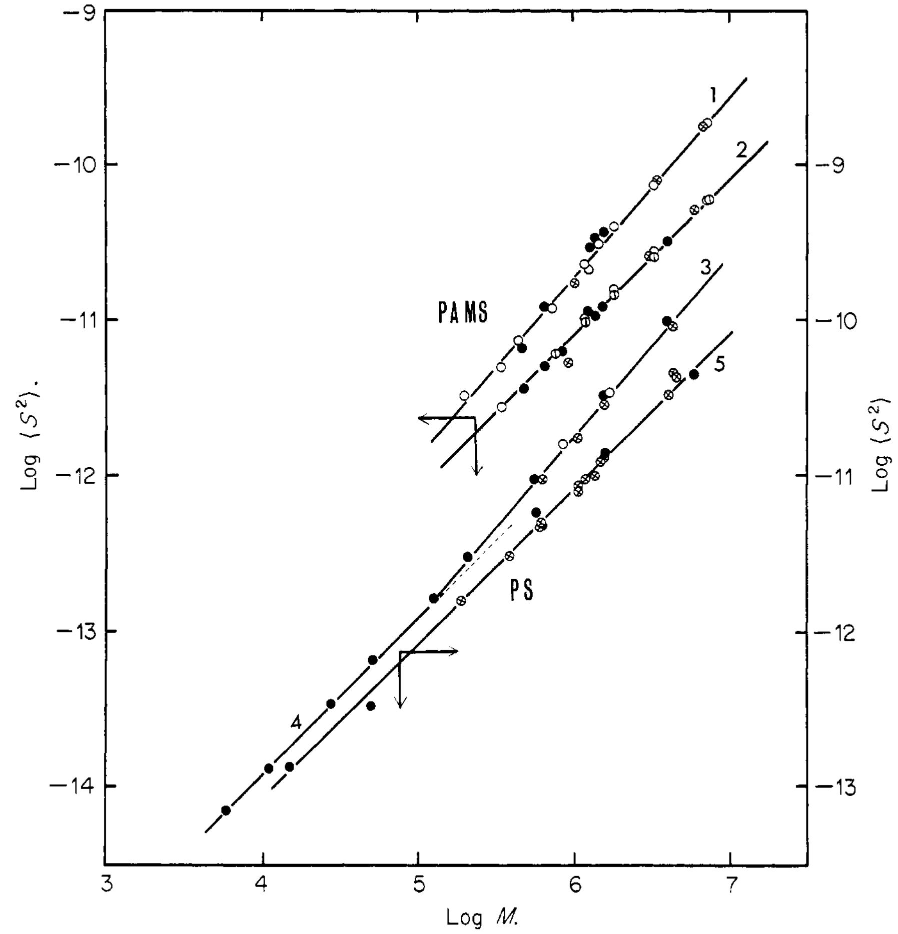

Figure 5. Molecular weight dependence of the radius of gyration. Lines 1 and 2 show the data for poly(α-methylstyrne), and lines 3, 4, and 5 show the data for polystyrenes. Line 1, the best fit to the present data in toluene at 25° (○); ●, the data of Cowie, Bywater, and Worsfold[43] in toluene at 37°; ⊗, the data of Mijnlieff, *et al.*,[35] at 23°. Line 2, the best fit to the present data in cyclohexane at 35° (○); ◐, that in *trans*-decalin at 9.5°; ●, Cowie, *et al.*, in cyclohexane at 37°; ⊗, Mijnieff, *et al.*, in cyclohexane 35°. Line 3, the best fit to the data of Kirste, *et al.*,[41] (●) in toluene at 25° and our data (○) in toluene at 25°; ⊗, Berry in toluene at 12°. Line 4, the data of Kirste, *et al.*, for lower molecular weight samples. Line 5, the data of Kirste, *et al.*, (●) and Berry (⊗) in Θ solvents.

the method of Debye[34] together with this assumption, Ptitsyn obtained the following equation for $P^{-1}(\theta)$ in good solvents

$$P^{-1}(\theta) = \frac{(1+\epsilon)(1+5\epsilon/6+\epsilon^2/6)^{1/(1+\epsilon)}x^{1/(1+\epsilon)}}{2\Gamma\{1/(1+\epsilon)\}} + \frac{(1+\epsilon)\Gamma\{2/(1+\epsilon)\}}{2\Gamma^2\{1/(1+\epsilon)\}} \quad (19)$$

It was suggested that ϵ may be determined from the relationships between radius of gyration or limiting viscosity number and molecular weight (see eq 18). Experimental tests of both Debye's and Ptitsyn's theories were reported by Smith and Carpenter.[40] They showed that as long as the molecular weight of polymer was less than a few million, eq 10 fits the experimental results better than eq 19. For molecular weights greater than a few million, however, it was necessary to use the Ptitsyn function to fit the data, but with an excluded volume parameter ϵ smaller than the *a priori* value calculated from viscosity data.

For poly(α-methylstyrene) in toluene, we obtain ϵ = 0.15 from the experimental molecular weight dependence of $\langle S^2\rangle$, as shown in Figure 5. The values of ϵ agree with the values estimated from the molecular weight dependence of $[\eta]$. The values of $P^{-1}(\theta)$ calculated from eq 19, assuming ϵ = 0.15 and the same value of $\langle S^2\rangle$ as used for the line D, are also shown by a solid line P in Figure 4. The agreement between theory and experiment is much poorer than that found between the theory of Debye (eq 10) and the experimental data. This result is in accord with the results of Smith and Carpenter. In order to have good agreement between the calculated values and the observed ones at higher angles, it is necessary to reduce ϵ or to increase $\langle S^2\rangle$. However, there is no theoretical basis for adjusting the value of ϵ, but there is indeed a possibility that $\langle S^2\rangle$ might be larger than that calculated applying the Debye theory.[34] If we choose a larger value for $\langle S^2\rangle$ to have good agreement between the calculated and the observed $P(\theta)$ at higher angles, however, clear disagreement is found at lower scattering angles as shown by broken line in Figure 4.[35]

The reason for the failure of the theory of Ptitsyn[38] and others[39] may become clear if we plot the experimental values of radius of gyration against molecular

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(40) T. E. Smith and D. K. Carpenter, *Macromolecules*, **1**, 204 (1968).

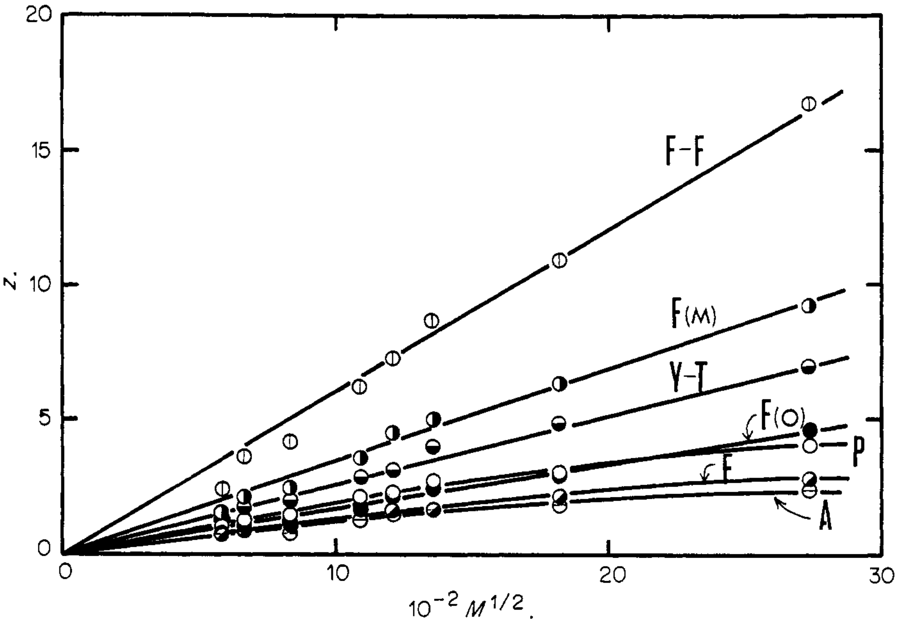

Figure 6. Relationships between z molecular weight for poly(α-methylstyrene) in toluene at 25°: ⦶, for which z was estimated from the theory of Flory and Fisk;[4] ◑, from the theory of Flory modified by Stockmayer;[9] ◒, the theory of Yamakawa and Tanaka;[11] ●, the theory of Flory;[1-3] ○, the theory of Ptitsyn;[10] ◔, the theory of Stockmayer and Fixman;[7] ⊖, the theory of Alexandrowicz.[12]

weight over a wide range of molecular weight. Figure 5 gives the radius of gyration of polystyrenes as a function of molecular weight reported by Kirste and Wild[41] and Berry,[15] together with our present data for poly(α-methylstyrenes) and also for a few samples of polystyrenes of Pressure Chemical Co. It is clear that we underestimate the mean square length of short chains in the theory of Ptitsyn. The value of ϵ for polystyrenes with higher molecular weights is 0.15, whereas the value of ϵ for the samples with molecular weights lower than 10^5 is nearly zero. Thus, we might have better agreement between theory and experiments if we express ϵ as a function of chain length. It should also be recalled that the distance between two repeating units i and j in a molecule is determined not only by the excluded volume effect of the segments between i and j but also by the effect of the remaining parts of the molecule, so that the polymer chain may be expanded more uniformly than predicted from the theory of Ptitsyn.[38]

Thus, we conclude that the theory of Debye, eq 10, can be used even when we determine the radius of gyration of very high molecular weight samples in good solvent media. The disagreement between the theory of Debye and the experimental data at high angles in Figure 4 should not be taken seriously since the disagreement might be due to the non-Gaussian character of polymer conformation. In order to improve the theory of Ptitsyn, McIntyre, Mazur, and Wims[42] introduced a parameter t to modify the distribution function $W(i,j)$ into a non-Gaussian form (see eq 9 of ref 42). In practice, if we assume $t = 3$ with $\epsilon = 0.15$, we can find satisfactory agreement between the calculated values and the experimental data by using the same value of $\langle S^2 \rangle$ as used to calculate the lines D and P. However, it is outside the scope of this paper to discuss on the validity of the theory of McIntyre, *et al.* It is sufficient for the present purpose if we can confirm that the reliable radius of gyration can be obtained from the theory of Debye[34] even in good solvent media.

Expansion Factor. Norisuye, *et al.*,[13] and Tanaka, *et al.*,[17] suggested that the validity of the theories presented by previous authors may be examined by checking the proportionality of z calculated from those theories to $M^{1/2}$. The values of z estimated from the present experimental data of α_s in toluene were plotted againt $M^{1/2}$ in Figure 6. It is observed, in agreement with the conclusions of previous investigators,[13,17] that the theories of Flory[3] and also the theory of Yamakawa and Tanaka[11] of the α^4-type show better agreement with our experimental results than the theory of Stockmayer and Fixman (the α^3-type).[7] Here, however, we would like to point out that if the molecular weights are low it is difficult to find the nonproportionality of z to $M^{1/2}$ from such plots of z *vs.* $M^{1/2}$, since the deviation is found *at low molecular weights.* This can be shown by replotting the data in the form of $z/M^{1/2}$ *vs.* log M. Figure 7 shows the plots of $(\alpha_s^5 - \alpha_s^3)/M^{1/2}$ as well as $(\alpha_s^3 - 1)/M^{1/2}$ *vs.* log M in toluene. It is clear that $(\alpha_s^5 - \alpha_s^3)/M^{1/2}$ is independent of M if M is higher than 10^6. As M decreases, however, $(\alpha_s^5 - \alpha_s^3)/M^{1/2}$ appears to show deviation from the constant value. Figure 7 also shows the plot of $(\alpha_s^3 - 1)/M^{1/2}$ *vs.* log M, in which it appears that $(\alpha_s^3 - 1)/M^{1/2}$ becomes constant at M lower than 10^6. The nonproportionality of $(\alpha_s^3 - 1)$ to $M^{1/2}$ can easily be detected since deviation from the linear relationship manifests itself *at high molecular weights.* Thus, we may conclude that the theory of Flory (the α^5-type equation) is valid in toluene at least if M is higher than, say, 10^6, but we reserve our conclusion on the behavior of low molecular weight polymers.

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(41) R. G. Kirste and G. Wild, *Makromol. Chem.*, **121**, 174 (1969).

(42) D. McIntyre, J. Mazur, and A. M. Wims, *J. Chem. Phys.*, **49**, 2887 (1968); and J. Mazur, D. McIntyre, and A. M. Wims, *ibid.*, **49**, 2896 (1968).

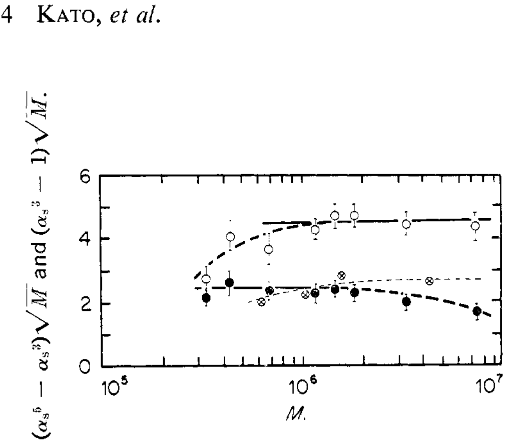

Figure 7. Plots of $(\alpha_s^5-\alpha_s^3)/M^{1/2}$ (○) as well as $(\alpha_s^3-1)M^{1/2}$ (●) *vs.* log M for poly(α-methylstyrene) in toluene at 25°: ⊗, $(\alpha_s^5-\alpha_s^3)/M^{1/2}$ of Berry[15] for polystyrene.

The expansion factor α_s in *trans*-decalin is not high enough to examine the validity of the theories by the above method, but at least it is sure that the theory of Flory is valid if M is higher than 10^6 where reliable data are available.

For the samples of molecular weights higher than 10^6 in *trans*-decalin, $(\alpha_s^5-\alpha_s^3)$ is plotted against the experimental values of $(1-\Theta/T)\,(\langle S^2\rangle_0/M)^{-3/2}M^{1/2}$ in Figure 8. The straight line passing through the origin shows the validity of the proportionality of $(\alpha_s^5-\alpha_s^3)$ to $M^{1/2}$. The value of B_0 in decalin calculated from the slope of the straight line is $B_0 = 1.52 \times 10^{-28}$ according to $(\alpha_s^5-\alpha_s^3) = (134/105)z$ and $B_0 = 0.75 \times 10^{-28}$ according to $(\alpha_s^5-\alpha_s^3) = 2.60z$ (see eq 1). If we estimate the values of z from the theory of Yamakawa and Tanaka[11] as well as from the theory of Flory and Fisk,[4] we have $B_0 = 1.28 \times 10^{-28}$ and 2.59×10^{-28}, respectively. Furthermore, B_0 can be estimated from the temperature dependence of second virial coefficient as proposed by Berry[15] if the temperature is close to Θ. The plot of $A_2/h(\bar{z})$ *vs.* $(1-\Theta/T)$ in decalin, where $h(\bar{z})$ is the function representing the interpenetration of two molecules as explained later, is shown in Figure 9 in which the line with $B_0 = 1.52 \times 10^{-28}$ appears to be reasonable, but the lines with other B_0 values, for examples, $B_0 = 0.75 \times 10^{-28}$ and 1.28×10^{-28}, are clearly outside the range of experimental points. Thus, we employ $B_0 = 1.52 \times 10^{-28}$ in decalin for the further discussion in this work.

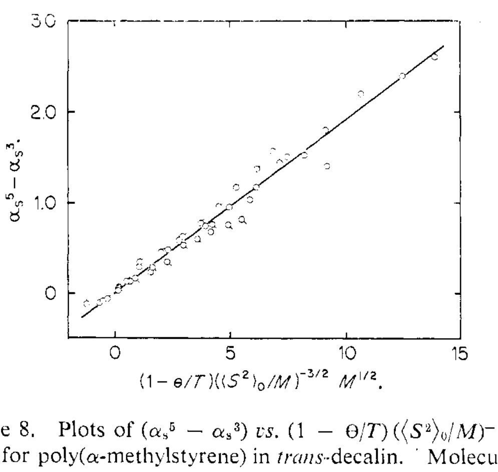

Figure 8. Plots of $(\alpha_s^5-\alpha_s^3)$ *vs.* $(1-\Theta/T)\,(\langle S^2\rangle_0/M)^{-3/2}M^{1/2}$ for poly(α-methylstyrene) in *trans*-decalin. Molecular weights of the samples are higher than 10^6, *i.e.*, ○, for PαS-14; ○, for PαS-13; ○, for PαS-12; ○, for PαS-9.

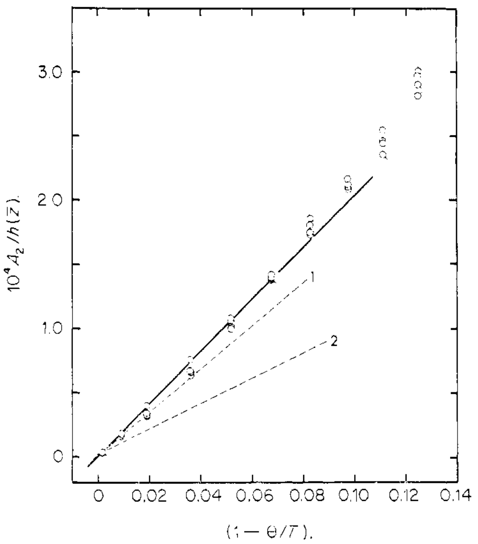

Figure 9. Plots of $A_2/h(\bar{z})$ *vs.* $(1-\Theta/T)$ for poly(α-methylstyrene) in *trans*-decalin. Pips show the same samples as in Figure 8. The solid line shows $B_0 = 1.52 \times 10^{-28}$. Line 1 and line 2 show $B_0 = 1.28 \times 10^{-28}$ and $B_0 = 0.75 \times 10^{-28}$, respectively.

Thus, we may conclude that $(\alpha_s^5-\alpha_s^3) = (134/105)z$ can account for the z dependence of the expansion factor both in good solvent and in poor solvent if the molecular weight is higher than 10^6. The z values in toluene may, therefore, be calculated from α_s using eq 1 if M is higher than 10^6. In practice, we have

$$z = 1.1 \times 10^{-28}(1-\Theta/T)(\langle S^2\rangle_0/M)^{-3/2}M^{1/2} \quad (20)$$

in cyclohexane

$$z = 1.52 \times 10^{-28}(1-\Theta/T)(\langle S^2\rangle_0/M)^{-3/2}M^{1/2} \quad (21)$$

in *trans*-decalin

$$z = 3.45 \times 10^{-3}M^{1/2} \quad (22)$$

in toluene.

Here, it is pertinent to compare our situation with the situations of previous workers. The values of $A_2M^{1/2}$ in decalin and toluene are plotted against the z values estimated from the above equations in Figure 10, to confirm that z values thus calculated in decalin can be connected smoothly to z values in toluene. Figure 10 shows that the method of Berry[15] to estimate z in good solvent is correct if B_0 determined from the temperature dependence of A_2 (Figure 9) is reliable. However, we found it fairly difficult to determine B_0 from the temperature dependence of A_2 in the vicinity of Θ, as was pointed out by Yamakawa[16] and also as can be seen in Figure 9. On the other hand, Norisuye, *et al.*,[13] determined z from the data of α_s using the equation of Yamakawa and Tanaka.[11] If we apply this method to our data to calculate z, $A_2M^{1/2}$ *vs.* z plot in toluene thus obtained does not make a single curve together with $A_2M^{1/2}$ *vs.* z plot in *trans*-decalin determined with $B_0 = 1.52 \times 10^{-28}$, as shown in Figure 10. The same thing can be found for the theory of Flory and Fisk.[4] If the theory of Flory (eq 1) is used and also if M is higher than, say, 10^6, no contradiction is found as seen in Figure 10. Thus, when M is high enough to get reliable data of α_s, that is, if M

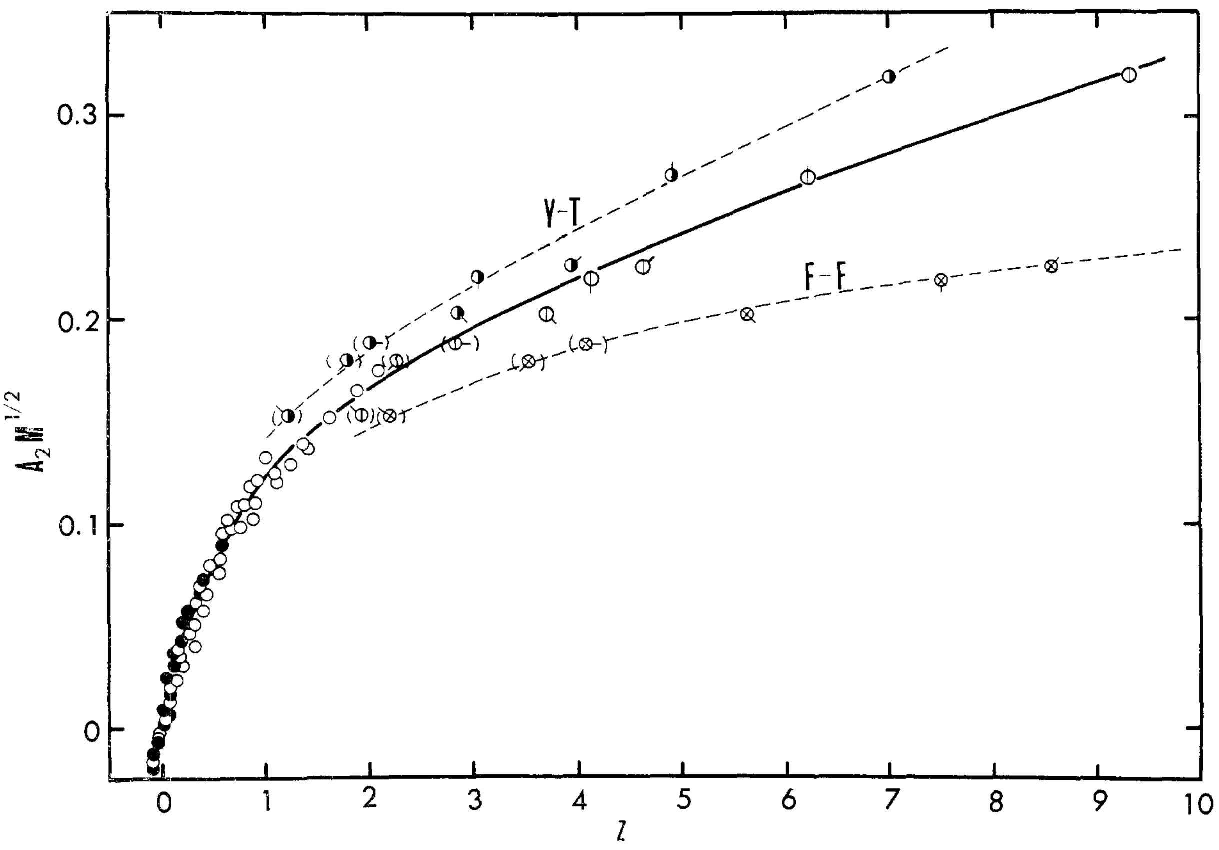

Figure 10. Relationship between $A_2M^{1/2}$ and the calculated z for poly(α-methylstyrene): ●, z in cyclohexane calculated from eq 20; ○, z in *trans*-decalin calculated from eq 21; ⦶, z in toluene calculated from eq 22. Curve Y–T shows the best fit to z calculated from the equation of Yamakawa and Tanaka[11] (◑); curve F–F shows the best fit to z calculated from the equation of Flory and Fisk[4] (⊗). Parentheses show the data for samples with molecular weight lower than 10^6, that is, ⦶, PαS-7; ⦶, PαS-6; ⦶, PαS-5. The other pips show the same samples as in Figure 8.

is higher than, say, 10^6, we agree with previous workers that the theory of Flory is the best of all theories on α_s.

If M is lower than 10^6, however, the theory of Flory appears to become inapplicable in toluene as can be seen in Figure 7, but the error in the determination of α_s prevents us from having any definite conclusion on this problem in this paper. From experimental data of α_s for polymers of low molecular weights found in the literature, too, we cannot obtain any conclusion. For example, the data of Berry[15] are shown in Figure 7. The data of Kirste, *et al.*,[41] on polystyrenes and poly(methyl methacrylates) indicate that $(\alpha_s^5 - \alpha_s^3)/M^{1/2}$ deviate from a constant value as M decreases, but the directions of deviation are different with the samples—upward for polystyrene, downward for poly(methyl methacrylate). The data of Norisuye, *et al.*,[13] give a constant value to $(\alpha_s^5 - \alpha_s^3)/M^{1/2}$ over the whole range of molecular weight. It is our opinion that the reason for the variety of conclusions reported is in the ambiguity of $\langle S^2\rangle$, particularly of $\langle S^2\rangle_0$. Small discrepancy found between the data of Cowie, *et al.*,[43] and ours in Figure 5, small discrepancy between the data of Norisuye, *et al.*, and those of Hanafusa, Teramoto, and Fujita[44] on $\langle S^2\rangle_0$ of polychloroprene and the difference between the behavior of polystyrene and that of poly(methyl methacrylate) reported by Kirste, *et al.*,[41] are big enough to change the conclusion entirely. Therefore, we cannot conclude that the theory of Flory on α_s is valid over the whole range of molecular weight. The problem of the behavior of low molecular weight samples will be discussed further in the accompanying paper.

Second Virial Coefficient. The second virial coefficient A_2 is, in general, given by

$$A_2 = 4\pi^{3/2}N_A(\langle S^2\rangle^{3/2}/M)\bar{z}h(\bar{z}) \qquad (23)$$

and

$$\bar{z} = z/\alpha_s^3$$

where the function of $h(\bar{z})$ represents the effect of interpenetration of two molecules on A_2. A summary of $h(\bar{z})$ functions presented by various authors is given by Norisuye, *et al.*,[13] and others.[45] Here we show only two representatives

Flory, Krigbaum, and Orofino[46]

$$\bar{z}h(\bar{z}) = (1/C')\ln(1 + C'\bar{z}) \qquad (24)$$

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(43) J. M. G. Cowie, S. Bywater, and D. J. Worsfold, *Polymer*, 8, 105 (1967).

(44) K. Hanafusa, A. Teramoto, and H. Fujita, *J. Phys. Chem.*, 70, 4004 (1966).

(45) M. Kurata, M. Fukatsu, H. Sotobayashi, and H. Yamakawa, *J. Chem. Phys.*, **41**, 139 (1964).

(46) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950); T. A. Orofino and P. J. Flory, *ibid.*, **26**, 1067 (1957).

(47) E. F. Casassa and H. Markovitz, *ibid.*, **29**, 493 (1958); E. F. Casassa, *ibid.*, **31**, 800 (1959).

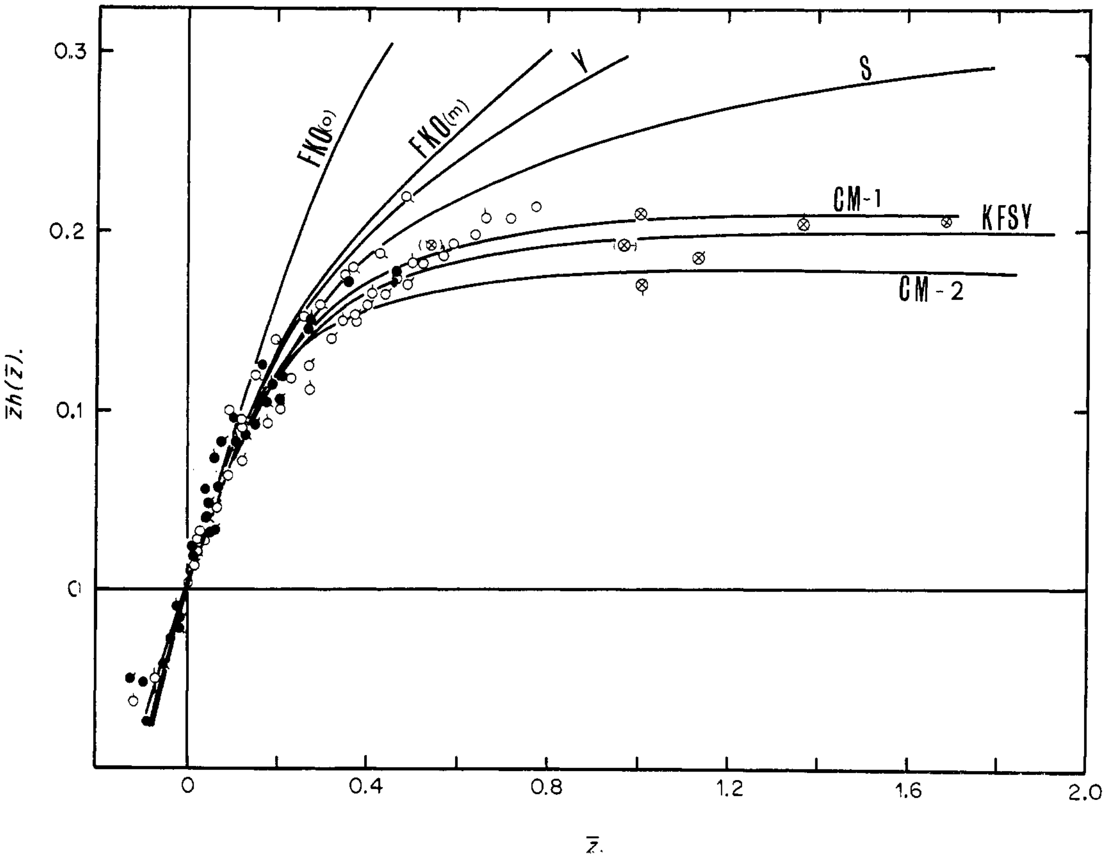

Figure 11. Comparison between the interpenetration function $\bar{z}h(\bar{z})$ and the theories. FKO(o) denotes the theory of Flory, Krigbaum, and Orofino;[46] FKO(m), that modified by Stockmayer;[9] Y, theory of Yamakawa;[16] S, theory of Stockmayer;[9] CM-1, theory of Casassa and Markovitz[7] combined with eq 28; CM-2, that combined with eq 27; KFSY, theory of Kurata, *et al.*;[45] ●, the data in cyclohexane; ○, in *trans*-decalin; ⊗, in toluene. Pips show the same samples as in Figures 8 and 10.

Casassa and Markovitz[47]

$$\bar{z}h(\bar{z}) = \{(\alpha_2/\alpha_s)^3/5.73\}(1 + \exp(-5.73\bar{z}(\alpha_2/\alpha_s)^3) \quad (25)$$

where C' is the numerical constant, *i.e.*, 2.30 according to Flory, *et al.*,[3,46] and 5.73 if modified corresponding to eq 1.[9] While α_s is the intramolecular expansion factor, α_2, in eq 25, is the intermolecular expansion factor. According to Casassa and Markovitz,[47] the latter is given by

$$\alpha_2^5 - \alpha_2^3 = (1.858\sim2.043)\bar{z} \quad (26)$$

If we assume $\alpha_s = \alpha_2$, we have

$$\bar{z}h(\bar{z}) = (1/5.73)(1 - \exp(-5.73\bar{z})) \quad (27)$$

This equation is practically equal to the equation of Kurata, *et al.*,[45] which was based on the same idea as used for eq 2.

Figure 10 shows that $A_2M^{1/2}$ is a function of z only over the whole range of solvent power. In order to compare our experimental data of A_2 with various theories, the interpenetration function $\bar{z}h(\bar{z})$ is calculated from the data using $\bar{z}h(\bar{z}) = (^1/_4\pi^{3/2}N_A)\,(A_2M^2/\langle S^2\rangle^{3/2})$ and are plotted against $\bar{z}$ in Figure 11. The observed values at large $\bar{z}$ are found to be between the curve of Casassa and Markovitz[47] and that of Flory.[46]

Our experimental results are in coincidence with the data of Berry,[15] Norisuye, *et al.*,[13] and Tanaka, *et al.*,[17] but are slightly lower than them at the limit of large $\bar{z}$. The difference between their results and ours, however, cannot be regarded as significant, if we take into account the effect of molecular weight distribution on $A_2M^2/\langle S^2\rangle^{3/2}$.

Calculated values of A_2 from various theories are shown in Figure 11 to be compared with the present experimental data. We may have the best agreement between theory and experiments if we assume

$$\alpha_2^5 - \alpha_2^3 = 1.858z \quad (28)$$

in the theory of Casassa and Markovitz.[47] The theory of Kurata, *et al.*,[45] is also in good agreement with the experimental data. This conclusion cannot be changed even if we allow a small variation of B_0. This conclusion can be confirmed by eliminating z from the equations of α_s and A_2 and then comparing the experimental plot of $\bar{z}h(\bar{z})$ *vs.* $(\alpha_s^2 - 1)$ with theories, as is commonly done.

Acknowledgment. We wish to thank Mr. T. Kitano for his contribution to the comparison between A_2^{LS} and A_2^{osmo}.