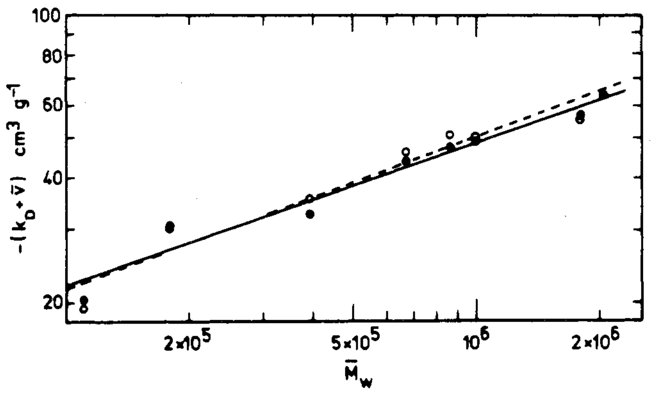

Figure 3. Variation of $-(k_D + \bar{v})$ with $\bar{M}_w$ at 25.0 °C (○) and 25.5 °C (●).

Another theory by Imai[11] gives the same expression for k_f^θ as Yamakawa's theory. All the theories predict that k_f^θ should be proportional to $\bar{v}_h$. In Table I we also list the values of $\bar{v}_h$ and $-(k_D + \bar{v})/\bar{v}_h$ $(=k_f^\theta/\bar{v}_h)$ for different $\bar{M}_w$. The quotient of the latter term is seen to lie between 1.2 and 2, intermediate between the predictions of Yamakawa (and Imai) and the soft-sphere model of Pyun and Fixman.

Another way of displaying the results is to plot log $(-k_D - \bar{v})$ against log $\bar{M}_w$ as shown in Figure 3 for the data at 25.0 and 25.5 °C. The slope at 25.5 °C is 0.35 ± 0.04 and at 25.0 °C is 0.37 ± 0.05. These values are not in agreement with the theoretical prediction of 0.5. In the only reported work in a single solvent (cyclohexane) at the theta temperature, King et al.[12] obtained an index slightly less than 0.5 (0.48 ± 0.04). This is in closer agreement than our result with the theory, and it may be that the theory for k_D in a binary solvent requires more careful consideration.

No systematic change in k_D was detected on increasing the temperature from 25.0 to 25.5 °C, and indeed the values reproduce to a few percent. However, Takashima et al.[2] have shown that A_2M and $A_2{}^*M^*$ change by about 10 cm^3 g^{-1} over this temperature interval for high $\bar{M}_w$, and according to the theories for k_f this should produce a detectable change in k_D. For example in Yamakawa's theory (eq 2) the fractional change in $(k_D + \bar{v})$ for a change in temperature of 0.5 °C should be $8/\bar{v}_h$. For $\bar{M}_w = 10^6$, the fractional change is $8/35 \simeq 0.2$; such a change should be easily detectable but none was found.

This work, which forms part of a wider investigation on binary solvents, shows that it is now possible to obtain accurate values for D which can prove a sensitive test of current theories of polymer solutions.

Acknowledgment. We should like to thank the (British) Science Research Council for the award of a studentship to one of us (R.A.F.) and also for an equipment grant.

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Frictional Coefficient and Its Concentration Dependence for Monodisperse Poly(α-methylstyrene) in Solution

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ABSTRACT: The sedimentation coefficient and its polymer concentration dependence for monodisperse poly(α-methylstyrenes) were measured in theta and nontheta solvents over a wide range of molecular weights. The expansion factor of the dimension of polymer coil estimated from the frictional coefficients agrees with the α^5-type theory of Flory. The polymer concentration dependence of the frictional coefficient in good solvents agrees with the theory of Pyun and Fixman at small excluded volumes but deviates from the theory at large excluded volumes. It is suggested that the variation of the concentration dependence of frictional coefficient with excluded volume may be similar to that of the second virial coefficient.

It is no doubt important to study the hydrodynamic interaction between two polymer coils in solution as well as the hydrodynamic properties of a polymer coil at infinite dilution. Many theoretical[1] and experimental works[2] have so far been carried out not only on intrinsic viscosity but also on concentration dependence of specific viscosity of linear polymers. However, less attention has been paid to the concentration dependence of the translational frictional coefficient of linear polymers. To study the hydrodynamic properties of linear polymers, it may be more desirable to measure the translational frictional coefficient rather than the intrinsic viscosity, since more rigorous theories have been presented for the translational frictional coefficient and its concentration dependence.[1,3]

In order to examine the existing theories without ambiguity, it is also important to obtain experimental data on translational frictional coefficient of linear polymers together with the data on their thermodynamic properties. Although several experimental studies of the frictional coefficient and its concentration dependence for linear polymers have been carried

Table I
Molecular Weights, Sedimentation and Intrinsic Frictional Coefficients, and Concentration Dependence Coefficients of Poly(α-methylstyrene)

		In cyclohexane at 34.5 °C			In *trans*-decalin at 20 °C			In *trans*-decalin at 20 °C		
Samples	$\overline{M}_w \times 10^{-4}$	$S_0{}^0 \times 10^{13}$, s	$[f] \times 10^4$, cm	k, dL/g	$S_0{}^0 \times 10^{13}$,s	$[f] \times 10^4$, cm	k, dL/g	$S_0{}^0 \times 10^{13}$, s	$[f] \times 10^4$, cm	k, dL/g
PαS-14	747	$49._8$	1.06	1.3_4	10.6	0.97_3	1.0_6	11.4	1.15	3.5_3
PαS-13	330	$33._0$	0.70_3	1.1_9	6.8_5	0.66_5	0.8_9	7.4_1	0.78_2	1.7_8
PαS-12	182	$24._3$	0.52_1	0.6_8	5.1_5	0.48_2	0.5_7	5.7_1	0.553	1.3_7
PαS-9	119	$21._6$	0.38_7	0.9_1	4.4_1	0.37_2	0.6_2	4.9_8	0.41_9	1.0_9
PαS-8	76.8	16.5	0.34_1	0.3_8	3.4_0	0.31_2	0.3_8			
PαS-6	44.4	11.7	0.26_0	0.3_6	2.4_2	0.24_7	0.2_7			
PαS-4	20.4	8.0_6	0.17_8	0.2_0	1.74	0.16_2	0.2_9			

		In *trans*-decalin at 40 °C			In toluene at 25 °C		
Samples	$\overline{M}_w \times 10^{-4}$	$S_0{}^0 \times 10^{13}$,s	$[f] \times 10^4$, cm	k, dL/g	$S_0{}^0 \times 10^{13}$, s	$[f] \times 10^4$, cm	k, dL/g
PαS-14	747	14.3	1.38	6.2_8	$33._8$	1.65	14.5
PαS-13	330	10.3	0.87_4	3.5_6	$22._7$	1.09	7.4_3
PαS-12	182	7.4_1	0.64_3	2.0_7	17.2	0.78_1	4.5_7
PαS-9	119	6.4_1	0.49_1	1.6_7	15.1	0.60_4	3.5_3
PαS-8	76.8	5.2_6	0.38_6	1.3_4	12.0	0.47_8	2.4_7
PαS-6	44.4	3.3_8	0.29_5	0.8_2	9.2_6	0.34_9	1.6_7
PαS-4	20.4	2.7_1	0.19_9	0.4_5	6.7_6	0.22_5	0.9_1

out,[2] there are very few accompanied by thermodynamic data. Moreover, the samples used should have well-defined structures.

In the present work we study the frictional coefficient and its concentration dependence for monodisperse poly(α-methylstyrenes) over a wide range of molecular weights. The experimental conditions are the same as in our previous works[4,5] on light scattering and viscosity which were carried out with the same samples. Some experimental data on the sedimentation coefficient of the same polymer series at lower molecular weights were already reported.[6]

Experimental Section

The monodisperse poly(α-methylstyrenes) used as samples are the same as used in the previous works.[4,5] Solvents used here are cyclohexane, *trans*-decalin, and toluene. The purification methods for the solvents have also been described previously.[4,5]

Ultracentrifugation was carried out in cyclohexane at 34.5 °C (theta temperature), in *trans*-decalin at 9.5 (theta), 20, and 40 °C, and also in toluene at 25 °C with a Beckman/SPINCO Model E ultracentrifuge equipped with a schlieren system and a RTIC temperature control unit. Since an apparent sedimentation coefficient depends on the position of boundary owing to the pressure dependence of the density and viscosity of solvents used, the angular velocity of the rotor in the ultracentrifugation was selected to be as low as possible, and the observed apparent sedimentation coefficients were extrapolated to the value at 1 atm by two methods described previously.[6] The relative difference between sedimentation coefficients obtained by the two methods was less than 2% and the differences between the values observed at different angular velocities were also less than 2%.

Density measurements of poly(α-methylstyrene) solutions were carried out, to obtain the partial specific volumes of the samples in the solvents, by a modified Gay-Lussac pycnometer of 100 mL capacity under the same experimental conditions as used in the ultracentrifugation.

Results

The sedimentation coefficient at 1 atm, S^0, was extrapolated to infinite dilution by,

$$1/S^0 = (1/S_0{}^0)[1 + kC] \qquad (1)$$

where $S_0{}^0$ is the sedimentation coefficient at infinite dilution, C is the concentration (g/100 cm³) and k is the concentration dependence coefficient. Examples of the concentration dependence of the sedimentation coefficient of poly(α-methylstyrenes) are shown in Figure 1.

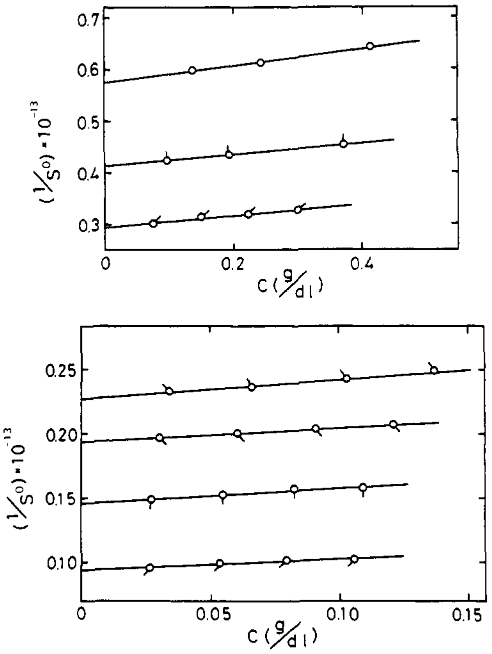

Figure 1. Concentration dependences of the sedimentation coefficient of poly(α-methylstyrenes) in *trans*-decalin at 9.5 °C: (ϙ), PαS-14; (ϙ) PαS-13; (ⵕ) PαS-12; (ȸ) PαS-9; (ȯ) PαS-8; (ȯ) PαS-6; (○) PαS-4.

All data for the sedimentation coefficients and their concentration dependence coefficients are listed in Table I. Double logarithmic plots of sedimentation coefficient against weight-average molecular weight ($\overline{M}_w$) are shown in Figure 2. From those plots we have

$$S_0{}^0 = 1.8 \times 10^{-15}\, \overline{M}_w{}^{0.5} \text{ in cyclohexane at 34.5 °C} \qquad (2)$$

$$S_0{}^0 = 3.9 \times 10^{-16}\, \overline{M}_w{}^{0.5} \text{ in } \textit{trans}\text{-decalin at 9.5 °C} \qquad (3)$$

$$S_0{}^0 = 3.6 \times 10^{-15}\, \overline{M}_w{}^{0.43} \text{ in toluene at 25 °C} \qquad (4)$$

The data in the previous paper[6] are also in good agreement with the above equations. The intrinsic frictional coefficients $[f]$ in Table I are calculated from the sedimentation coefficient $S_0{}^0$ using eq 5,

$$[f] = \overline{M}_w(1 - \bar{v}\rho)/S_0{}^0 N_A \eta_0 \qquad (5)$$

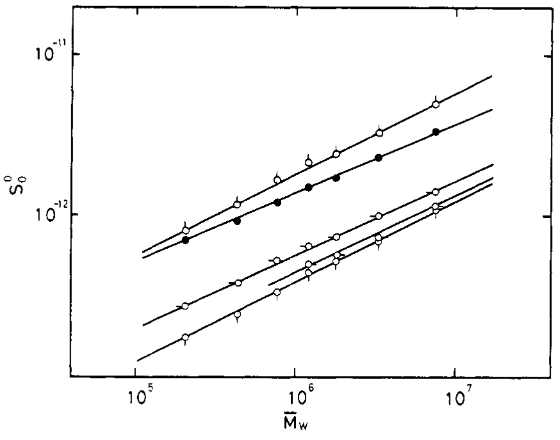

Figure 2. Log S_0^0 vs. log $\overline{M}_w$ plots for poly(α-methylstyrenes): in cyclohexane at 34.5 °C (ό); in *trans*-decalin at 9.5 °C (ϙ), at 20 °C (O-), at 40 °C (-O); and in toluene at 25 °C (●).

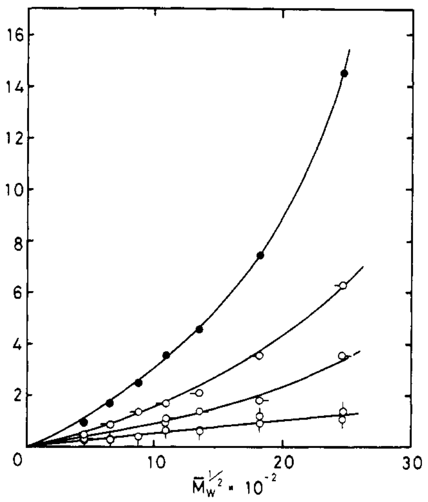

Figure 3. Plots of concentration dependence vs. $\overline{M}_w^{1/2}$: in cyclohexane at 34.5 °C (ό); in *trans*-decalin at 9.5 °C (ϙ), at 20 °C (O-), and at 40 °C (-O); and in toluene at 25 °C (●).

where N_A is Avogadro's number, $\bar{v}$ is the partial specific volume of the polymer, and ρ and η_0 are the density and viscosity of solvent, respectively. These values are given in Table II. The data in cyclohexane and toluene are in good agreement with the data reported previously.[7]

The concentration dependence coefficients k in eq 1 are plotted against the square root of molecular weight as shown in Figure 3.

Discussion

Frictional Coefficient. Theoretical studies show that the intrinsic frictional coefficient of a nondraining coil in theta solvents $[f]_\Theta$ is proportional to the unperturbed radius of gyration $\langle s^2\rangle_\Theta^{1/2}$:

$$[f]_\Theta = P_\Theta \langle s^2\rangle_\Theta^{1/2} \tag{6}$$

where the subscript Θ denotes the values in theta solvents and $P_\Theta = 12.5_3$ according to Kirkwood and Riseman.[8] In nontheta solvents, the intrinsic frictional coefficient $[f]$ is affected by the expansion of the polymer coil. If we define α_f by the ratio of $[f]$ to $[f]_\Theta$ such as

$$[f]/[f]_\Theta \equiv \alpha_f \tag{7}$$

we have

$$[f] = P_\Theta(\alpha_f/\alpha_s)\langle s^2\rangle^{1/2} \tag{8}$$

Table II
Densities and Viscosities of Solvents and Partial Specific Volumes of Poly(α-methylstyrenes) in These Solvents

Solvents	Temp, °C	ρ	η_0, cP	$\bar{v}$
Cyclohexane	34.5	0.765_5	0.76_0	0.88_6
trans-Decalin	9.5	0.877_8	2.59	0.89_4
trans-Decalin	20	0.870_0	2.12	0.89_2
trans-Decalin	40	0.855_3	1.49	0.89_2
Toluene	25	0.862_3	0.55_0	0.87_3

where $\langle s^2\rangle^{1/2}$ is the radius of gyration in nontheta solvent and α_s is defined by

$$\langle s^2\rangle/\langle s^2\rangle_\Theta \equiv \alpha_s^2 \tag{8'}$$

For a flexible chain with small excluded volume, perturbation theory[9] gives

$$\alpha_s^2 = 1 + \frac{134}{105}z + \ldots \tag{9}$$

with

$$z = B(A_0)^{-3/2}M^{1/2}, \qquad A_0 = \langle s^2\rangle_\Theta/M, \qquad \text{and } B = (1/4\pi)^{3/2}\beta/m_s^2 \tag{9'}$$

where M and m_s are the molecular weights of polymer and segment, respectively, and β is the binary cluster integral. Although there is no definite conclusion on a closed expression of expansion factor over a wide range of z, it was shown that the experimental data of α_s for the polymer with molecular weights higher than ca. 10^6 are in good agreement with the α^5-type equation of Flory,[4,10]

$$\alpha_s^5 - \alpha_s^3 = \frac{134}{105}z \tag{10}$$

where its numerical constant is chosen so that eq 10 may tend to eq 9 at the limit of small z.

According to Albrecht and Stockmayer,[11] perturbation theory for the frictional coefficient gives

$$\alpha_f = 1 + 0.609z + \ldots \tag{11}$$

If we assume that the procedure in transforming eq 9 into eq 10 is applicable to α_f, we have the following equation from eq 11.

$$\alpha_f^5 - \alpha_f^3 = 1.22z \tag{12}$$

The experimental data of α_f, including the data of poly(α-methylstyrene) at 25 °C by Ooms, Mijnlieff, and Beckers,[12] are plotted against the values of the excluded volume parameter z determined in the previous work[4] in Figure 4. The calculated value of eq 12 is also shown in the figure for the comparison. It is clear that eq 12 is in good agreement with the experimental data. Moreover, it is obvious from the comparison between eq 10 and 12 that the variation of α_f with z is similar to that of α_s. Thus, it may be expected from eq 8 that $[f]$ is almost proportional to $\langle s^2\rangle^{1/2}$ irrespective of solvent power. In practice, we have a good proportionality between $[f]$ and $\langle s^2\rangle^{1/2}$ over a wide range of molecular weight, as shown in Figure 5.

Concentration Dependence of Frictional Coefficient. Since the intermolecular hydrodynamic interaction depends on the spatial distribution of polymer molecules in solution, the concentration dependence of the frictional coefficient is obviously affected by intermolecular thermodynamic interactions.

Using a soft interpenetrable sphere model, Pyun and Fixman[13] presented a theory on the concentration dependence of the frictional coefficient of a flexible polymer expressed in

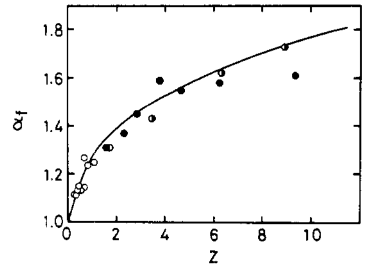

Figure 4. Plots of α_f vs. z in *trans*-decalin at 20 and 40 °C (○) and in toluene at 25 °C (●). ◑ denotes the data of Ooms, Mijnlieff, and Beckers for poly(α-methylstyrene) in toluene at 25 °C. The curve denotes α_f according to eq 12.

terms of the thermodynamic interactions. If we assume that the hydrodynamic radius of a polymer coil is equal to the Stokes radius $[f]/6\pi$, the concentration dependence coefficient k at the concentration C in g/100 cm^3 is given by

$$k = \left(\frac{4\pi}{300}\right)\left(\frac{1}{6\pi}\right)^3 N_A \frac{[f]^3}{M}[7.16 - \kappa(A)] \qquad (13)$$

and

$$A = 3n^2x/8\pi a^3 \qquad (13')$$

where $\kappa(A)$ is a function of thermodynamic interaction parameter A, n is the number of segments, a is the radius of polymer, and x is the second virial coefficient for segment–segment interaction, which is equal to β in eq 9′.[1] Let us rewrite A in terms of the excluded volume parameter z for the comparison with experimental data: If we assume that a is equal to the radius of gyration, from the comparison between eq 9′ and 13′ we have[14]

$$A = 3\pi^{1/2}(z/\alpha_s^3) = 3\pi^{1/2}\bar{z} \qquad (14)$$

On the other hand, if the second virial coefficient of the same uniform density sphere at the limit of small excluded volume is adjusted to fit the first-order pertubation theory, we have[1,15]

$$A = 8.85\bar{z} \qquad (15)$$

Using a flexible chain model Yamakawa[16] also presented a theory on the concentration dependence coefficient expressed in terms of second virial coefficient. His equation for k at the concentration C in g/100 cm^3 is given by

$$k = \left(\frac{4\pi}{300}\right)\left(\frac{1}{6\pi}\right)^3 N_A \frac{[f]^3}{M} + \frac{\lambda(\bar{z})}{100}A_2M \qquad (16)$$

where λ is a function of $\bar{z}$ but is almost equal to 1.2 in our experimental range. Here we also assumed that the hydrodynamic volume of a polymer coil is equal to that of a sphere with radius $R = [f]/6\pi$.

Since there are no thermodynamic interactions between polymers in a theta solvent, that is, $\bar{z} = 0$ or $A_2 = 0$, from eq 13 and 16, the concentration dependence coefficient in a theta solvent k_Θ is given by

$$k_\Theta = k_\Theta'\left(\frac{4\pi}{300}\right)\left(\frac{1}{6\pi}\right)^3 N_A \frac{[f]_\theta^3}{M} \qquad (17)$$

where k_Θ' is a numerical constant. In the theory of Pyun and Fixman $k_\Theta' = 7.16 - \kappa(0)$ where $\kappa(0) = 4.20$, 4.56, or 4.93 depending on the three approximations for the binary clusters of overlapping spheres, while in the theory of Yamakawa $k_\Theta' = 1$. Substituting eq 6 into eq 17 and using the relationship, $A_0 = \langle s^2\rangle_\Theta/M$, we have

$$k_\Theta = 7.41 \times 10^{21}\, k_\Theta' A_0^{3/2} M^{1/2} \qquad (18)$$

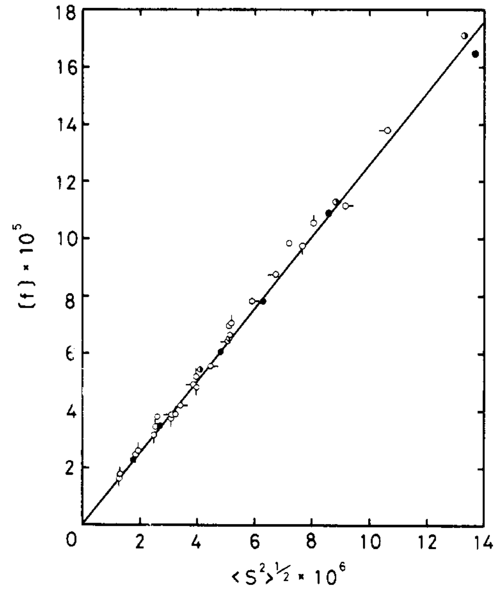

Figure 5. Relationship between $[f]$ and $\langle s^2\rangle^{1/2}$: in cyclohexane at 34.5 °C (ό); in *trans*-decalin at 9.5 °C (ϙ), at 20 °C (O-), and at 40 °C (-O); and in toluene at 25 °C (●). O and ◑ denote the data of Ooms, Mijnlieff, and Beckers for poly(α-methylstyrene) in cyclohexane at 35 °C and in toluene at 25 °C, respectively. The line denotes the proportionality between $[f]$ and $\langle s^2\rangle^{1/2}$ with the proportional constant 12.5$_3$ according to Kirkwood and Riseman.

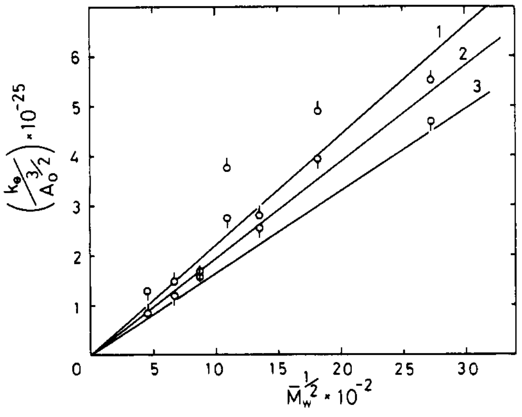

Figure 6. Plots of $k_\Theta/A_0^{3/2}$ vs. $\bar{M}_w^{1/2}$ in cyclohexane at 34.5 °C (ό) and in *trans*-decalin at 9.5 °C (ϙ). Lines 1, 2, and 3 denote the theory of Pyun and Fixman for $\kappa(0) = 4.20$, 4.56, and 4.93, respectively.

Imai[17] also gave the same equation as eq 18 though his constant is smaller than that of Pyun and Fixman.

To eliminate the difference between the unperturbed dimensions of poly(α-methylstyrene) in cyclohexane and in *trans*-decalin,[4] $k_\Theta/A_0^{3/2}$ is plotted against $M^{1/2}$ for the three values of k_Θ' given by Pyun and Fixman as shown in Figure 6. It is clear from the figure that the experimental data are in good agreement with the theory of Pyun and Fixman over a wide range of molecular weights, as already shown[6] for the samples with lower molecular weights than 10^6.

For the sake of comparison between the theories and the experimental results in good solvents, let us rewrite the theory of Pyun and Fixman as

$$\frac{k}{k_\Theta\alpha_f^3} = \frac{7.16 - \kappa(\bar{z})}{7.16 - \kappa(0)} = 1 + \frac{\kappa(0) - \kappa(\bar{z})}{7.16 - \kappa(0)} \qquad (19)$$

where we divided eq 13 by eq 17 and used eq 7. Here, it may be meaningful to note that $k/k_\Theta\alpha_f^3$ has the physical meaning of the ratio of the concentration dependence coefficients in

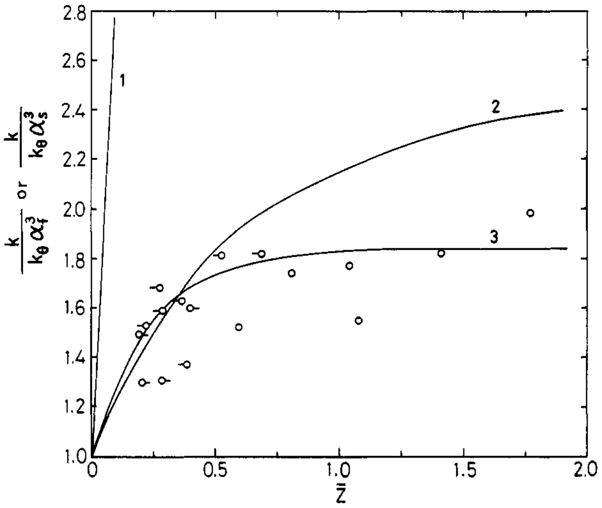

Figure 7. The effect of excluded volume on the concentration dependence coefficient. The symbols O–, –O, and O are the data in *trans*-decalin at 20 and 40 °C and in toluene at 25 °C, respectively. Curves 1 and 2 denote the theoretical equations of Yamakawa and of Pyun and Fixman, respectively. Curve 3 denotes empirical eq 22.

the plots of frictional coefficient vs. volume fraction of polymer spheres in nontheta and theta solvents.

The theory of Yamakawa can also be transformed into

$$\frac{k}{k_\Theta \alpha_f^3} = 1 + \frac{648\pi^{7/2}}{P_\Theta^3}\lambda(\bar{z})\bar{z}h(\bar{z}) \tag{20}$$

Here, we assumed $\alpha_f = \alpha_s$ and used eq 16, 17, 6, and 7, together with the general relationship between A_2 and the penetration function $\bar{z}h(\bar{z})$,

$$A_2 = 4\pi^{3/2}N_A \frac{\langle s^2\rangle^{3/2}}{M^2}\bar{z}h(\bar{z}) \tag{21}$$

In his original paper[16] the modified Flory–Krigbaum–Orofino expression was used for $\bar{z}h(\bar{z})$, that is, $\bar{z}h(\bar{z}) = \ln(1 + 5.73\bar{z})/5.73$.[1,18] As is obvious from eq 19 and 20, the theories predict that $k/k_\Theta\alpha_f^3$ is a function of $\bar{z}$ only.

In Figure 7, the experimental data for $k/k_\Theta\alpha_s^3$ are plotted against $\bar{z}$ as determined in our previous work on light scattering from the same polymer solutions. Here it is noted that we used α_s instead of α_f because α_s is almost equal to α_f, as already shown, and α_s is measured more accurately than α_f. In the figure, the calculated values of $k/k_\Theta\alpha_f^3$ from the theories of Pyun and Fixman and of Yamakawa are also shown in comparison with the experimental data. Here, we assumed eq 14 and used $\kappa(0) = 4.93$ in eq 19, since the numerical values of κ are given only for this case in the original paper of Pyun and Fixman. From the figure, it appears that the experimental data of $\kappa/\kappa_\Theta\alpha_f^3$ may be expressed in terms of $\bar{z}$, as expected from the theories. Quantitatively speaking, however, the theory of Pyun and Fixman is found to be in good agreement with the experimental data at small excluded volumes[6,14,19] but deviates from the data at large excluded volumes. If eq 15 is assumed instead of eq 14, the theory deviates the data at the smaller excluded volumes.

The theory of Yamakawa gives much higher values of the ratio $\kappa/\kappa_\Theta\alpha_f^3$ than the experimental data as shown in the figure. In his theory, k_Θ' is clearly underestimated but, moreover, the effect of thermodynamic interaction may be overestimated.

At the limit of large $\bar{z}$, $\kappa/\kappa_\Theta\alpha_f^3$ tends to a constant which is a ratio of the concentration dependence coefficient for hard spheres to that for soft penetrable spheres in theta solvents (at the volume fraction concentration unit) in the theory of Pyun and Fixman. Its values are 2.41, 2.75, and 3.21 depending on the three approximations. From Figure 7, it appears that the experimental data of $\kappa/\kappa_\Theta\alpha_f^3$ level off approximately at $\bar{z} = 0.5$ and tend to about 1.8–2.0 at the limit of large $\bar{z}$, which is smaller than the limiting values of Pyun and Fixman. This may imply that a polymer coil in good solvents may behave like a hard sphere but is not literally hard in the intermolecular hydrodynamic interaction as well as in the intermolecular thermodynamic interaction. In the theory of Yamakawa, moreover, the limiting value of $\kappa/\kappa_\Theta\alpha_f^3$ depends on the value of $\bar{z}h(\bar{z})$ which is almost constant at the limit of large $\bar{z}$, though the value is much higher than the experimental data.

From the above discussion it is clear that the concentration dependence coefficient κ is determined not only by the hydrodynamic volume of the polymer but also by the intermolecular thermodynamic interaction, just as the second virial coefficient. That is, we can speculate that there may be a close relationship between $\kappa/\kappa_\Theta\alpha_f^3$ and the penetration function $\bar{z}h(\bar{z})$ as can be seen in the theory of Yamakawa. Here, we would like to present an empirical equation

$$\kappa/\kappa_\Theta\alpha_f^3 = 1 + g\bar{z}h(\bar{z}) \tag{22}$$

where g is a numerical constant which is approximately 4 and $\bar{z}h(\bar{z})$ is the penetration function of Cassasa and Markovitz,[20,21] which is in good agreement with the experimental second virial coefficients.[4] Equation 22 corresponds to eq 20 except for the numerical constant and the functional form of $\bar{z}h(\bar{z})$. If we use the value of k_Θ' which is in good agreement with the experimental data in the theta solvents instead of unity in the theory of Yamakawa, eq 20 reduces to eq 22 where g is about 8.

As seen in Figure 7, eq 22 shows good agreement with the experimental data. This may mean that the variation of the concentration dependence of the frictional coefficient with excluded volume is similar to that of the second virial coeffient.

Acknowledgment. We wish to thank Professor Mitsuru Nagasawa for his constant interest in this work and for critically reading the manuscript. We also wish to thank Dr. Teruo Fujimoto for his assistance in preparing the samples.

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