Thermodynamic and Hydrodynamic Properties of Linear Polymer Solutions. II. Limiting Viscosity Number of Monodisperse Poly(α-methylstyrene)[1]

Ichiro Noda, Kiyokazu Mizutani, Tadaya Kato,* Teruo Fujimoto, and Mitsuru Nagasawa

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan. Received May 19, 1970

ABSTRACT: The limiting viscosity numbers of monodisperse poly(α-methylstyrenes) used in the previous work are determined in Θ and good solvents. Expansion factors are calculated from the ratio of limiting viscosity number in good solvent to that in a Θ solvent and compared with the current theories. It is found that the viscosity expansion factor agrees with Flory's theory (α^5-type equation) if molecular weights are higher than, *e.g.*, 10^6. If molecular weights are lower, however, Stockmayer and Fixman's theory (α^3-type equation) appears to be more applicable than Flory's theory. Comparing the data with the recent results of Monte Carlo calculation by electronic computer and also with the expansion factor of radius of gyration reported previously, it is pointed out that one of the reasons for the failure of Flory's theory for low molecular weight samples would be due to the failure of the theory for expansion factor of the radius of gyration.

The limiting viscosity number of linear polymers, $[\eta]$ is given by[2,3]

$$[\eta] = \Phi(h,z)(\langle S^2\rangle_0/M)^{3/2}M^{1/2}\alpha_s^{3} \tag{1}$$

$$\alpha_s^{2} = \langle S^2\rangle/\langle S^2\rangle_0 \tag{1a}$$

$$h = (\zeta/3\pi\eta_0)(n^2/2\pi\langle S^2\rangle_0)^{1/2} \tag{1b}$$

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

where $B = B_0 g$, $\Phi(h,z)$ is a factor which is generally a function of drainage parameter h and excluded volume function z, $\langle S^2\rangle^{1/2}$ and $\langle S^2\rangle_0^{1/2}$ are the radii of gyration of the polymer in non-Θ and Θ solvents, respectively, η_0 is the solvent viscosity, n is the number of segments per molecule, ζ is the friction factor per segment, M is the molecular weight of the polymer, B_0 is a constant, and g, which is a function of $(1 - \Theta/T)$, is introduced taking into account the possibility that z is not linear with respect to $(1 - \Theta/T)$. Thus, the ratio of $[\eta]$ in good solvents to that in Θ solvents reduces to the form

$$[\eta]/[\eta]_0 = \alpha_\eta^{3} = [\Phi(h,z)/\Phi(h,0)]\alpha_s^{3} \tag{2}$$

Since, in general, $\Phi(h,z)$ changes with h and z, the relationship between α_η and α_s depends on the magnitudes of h and z. There are two extreme cases of hydrodynamic interaction. At the limit of free drainage, *i.e.*, at $h = 0$, we have, with no assumption[3]

$$\alpha_\eta^{3} = \alpha_s^{2} \tag{3}$$

At the limit of nondrainage, $h = \infty$, we have

$$\alpha_\eta^{3} = [\Phi(\infty,z)/\Phi(\infty,0)]\alpha_s^{3} \tag{4}$$

If $\Phi(\infty,z)/\Phi(\infty,0)$ is equal to unity irrespective of z, we have the familiar Flory and Fox relationship[4] which shows that α_η have the same z dependence of α_s

$$\alpha_\eta^{3} = \alpha_s^{3} \tag{5}$$

Even if eq 5 is not valid, α_η must be a unique function of z when $h = \infty$ in so far as α_s is a unique function of z. In the case of partial drainage, however, α_η is a complicated function of not only z but also h and, therefore, the dependence of α_η on molecular weight, solvent, and temperature may not always be equal to that of α_s. However, it should be noted that the nonunique dependence of α_η on z cannot necessarily be attributed to the presence of solvent drainage through polymer coil, as there is a possibility that α_s is not a unique function of z over the whole range of molecular weight.

As is discussed in the previous paper,[1] the experimental works[5–7] so far published agreed in that the behavior of α_s can be well explained by equations of the, so-called, α^5-type (*e.g.*, Flory's[8] and Flory–Fisk's[9] theories) at least when molecular weights are high enough to get reliable data of α_s. The α^3-type equations (*e.g.*, Kurata–Stockmayer–Roig's[10] or Stockmayer–Fixman's[11] theories) cannot explain the experimental data of α_s. Moreover, if molecular weight is high, α_η also agrees with the α^5-type equations.[12] On the other hand, it was experimentally shown by Kurata and Stockmayer[10] and, later, by many authors that the limiting viscosity number, *i.e.*, α_η agrees with the α^3-type equations if the excluded volume function, z, is small.

Concerning the relationship between the behavior of α_s and that of α_η, two quite different conclusions were

---

* To whom correspondence should be addressed.

(1) T. Kato, K. Miyaso, I. Noda, T. Fujimoto, and M. Nagasawa, *Macromolecules*, **3**, 777 (1970).

(2) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **16**, 565 (1948).

(3) M. Kurata and H. Yamakawa, *ibid.*, **29**, 311 (1958).

(4) P. J. Flory and T. G Fox, *J. Amer. Chem. Soc.*, **73**, 1904 (1951).

(5) G. C. Berry, *J. Chem. Phys.*, **44**, 4550 (1966).

(6) T. Norisuye, K. Kawahara, A. Teramoto, and H. Fujita, *ibid.*, **49**, 4330 (1968).

(7) G. Tanaka, S. Imai, and H. Yamakawa, *ibid.*, **52**, 2639 (1970).

(8) P. J. Flory, *ibid.*, **17**, 303 (1949).

(9) P. J. Flory and S. Fisk, *ibid.*, **44**, 2243 (1966).

(10) M. Kurata, W. H. Stockmayer, and A. Roig, *ibid.*, **33**, 151 (1960), and M. Kurata and W. H. Stockmayer, *Fortsch. Hochpolym.-Forsch.*, **3**, 196 (1963).

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

(12) G. C. Berry, *J. Chem. Phys.*, **46**, 1338 (1967).

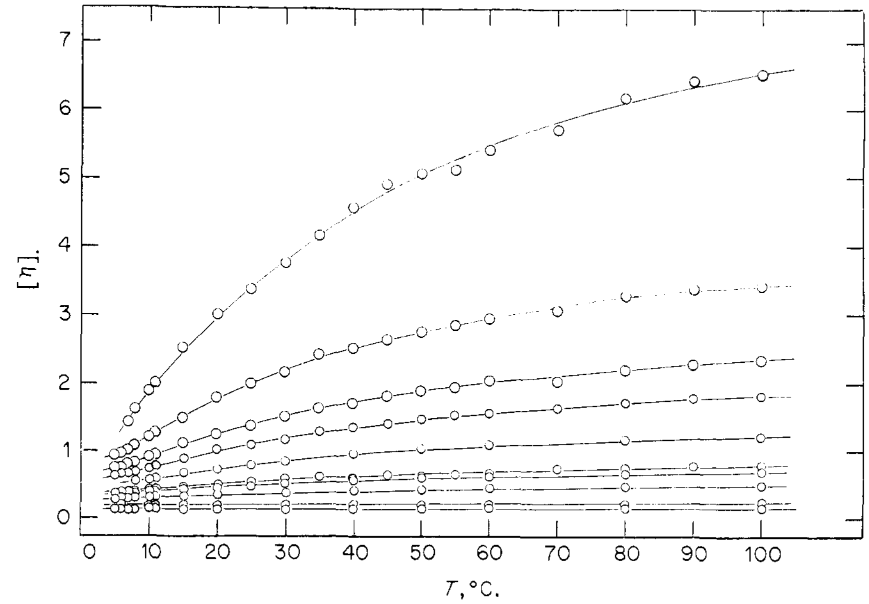

Figure 1. Temperature dependence of [η] for poly(α-methylstyrene) in *trans*-decalin. The curves are for samples PαS-14, PαS-13, PαS-12, PαS-9, PαS-8, PαS-6, PαS-5, PαS-4, PαS-2, and PαS-1 in order from the top to the bottom of the figure.

reported. Using monodisperse polystyrenes, Berry[12] reported that α_η of the samples of low molecular weights is not a unique function of z and, hence, [η] would be affected by a partial drainage. Kawahara, Norisuye, and Fujita,[13] on the other hand, concluded that polymer coils behave as nondraining coils even if the molecular weights are low, by analyzing their own data of polychloroprene and the data of Berry.[12] They further pointed out that eq 4 is valid and the difference between the behaviors of α_s and α_η may be interpreted as the variation of $\Phi(\infty,z)/\Phi(\infty,0)$ with z only.[14] Recently, Tanaka, Imai, and Yamakawa[7] supported the conclusion of Kawahara, *et al.*,[13] by using poly(p-methylstyrene).

These two different conclusions on the effect of hydrodynamic interaction among segments on α_η arises from the difference in their methods of determining z as was discussed in the previous paper.[1] In addition to the difference in z, however, it is to be pointed out that there is a clear difference between the molecular weight dependences of [η], as well as of $\langle S^2 \rangle$, reported by those investigators. Therefore, it seems necessary to accumulate more data on [η] and $\langle S^2 \rangle$ for different samples covering wider ranges of molecular weight. As in the previous paper,[1] we avoid using both methods of estimating z proposed by Berry[5] and by Norisuye, *et al.*[6,7] At the present stage of theories, it seems safe to use only molecular weight as a reliable parameter. In the experimental works so far published,[7,12,13] it was *a priori* assumed that an equation for α_s is applicable to the entire range of molecular weight if the equation is valid for high molecular weight. We feel that this assumption should be carefully studied before reaching a definite conclusion on the draining effect.

Experimental Section

The monodisperse poly(α-methylstyrenes) used here are the same as those listed in Table I of the previous paper.[1] The solvents were *trans*-decalin, cyclchexane, methylcyclohexane, and toluene. Purification was carried out in the same way as in the previous paper.[1]

Measurements of viscosity were carried out by using capillary viscometers of an Ubbelohde type and a rotational viscometer of a Zimm type for the samples of high molecular weight in good solvents. The capillary viscometers used for toluene and cyclohexane were the same as those described before.[15] The kinetic energy correction for the viscometers used for *trans*-decalin was less than 0.3% and, therefore, was neglected. The rotational viscometer was almost the same as the previous one.[16] Fluctuation of the temperature was less than ±0.02°. The results obtained by using both viscometers agreed with each other within the error of 2%. The polymer solutions for *trans*-decalin and toluene, prepared in the same way as in the previous paper,[1] were stocked together with the diluting solvent and volumetric pipets in an air thermostat regulated at 25°. The solutions and solvents were transferred from the stock vessels into the viscometer maintained at desired temperatures by using the pipets. Concentrations of the polymer solutions at different temperatures were calculated by taking into account the temperature dependence of the densities of solvents. Preparations and dilution of polymer solution in cyclohexane were carried out at 45° by the same method as for *trans*-decalin. Extrapolation of viscosity data was carried out by using plots of η_{sp}/c *vs.* c, of η_{sp}/c *vs.* η_{sp}, and ln η_{rel}/c *vs.* c, where η_{rel} and η_{sp} are the relative viscosity and the specific viscosity, respectively.[15]

Results

The limiting viscosity numbers of the samples in cyclohexane at 34.5° (Θ solvent), in *trans*-decalin at 9.5° (Θ solvent) and in toluene at 25° are given in Table I. The temperature dependence of [η] in *trans*-decalin for each different molecular weight is shown in Figure 1. Typical examples of the relationship between [η] and molecular weight are shown in Figure 2. Thus, we

---

(13) K. Kawahara, T. Norisuye, and H. Fujita, *J. Chem. Phys.* **49**, 4339 (1968).

(14) H. Yamakawa, *ibid.*, **48**, 2103 (1968).

(15) I. Noda, S. Saito, T. Fujimoto, and M. Nagasawa, *J. Phys. Chem.*, **71**, 4048 (1967).

(16) I. Noda, Y. Yamada, and M. Nagasawa, *ibid.*, **72**, 2890 (1968).

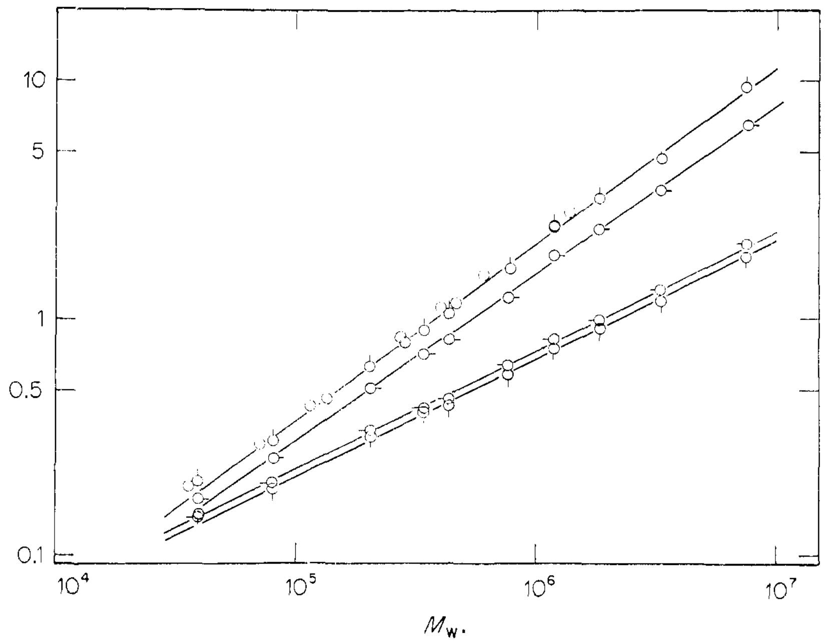

Figure 2. Double logarithmic plots of $[\eta]$ against M_w for poly(α-methylstyrene) in various solvents: ȯ, in toluene at 25°; O, in toluene at 25° reported previously;[15] O-, in *tert*-decalin at 100°; -O, in cyclohexane at 34.5°; ọ, in *tert*-decalin at 9.5°.

have the following Mark–Houwink–Sakura equations in the Θ solvents and in toluene

$$[\eta]_0 = 7.3 \times 10^{-4} M^{1/2} \text{ in cyclohexane at } 34.5° \quad (6)$$

$$[\eta]_0 = 6.7 \times 10^{-4} M^{1/2} \text{ in } trans\text{-decalin at } 9.5° \quad (7)$$

$$[\eta] = 7.0_6 \times 10^{-4} M^{0.744} \text{ in toluene at } 25° \quad (8)$$

It should be noted that $[\eta]$ of PαS-1 in *trans*-decalin at 9.5° markedly deviates from eq 7, while only a slight deviation is observed in cyclohexane. Since this deviation would be caused by the difference in the tacticity of PαS-1 from that of the samples having higher molecular weights as shown in the previous paper,[1] we did not use the data of PαS-1 in the following discussion. Equation 8 in toluene is slightly different from the equation reported previously[15] since the viscosity data of the samples having high molecular weights were not at hand for the previous paper. The difference between the unperturbed dimensions in cyclohexane at 34.5° and *trans*-decalin at 9.5°, both of which are the Θ temperatures, seems to be beyond the experimental error, as can be seen in Figure 2 and expressed by eq 6 and 7. Therefore, the temperature dependence of the unperturbed dimensions for poly(α-methylstyrene) appears to be significant. To find Θ solvents at different temperatures, we used mixtures of two solvents among *trans*-decalin, cyclohexane, and methylcyclohexane, each of which is a Θ solvent at different temperatures.[17] We found "an apparent Θ temperature" for the mixed solvents by using the cloud point method of Schultz and Flory,[18] though this method is not exactly valid for three-component systems. The unperturbed dimensions in those Θ solvents were determined from the intercept at $M = 0$ in the plot of $[\eta]/M^{1/2}$ *vs.* $M^{1/2}$, as suggested by Stockmayer and Fixman[11]

$$[\eta]/M^{1/2} = K_0 + 0.51\Phi(\infty,0)BM^{1/2} \quad (9)$$

with

$$K_0 = \Phi(\infty,0)(\langle S^2\rangle)_0/M^{3/2} \quad (10)$$

Although there have been many discussions on the validity of eq 9, it is well established that K_0 can be

TABLE I
THE LIMITING VISCOSITY NUMBERS OF POLY(α-METHYLSTYRENE)

Samples	$M_w \times 10^4$	$[\eta]_0$ *trans*-decaline $T = 9.5°$	$[\eta]_0$ cyclohexane $T = 34.5°$	$[\eta]$ toluene $T = 25°$
PαS-14	747	1.80	2.06	9.4
PαS-13	330	1.18	1.30	4.65
PαS-12	182	0.90_0	0.98_5	3.17_5
PαS-9	119	0.74_0	0.81_1	2.42_4
PαS-8	76.8	0.58_0	0.62_8	1.59
PαS-6	44.4	0.43_0	0.45_5	1.04_2
PαS-5	34.2	0.40_1	0.42_0	0.89_5
PαS-4	20.4	0.31_4	0.33_6	0.62_1
PαS-2	$(8.01)^a$	0.19_1	0.20_1	0.30_3
PαS-1	$(3.93)^a$	0.14_7	0.14_5	0.20_5

[a] M_n.

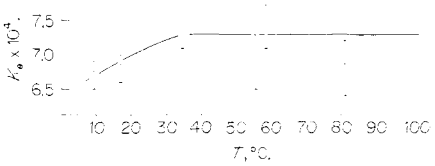

Figure 3. Plots of K_0 against temperature for poly(α-methylstyrene) in Θ and mixed "apparent Θ" solvents.

---

(17) A. Kotera, T. Saito, N. Yamaguchi, A. Wada, Y. Taniyama, S. Usami, and T. Sakai, Preprint, Meeting of Polymer Science of Japan, 1963, Nagoya.

(18) A. R. Schultz and P. J. Flory, *J. Amer. Chem. Soc.*, **74**, 4760 (1952).

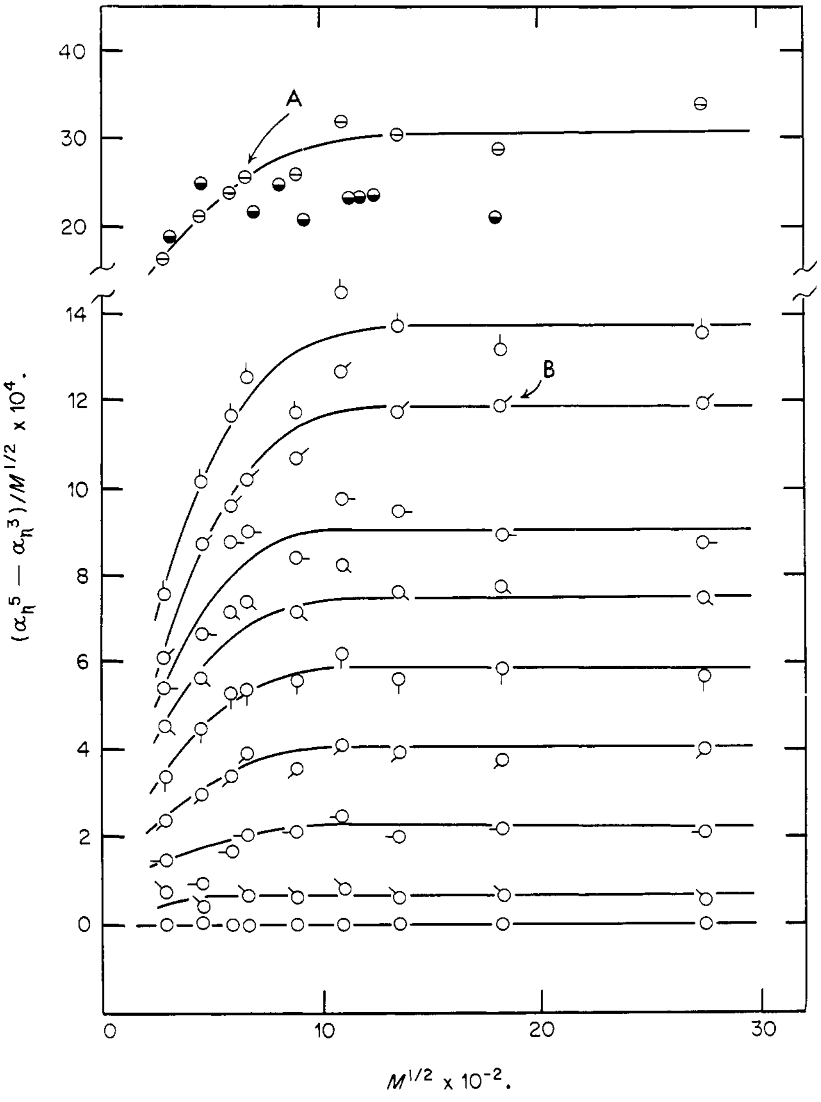

Figure 4. Examples of plots of $(\alpha\eta^5 - \alpha\eta^3)/M^{1/2}$ against $M^{1/2}$ for poly(α-methylstyrene) in toluene and *tert*-decalin at various temperatures: ⊖, in toluene at 25°; ◒, data of Cowie, *et al.*,[19] in toluene at 37°; ȯ, ♂, ○-, Q, ♀, ρ, -○, ○̀, and ○, in *tert*-decalin at 100, 80, 60, 50, 40, 30, 20, 12, and 9.5°, respectively.

obtained from the theory if the temperature is close to Θ. Variation of K_0 with temperature thus determined is given in Table II and in Figure 3. The disagreement between the radii of gyration $\langle S^2\rangle_0$ in *trans*-decalin and in cyclohexane at the respective Θ temperatures reported in the previous paper consistent with the difference between the corresponding values obtained from K_0 in both Θ solvents. Although it is difficult to determine whether the unperturbed dimensions of poly(α-methylstyrene) depend on temperature or on solvent species, we assumed that the value of K_0 depends on temperature only. That is, as shown in Figure 3, we assumed that K_0 increases with increasing temperature in the range from 9 to 34.5° where the effect of variation of unperturbed dimension on the expansion factor is relatively large, and simply assumed no temperature dependence above 34.5° where the experimental errors in K_0 are large but the effect of variation of unperturbed dimension is small. Even if we assume that the value of K_0 does not depend on temperature but depends on solvent species, however, the conclusion in the following discussion is not very much affected.

Table II

Temperature Dependence of K_0

Solvent	Volume ratio	T, °C	$K_0 \times 10^4$
trans-Decaline		9.5	6.7 ± 0.2
trans-Decaline–cyclohexane	1:1	17.0	6.8 ± 0.2
Cyclohexane		34.5	7.3 ± 0.2
trans-Decaline–methyl-cyclohexane	2:5	55.5	6.9 ± 0.4
Cyclohexane–methyl-cyclohexane	1:1	58.6	7.4 ± 0.3
trans-Decaline–methyl-cyclohexane	1:10	81.0	6.8 ± 0.4

Discussion

Let us now assume two different types of equations (11) and (12) for the molecular weight dependence of α_η, as we have for α_s. Since α_η might be a complicated

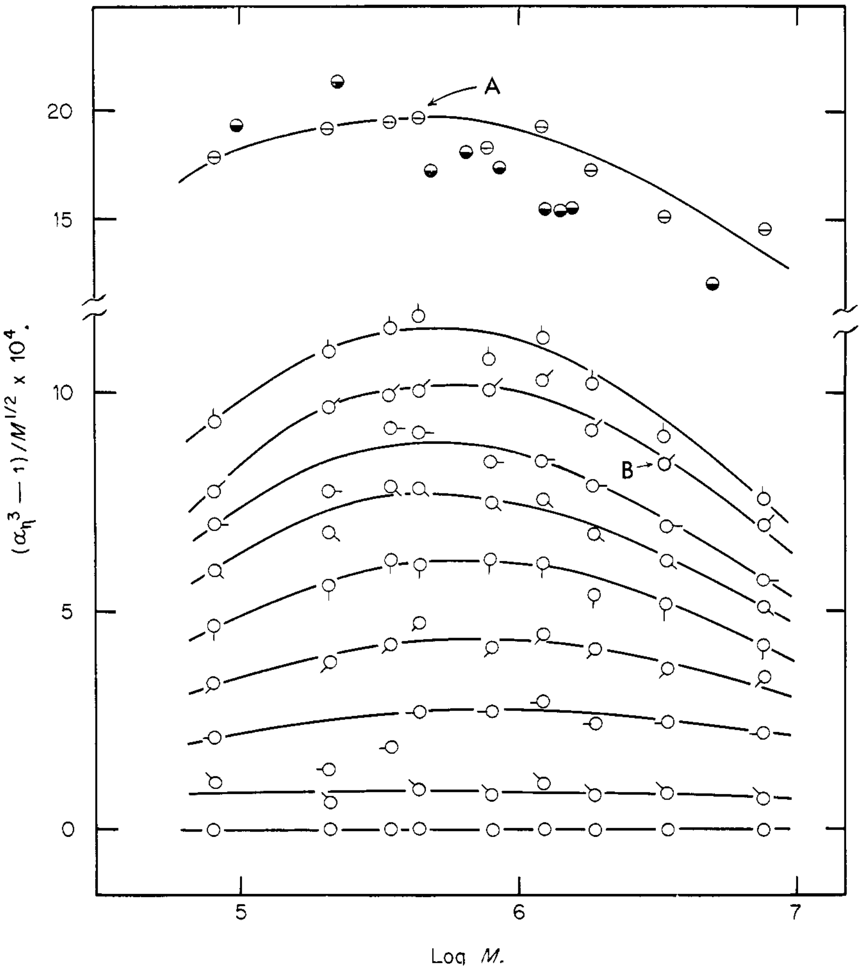

Figure 5. Examples of plots of $(\alpha_\eta^3 - 1)/M^{1/2}$ against log M for poly(α-methylstyrene) in toluene and *trans*-decalin at various temperatures; the symbols have the same significance as those in Figure 4.

function of z and h, eq 11 and 12 are the tentative assumption for the convenience of discussion

$$\alpha_\eta^5 - \alpha_\eta^3 = C_\eta B_0 g(\langle S^2\rangle_0/M)^{-3/2} M^{1/2} \qquad (11)$$

$$\alpha_\eta^3 - 1 = C_\eta' B_0 g'(\langle S^2\rangle_0/M)^{-3/2} M^{1/2} \qquad (12)$$

where C_η and C_η' are constants but do not necessarily agree with the constants in the corresponding equations for α_s (eq 1 and 2 in the previous paper[1]), since the relationship, eq 5, is not always valid, and g and g' are functions of $(1 - \Theta/T)$ but may not always be linear with respect to $(1 - \Theta/T)$. At a constant temperature, *i.e.*, if $B_0 g$ or $B_0 g'$ is constant, eq 11 predicts a constant value for $(\alpha_\eta^5 - \alpha_\eta^3)/M^{1/2}$ independent of molecular weight, whereas eq 12 predicts a constant value for $(\alpha_\eta^3 - 1)/M^{1/2}$. Both plots for the present data are shown together with the data of Cowie, Bywater, and Worsfold[19] in Figures 4 and 5. Both figures do not support either eq 11 or 12 well. Roughly speaking, however, it may be concluded that eq 11 is valid when M is higher than about 10^6, whereas $(\alpha_\eta^3 - 1)/M^{1/2}$ appears to be more nearly constant below $M = 10^6$ than $(\alpha_\eta^5 - \alpha_\eta^3)/M^{1/2}$, even if z is large.

Since we may conclude that eq 11 is applicable at high molecular weights, we may determine the functional form of g by plotting $(\alpha_\eta^5 - \alpha_\eta^3)/M^{1/2}$ against $(1 - \Theta/T)(\langle S^2\rangle_0/M)^{-3/2}$ in Figure 6. A linear relationship between them is observed in the temperature range from 5 to 100° in *trans*-decalin within experimental error so that we have $g = (1 - \Theta/T)$. In the previous paper, it was reported from the data of α_s that z is proportional to $(1 - \Theta/T)$ in the range between 8 and 50° in *trans*-decalin. The present data of α_η show that the proportionality may be extended to 100°. In the previous paper[1] we reported $B_0 = 1.52 \times 10^{-28}$, $\Theta = 9.5°$ for poly(α-methylstyrene) in *trans*-decalin, and $B = 0.82 \times 10^{-28}$ in toluene at 25°. Using these values of B_0 and B, we have $C_\eta = 0.97$ in *trans*-decalin and 0.94 in toluene for the samples having molecular weight higher than 10^6. Here, it is to be noted that the plot of $(\alpha_\eta^5 - \alpha_\eta^3)/M^{1/2}$ *vs.* $M^{1/2}$ for low molecular weight samples shows a clear deviation from constancy in Figure 4. It appears to be dangerous to discuss the temperature dependence of α_η or B using low molecular weight samples.

As was explained in the previous paper,[1] two different methods of determining z were reported in the literature.[5-7] Although some discrepancies were found, all as well as the present work agreed in that the α^5-type theory of Flory[8,9] is valid for α_s and, hence, z may be calculated from the data of α_s using the theory of Flory,

---

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

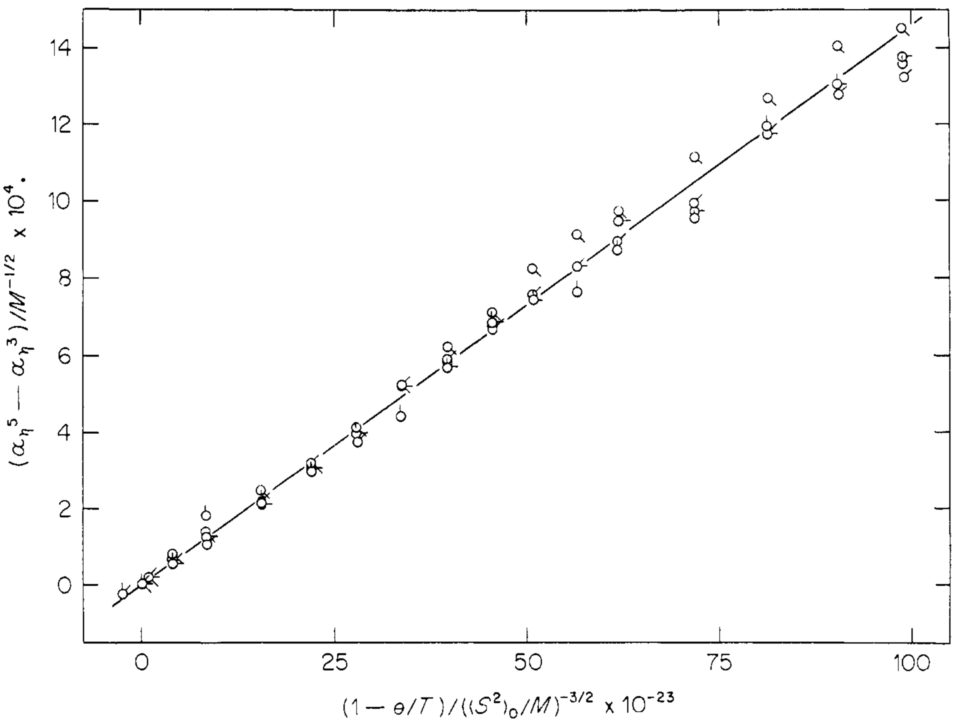

Figure 6. Plots of $(\alpha_\eta^5 - \alpha_\eta^3)/M^{1/2}$ against $(1 - \Theta/T)(\langle S^2\rangle_0/M)^{-3/2}$ for poly(α-methylstyrene), whose molecular weight is high, in *trans*-decalin at various temperatures: ○́, ○̀, ○̡ and -○, for samples PαS-14, PαS-13, PαS-12, and PαS-9, respectively.

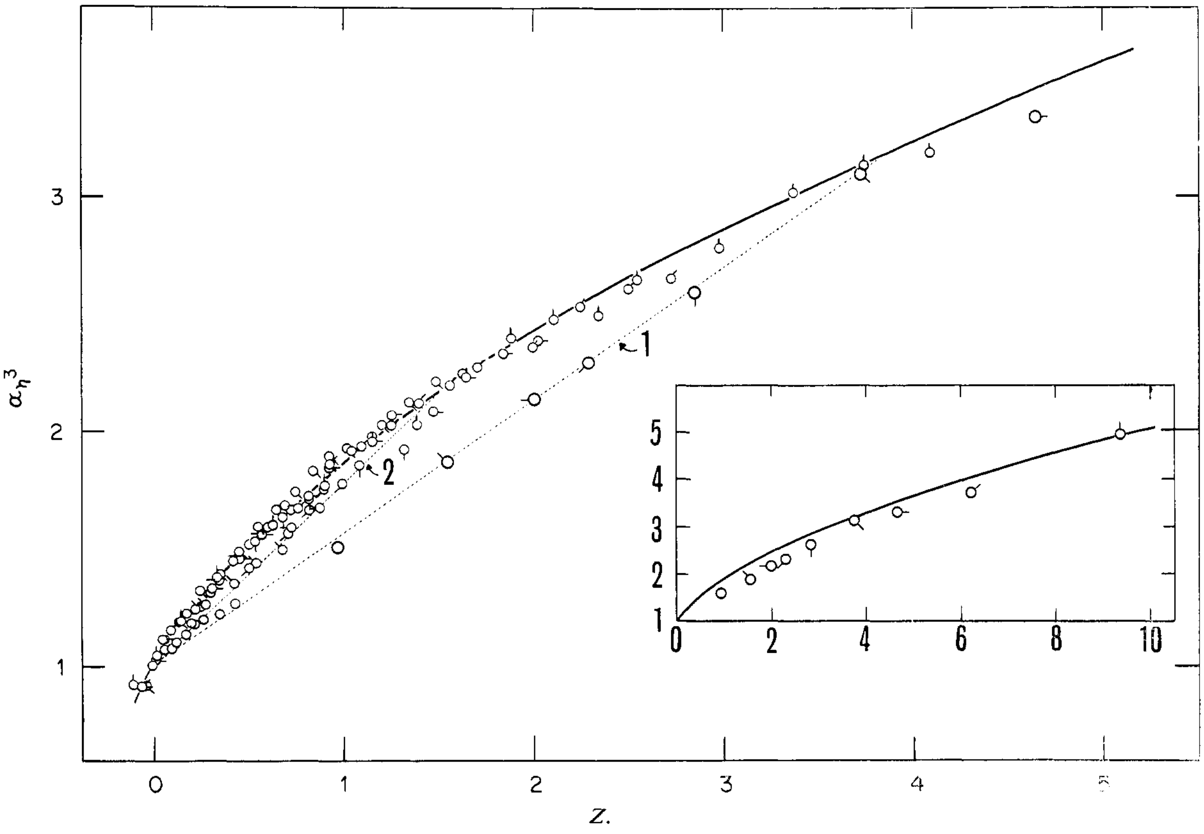

Figure 7. The dependence of α_η^3 on z for poly(α-methylstyrene) in toluene and *trans*-decalin; ○̍, ○́, ○̡, ○̦, ○̩, ○̗,-○, ○̀, and ○, for samples PαS-14, PαS-13, PαS-12, PαS-9, PαS-8, PαS-6, PαS-5, PαS-4, and PαS-2, respectively. Larger circles present in toluene and smaller circles present in *trans*-decalin. The dotted lines show the linear relationship between α_η^3 and $M^{1/2}$ for the samples with molecular weights lower than 10^6 in toluene at 25° (1) and in decalin at 100° (2).

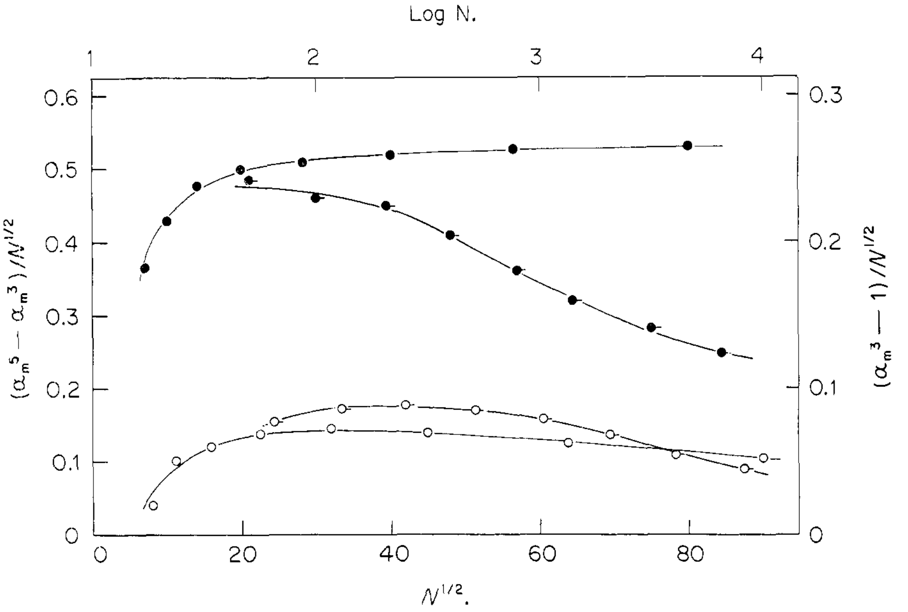

Figure 8. Plots of $(\alpha_m^5 - \alpha_m^3)/N^{1/2}$ against $N^{1/2}$, and of $(\alpha_m^3 - 1)/N^{1/2}$ against log N: O and O-, $(\alpha_m^5 - \alpha_m^3)/N^{1/2}$ against $N^{1/2}$ and $(\alpha_m^3 - 1)/N^{1/2}$ against log N for model of the tetrahedral lattice;[20] ● and ●-, $(\alpha_m^5 - \alpha_m^3)/N^{1/2}$ against $N^{1/2}$ and $(\alpha_m^3 - 1)/N^{1/2}$ against log N for model of the cubic lattice.[21]

at least if the molecular weight is higher than, say, 10^6. In Figure 7, α_η^3 for all samples used in this work is plotted against z thus estimated. As was pointed out by Berry,[12] α_η does not make a single composite curve but shows deviation depending on molecular weight. From this kind of graph, Berry concluded that α_η is not a function of z only but may be a function of z and draining parameter h.

However, Yamakawa,[14] Kawahara, *et al.*,[13] and Tanaka, *et al.*,[7] denied this conclusion by criticizing the assumption of Berry that B should be linear with respect to $(1 - \Theta/T)$. According to them, α_η can be expressed as a function of z only, and the splitting of the relationship between α_η^3 and z in Figure 7 may stem from the nonlinearity of B with respect to $(1 - \Theta/T)$. However, the parameters in z used in Figure 7 were determined from α_s for high molecular weight samples using Flory's theory, which all agreed is correct. Nevertheless, we can see that α_η cannot be expressed as a function of z only. Moreover, the fact that α_η cannot be expressed by a unique function of z can be shown irrespective of the method of determining z. That is, if α_η were expressed by unique function of z, the derivative $\partial\alpha_\eta^3/\partial z$ would be a constant independent of molecular weight at a constant value of α_η. However, this is not true for poly(α-methylstyrene) as shown in Figure 7. For example, sample PαS-6 in toluene at 25° (denoted by A in Figures 4 and 5) has almost the same value of α_η as sample PαS-13 in *trans*-decalin at 80° (denoted by B). However, both have different z dependence as is clear from Figures 4 and 5 where the shift of α_η from the α^3-type to the α^5-type occurs rather in term of molecular weight than in term of z.

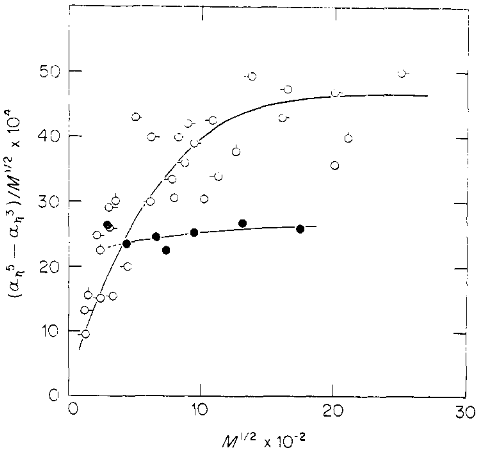

Figure 9. Plots of $(\alpha\eta^5 - \alpha\eta^3)/M^{1/2}$ against $M^{1/2}$ for various samples: -O, Ȯ, and O- data of Okada, *et al.*,[27] Berry,[12] and Krigbaum, *et al.*,[26] for polystyrene in good solvents, respectively; ●, data of Kawahara, *et al.*,[13] for polychloroprene in CCl_4.

Thus, we agree with Berry that α_η cannot be expressed as a unique function of z. The nonunique dependence of α_η on z may be attributed to the partial drainage of solvent through the polymer coils,[12] but it may not be the only reason. It is our impression that there is a possibility that the expansion factor α_s of the polymer coils of low molecular weights cannot be expressed by the same equation as for high molecular weight samples. Unfortunately, it was reported in the previous paper that the accuracy in light scattering measurements is not high enough to determine whether α_s for low molecular weight samples can be expressed by an equation of α^5-type or not. Here, therefore, we refer to the recent results of the Monte Carlo calculation on the conformation of long chains,[20,21] though there are some questions in applying the results for lattice models to the excluded volume effects of real polymers.[22] In Figure 8, the expansion factor α_m of radius of gyration calculated assuming the tetrahedral lattice[20] and of the end-to-end distance calculated assuming the cubic lattice[21] are

---

(20) K. Suzuki, *Bull. Chem. Soc. Jap.*, **41**, 538 (1968).
(21) Z. Alexandrowicz, *J. Chem. Phys.*, **51**, 561 (1969).
(22) E. Lotus and P. J. Gans, *ibid.*, **49**, 3828 (1968).

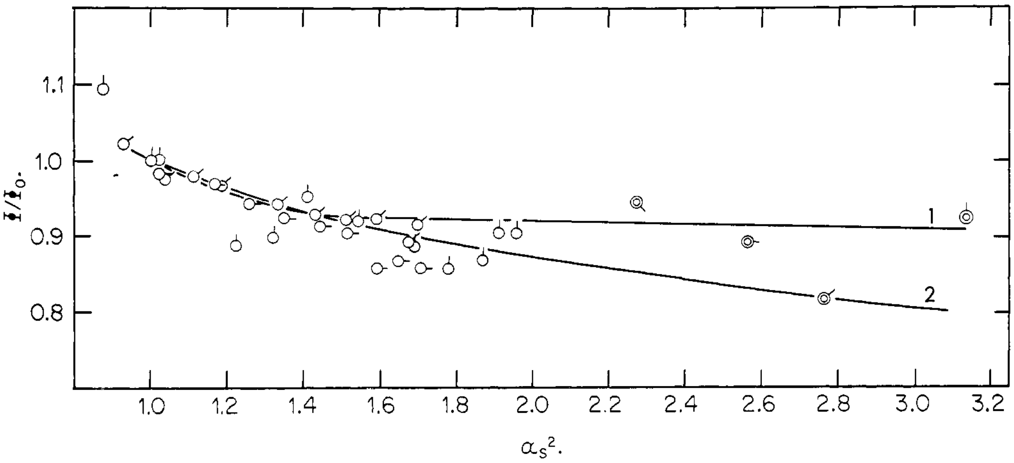

Figure 10. Plots of Φ/Φ_0 against $\alpha_s{}^2$ for poly(α-methylstyrene) in *trans*-decalin and toluene; the symbols have the same significance as those in Figure 7. Double circles present in toluene: curve 1, calculated from the relationship $\alpha_s{}^5 - \alpha_s{}^3 = 1.276z$ and $\alpha_\eta{}^5 - \alpha_\eta{}^3 = 0.97\ z$; curve 2, the recent theory of Fixman.[28]

shown in the forms of $(\alpha_m{}^5 - \alpha_m{}^3)/N^{1/2}$ *vs.* $N^{1/2}$ and $(\alpha_m{}^3 - 1)/N^{1/2}$ *vs.* log N, N being the number of chain elements. It can be concluded that the data on both lattices agree with the α^5-type equation when N is large, where as $(\alpha_m{}^3 - 1)/N^{1/2}$ is more nearly constant than $(\alpha_m{}^5 - \alpha_m{}^3)/N^{1/2}$ when N is small. The graphs obtained closely resemble the graphs in Figures 4 and 5 for α_η. Also, the behavior of α_s in Figure 7 of the previous paper[1] is similar. There are several theories[23-25] ranging between the α^5-types and the α^3-type, but none of them can explain the change from the α^3-type to the α^5-type at about $N = 500 \sim 1000$ satisfactorily. Moreover, it should be noted that the expansion factors calculated on both lattices seem to change from the α^3-type[11] to the α^5-type[8,9] in almost the same region of N, despite the fact that their values are much different from each other in that region. This fact suggests a possibility that the same expansion equation is not applicable to α_m over the whole range of molecular weight, just as found for α_η. The molecular weight dependence of α_s reported in the previous paper[1] is not in contradiction with the above results on α_m. Thus, the splitting may occur not only in the plot of $\alpha_\eta{}^3$ *vs.* z but also of $\alpha_m{}^3$ (or $\alpha_s{}^3$) *vs.* z. Therefore, we cannot always support the conclusion[12] that the deviations of α_η from the expansion equation which is valid for high molecular weight are caused by the draining effect only, unless the equation is proved to be valid for the low molecular weight where the deviations occur.

We have much experimental data on the relationship between limiting viscosity number and molecular weight, but the data useful to clarify the question raised here are not as plentiful. The values of $(\alpha_\eta{}^5 - \alpha_\eta{}^3)/M^{1/2}$ are plotted against $M^{1/2}$ for polystyrenes[12,26,27] and for polychoroprenes[13] in good solvents in Figure 9. The former is similar to the present data of poly(α-methylstyrene) but the latter as well as α_s for the same samples published by the same authors is in good agreement with the α^5-type equation even at low molecular weights. It was also reported that $(\alpha_\eta{}^5 - \alpha_\eta{}^3)/M^{1/2}$ for polyisobutylene is fairly constant independent of M (actually, exhibit a maximum) if the molecular weights are not too low.[26] These controversial facts may imply that the structure of polymer unit might affect the expansion behavior of polymer chains of low molecular weights. At present, therefore, it may be advisable to avoid a definite conclusion on the expansion behavior for the low molecular weight and the draining effect and to accumulate more data of both α_s and α_η for the same samples. Under the present stage of research it is impossible to make any assertion about the correct function of α_η for low molecular weight samples. Equation 12 appears to be more applicable than eq 11 if M is lower than, *e.g.*, 10^6, but $(\alpha_\eta{}^3 - 1)/M^{1/2}$ is not perfectly constant. There may be many other possible functions giving better agreement with experimental data. At least, however, it seems certain that not only α_η but also α_s do *not always* agree with the theory of Flory (α^5-type),[8,9] if the molecular weight is low.

Finally we will mention the difference between α_η and α_s when the molecular weight is high. Plotting the ratio $\alpha_\eta{}^3/\alpha_s{}^3$, which is equal to $\Phi(h,z)/\Phi(h,0)$ against $\alpha_s{}^2$ for the samples having molecular weight higher than 10^6 in Figure 10, $\Phi(h,z)/\Phi(h,0)$ is found to decrease slightly with increasing z. The decreasing behavior corresponds to the fact that $C_\eta = 0.97$ (or 0.94) in eq 11 is smaller than $C_s = 1.28$ and it can be explained by the recent theory of Fixman[28] at $h = \infty$. That is, despite the fact that both α_η and α_s can be expressed by the α^5-type equation, α_η/α_s is a function of z.

(23) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **47**, 3991 (1967).

(24) Z. Alexandrowicz, *ibid.*, **46**, 3789 (1967).

(25) M. Kurata, *J. Polym. Sci., Part A-2*, **6**, 1607 (1968).

(26) W. R. Krigbaum and P. J. Flory, *ibid.*, **11**, 37 (1953).

(27) R. Okada, Y. Toyoshima, and H. Fujita, *Makromol. Chem.*, **59**, 137 (1963).

(28) M. Fixman, *J. Chem. Phys.*, **45**, 793 (1966).