

Primary Structure of Poly(*N*-isopropylacrylamide) Synthesized by Radical Polymerization. Effects of Polymerization Solvents

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The mean-square radius of gyration (S^2), second virial coefficient A_2 , and intrinsic viscosity $[\eta]$ were determined in methanol at 25.0 °C for two kinds of poly(*N*-isopropylacrylamide) (PNIPA) synthesized by radical polymerization in *tert*-butanol and benzene by the use of azobis(isobutyronitrile) as an initiator. In all cases of the three quantities, it is found that the value is smaller for the PNIPA synthesized in benzene than for that synthesized in *tert*-butanol and the difference between the two kinds of PNIPA increases with increasing the weight-average molecular weight M_w . The average chain dimension of the former PNIPA should then be smaller than that of the latter. Since the two kinds of PNIPA were shown to have the same stereochemical composition (and also the same chain end group), the difference in the average chain dimension may be regarded as arising from the difference in the primary structure, *i.e.*, the number of branch points. Considering the fact that the average dimension of a given polymer chain in general decreases with increasing the number of branch points, it may be concluded that the number is larger in the former PNIPA than in the latter. The behavior of the interpenetration function Ψ and the Flory–Fox factor Φ as functions of M_w is also examined, confirming the conclusion.

KEY WORDS: Poly(*N*-isopropylacrylamide) / Primary Structure / Mean-Square Radius of Gyration / Second Virial Coefficient / Intrinsic Viscosity / Interpenetration Function / Flory–Fox Factor /

In a previous paper,¹ we have reported results for the cloud point in aqueous solutions of four kinds of poly(*N*-isopropylacrylamide) (PNIPA) samples synthesized by radical polymerization in *tert*-butanol, methanol, benzene, and 1,4-dioxane by the use of azobis(isobutyronitrile) (AIBN) as an initiator. It has been shown that the cloud point so determined is definitely lower for the samples synthesized in benzene and 1,4-dioxane than for those synthesized in *tert*-butanol and methanol, although all the samples have almost the same stereochemical composition and the same end group. It has then been conjectured that the difference in the cloud point may be regarded as arising from the difference in the primary structure, *i.e.*, the number of branch points, between the samples synthesized in the solvents of different quality (good or poor). In this paper, we actually perform a detailed examination of the primary structure of the PNIPA samples synthesized in *tert*-butanol (good solvent) and benzene (poor or nonsolvent) in order to confirm the conjecture.

Previously,¹ we have not been able to verify the existence of branch points in the PNIPA samples by means of ¹H NMR. It may be considered that the number of branch points, which form through side-chain reactions such as the chain transfer during the radical polymerization, is not large enough to be detected by ¹H or ¹³C NMR or by other spectroscopic methods, since the intensity of such a spectroscopic signal is in principle proportional to the number of atoms which belong to the branch points. On the other hand, the average dimension of a polymer chain represented by its mean-square radius of gyration (S^2) and/or the intrinsic viscosity $[\eta]$ is considered to be sensitive to its primary structure and is expected to be useful

to detect branch points in it even if they are only a few. In this study, therefore, we determine (S^2) and the second virial coefficient A_2 by light scattering (LS) measurements and $[\eta]$ by viscosity measurements and then examine the difference in the average chain dimension between the PNIPA samples synthesized in *tert*-butanol and benzene.

EXPERIMENTAL

Materials

Two kinds of (original) PNIPA samples were synthesized by radical polymerization in *tert*-butanol and benzene by the use of AIBN as an initiator. In each solvent, *N*-isopropylacrylamide (*ca.* 20 g), which had been recrystallized three times from a 8/2 mixture of *n*-hexane and benzene and then dried in a vacuum for 12 h, was polymerized in the solvent (*ca.* 150 mL) with AIBN (*ca.* 1 mol %) under dry nitrogen at 60 °C for 30 h, the conversion being almost 100%. The original samples so synthesized were purified by reprecipitation from acetone solutions into *n*-hexane and then separated into fractions of narrow molecular weight distribution by fractional precipitation using acetone as a solvent and *n*-hexane as a precipitant, or by a column elution method with a mixture 6/4 of *n*-hexane and acetone as an eluent. The test samples so prepared were dissolved in 1,4-dioxane, then filtered through a Teflon membrane of pore size 1.0 μm, and finally freeze-dried from their 1,4-dioxane solutions. They dried in a vacuum at *ca.* 80 °C for *ca.* 12 h just prior to use.

In the first and fourth columns of Table I are given the codes of all the 17 samples used in this work, the first letters T and B

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Table I. Poly(*N*-isopropylacrylamide) samples synthesized in *tert*-butanol and benzene

in <i>tert</i> -butanol			in benzene		
sample	M_w/M_n	f_r	sample	M_w/M_n	f_r
T5	1.14	0.52	B5	1.17	0.52
T7	1.11		B11	1.22	
T13	1.23	0.52	B14	1.14	0.51
T23	1.18		B20	1.18	
T38	1.12		B62	1.22	
T54	1.16		B130	1.21	
T96	1.19		B170	1.24	
T120	1.23		B270	1.26	0.52
T220	1.20	0.52			

in the codes indicating the solvents used for radical polymerization, *i.e.*, *tert*-butanol and benzene, respectively. We note that the samples T5, T13, B5, and B14 are the same as those used in the previous study.¹ In the second and fifth columns of the table are given the values of the ratio of the weight-average molecular weight M_w to the number-average molecular weight M_n , which were determined from analytical gel permeation chromatography (GPC) in the same manner as before¹ using tetrahydrofuran as an eluent and 12 standard polystyrene (PS) samples (Tosoh, $M_w = 2.8 \times 10^3 - 8.4 \times 10^6$, $M_w/M_n = 1.02 - 1.17$) as reference standards. In the table are also given the values of the fraction f_r of racemo diads for the samples T5, T13, T220, B5, B14, and B270 in the third and sixth columns, which were determined from ¹H NMR spectra in the same manner as before¹ on the basis of the assignments of the ¹H signals proposed by Isobe *et al.*² Each of the two series of samples Tx and Bx came from one original sample, so that all the samples listed in the Table I should have almost the same stereochemical composition.

The solvent methanol used for LS and viscosity measurements was purified by distillation after refluxing over calcium hydride for *ca.* 6 h. The solvents tetrahydrofuran used for analytical GPC and deuterated dimethyl sulfoxide used for NMR spectroscopy were of reagent grade.

Light Scattering

LS measurements were carried out to determine M_w and A_2 for all the 17 samples and $\langle S^2 \rangle$ for 13 samples with $M_w \gtrsim 1.3 \times 10^5$, in methanol at 25.0 °C. A Fica 50 light-scattering photometer was used for all the measurements with vertically polarized incident light of wavelength $\lambda_0 = 436$ nm. For a calibration of the apparatus, the intensity of light scattered from pure benzene was measured at 25.0 °C at a scattering angle of 90°, where the Rayleigh ratio $R_{Uu}(90^\circ)$ of pure benzene was taken as $46.5 \times 10^{-6} \text{ cm}^{-1}$.³ The depolarization ratio ρ_u of pure benzene at 25.0 °C was determined to be 0.41 ± 0.01 . Scattered intensity was measured at seven or eight different concentrations and at scattering angles θ ranging from 15.0 to 142.5°, and then converted to the excess unpolarized (Uv) components ΔR_{Uv} of the reduced scattered intensity by the use of the scattered intensity from the solvent methanol. The data obtained were treated by using the Berry square-root plot.⁴ For

all the samples, corrections for the optical anisotropy were unnecessary since the degree of depolarization was negligibly small.

The most concentrated solution of each sample was prepared gravimetrically and made homogeneous by continuous stirring at room temperature for 1–3 d. It was optically purified by filtration through a Teflon membrane of pore size 1.0, 0.45, or 0.10 μm . The solutions of lower concentrations were obtained by successive dilution. The weight concentrations of the test solutions were converted to the polymer mass concentrations c by the use of the densities of the respective solutions calculated with the partial specific volumes v_2 of the samples and with the density ρ_0 of the solvent methanol. The values of v_2 in methanol at 25.0 °C were determined to be 0.903 cm^3/g for all the samples independently of the kinds of solvents used for radical polymerization and M_w , by the use of a pycnometer of the Lipkin–Davison type having a volume of 10 cm^3 . For the value of ρ_0 of methanol at 25.0 °C, we used the literature value 0.7866 g/cm^3 .⁵

The refractive index increment $\partial n/\partial c$ was measured at the wavelength of 436 nm by the use of a Shimadzu differential refractometer DR-1. The values of $\partial n/\partial c$ in methanol at 25.0 °C were determined to be 0.184₄, 0.183₀, and 0.183₇ cm^3/g for the samples T5, T7, and T13, respectively, 0.185₄ cm^3/g for the samples T23–T220 independently of M_w , 0.182₂ and 0.183₈ cm^3/g for the samples B5 and B11, respectively, and 0.185₇ cm^3/g for the samples B14–B270 independently of M_w . For the refractive index n_0 of methanol at 25.0 °C at the wavelength of 436 nm, we used the literature value 1.3337.⁵

Viscosity

Viscosity measurements were carried out for all the 17 samples in methanol at 25.0 °C by the use of a conventional capillary viscometer of the Ubbelohde type. The flow time was measured to a precision of 0.1 s, keeping the difference between those of the solvent and solution larger than 20 s. The test solutions were maintained at a constant temperature within ± 0.005 °C during the measurements.

The most concentrated solution of each sample was prepared in the same manner as in the case of the LS measurements. The solutions of lower concentrations were obtained by successive dilution. The polymer mass concentrations c were calculated from the weight fractions with the densities of the solutions. Density corrections were also made in the calculations of the relative viscosity η_r from the flow times of the solution and solvent. The data obtained for the specific viscosity η_{sp} and η_r in the range of $\eta_r < 1.8$ were treated as usual by the Huggins (η_{sp}/c vs c) and Fuoss–Mead ($\ln \eta_r/c$ vs c) plots, respectively, to determine $[\eta]$ and the Huggins coefficient k' . (Note that the two plots have the same intercept.)

RESULTS AND DISCUSSION

The values of M_w , $\langle S^2 \rangle$, and A_2 determined from LS measurements and those of $[\eta]$ and k' from viscosity measure-

Table II. Results of LS and viscosity measurements for poly(*N*-isopropylacrylamide) in methanol at 25.0 °C

sample	M_w	$10^{-4}\langle S^2 \rangle$ (\AA^2)	$10^4 A_2$ ($\text{cm}^3 \text{mol/g}^2$)	$[\eta]$ (dL/g)	k'	Ψ	$10^{-23}\Phi$ (mol^{-1})
samples synthesized in <i>tert</i> -butanol							
T5	5.17×10^4		6.05	0.308	0.40		
T7	7.19×10^4		5.35	0.389	0.39		
T13	1.31×10^5	1.8 ₇	4.71	0.606	0.36	0.23 ₇	2.1 ₂
T23	2.27×10^5	3.3 ₄	3.96	0.926	0.38	0.24 ₉	2.3 ₄
T38	3.76×10^5	6.1 ₂	3.58	1.27	0.36	0.25 ₀	2.1 ₄
T54	5.35×10^5	9.2 ₉	3.25	1.73	0.35	0.24 ₅	2.2 ₃
T96	9.63×10^5	17.4	2.90	2.47	0.36	0.27 ₇	2.2 ₄
T120	1.16×10^6	22.6	2.76	2.84	0.35	0.25 ₇	2.0 ₈
T220	2.20×10^6	45.5	2.39	4.33	0.39	0.28 ₁	2.1 ₁
samples synthesized in benzene							
B5	4.65×10^4		5.73	0.275	0.42		
B11	1.11×10^5		4.48	0.484	0.39		
B14	1.44×10^5	1.9 ₃	4.31	0.591	0.40	0.25 ₁	2.1 ₇
B20	1.97×10^5	2.6 ₃	3.94	0.683	0.39	0.26 ₈	2.1 ₅
B62	6.21×10^5	8.9 ₈	2.88	1.40	0.39	0.30 ₈	2.2 ₀
B130	1.30×10^6	17.7	2.34	2.17	0.38	0.39 ₅	2.5 ₇
B170	1.72×10^6	22.4	2.02	2.61	0.39	0.42 ₄	2.8 ₉
B270	2.69×10^6	34.2	1.79	3.17	0.40	0.48 ₄	2.9 ₀

ments for the PNIPA samples in methanol at 25.0 °C are given in the second through sixth columns, respectively, in Table II. In the table, the values of $\langle S^2 \rangle$ for the samples T5, T7, B5, and B11 with smaller M_w have been omitted because the slopes of the Berry square-root plots against the square of the magnitude of the scattering vector for those samples are not sufficiently large to evaluate $\langle S^2 \rangle$ accurately. The values of A_2 are of order $10^{-4} \text{ cm}^3 \text{ mol/g}^2$ and those of k' are in the range of $0.3 \lesssim k' \lesssim 0.4$, indicating that methanol at 25.0 °C is a good solvent for PNIPA.

Mean-Square Radius of Gyration

Figure 1 shows double-logarithmic plots of $\langle S^2 \rangle$ (in \AA^2) against M_w for PNIPA in methanol at 25.0 °C. The circles and triangles represent the values for the PNIPA samples synthesized in *tert*-butanol and benzene, respectively. The solid curve connects smoothly the data points for the samples synthesized in each solvent. It is seen from the figure that the data points for the samples synthesized in benzene deviate downward from those synthesized in *tert*-butanol in the whole range of M_w examined, and the deviation increases with increasing M_w . The slopes of the data points in the range of $M_w \gtrsim 10^6$ are 1.1₂ and 0.9₀ for the samples synthesized in *tert*-butanol and benzene, respectively. Note that the former value 1.1₂ is somewhat smaller than 1.2 for linear flexible polymers with very large M_w in good solvents and further that the latter value 0.9₀ is even smaller than unity for unperturbed linear flexible polymers. It implies that the primary structure of PNIPA synthesized by radical polymerization is not linear.

The average dimension of a given polymer chain in dilute solution may in general be affected by chain stiffness and local chain conformation⁶ which are mainly determined by the chemical structure and stereochemical composition of the chain, by the intramolecular excluded-volume effect^{6,7} which is

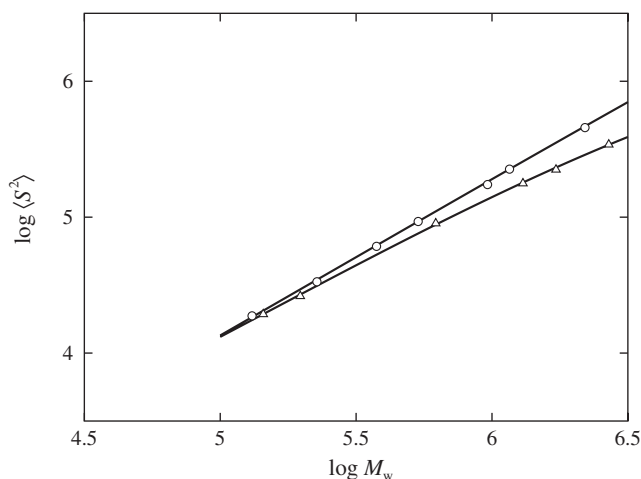


Figure 1. Double-logarithmic plots of $\langle S^2 \rangle$ (in \AA^2) against M_w for PNIPA in methanol at 25.0 °C: (O) samples synthesized in *tert*-butanol; (Δ) samples synthesized in benzene. The solid curve connects smoothly the data points for the samples synthesized in each solvent.

determined by interactions between polymer segments and solvent molecules, and by the primary structure of the chain.⁷ The stereochemical compositions of all the PNIPA samples used in the present study have been confirmed to be almost identical with each other, as already mentioned in the preceding section. The difference in $\langle S^2 \rangle$ between the two kinds of samples, both having the same chemical structure and stereochemical composition and both measured in the same solvent condition, therefore, is considered to be caused by the difference in the primary structure, *i.e.*, the number of branch points. Then the number of branch points in the PNIPA sample synthesized in benzene seems larger than that in the sample synthesized in *tert*-butanol, since in general the larger the

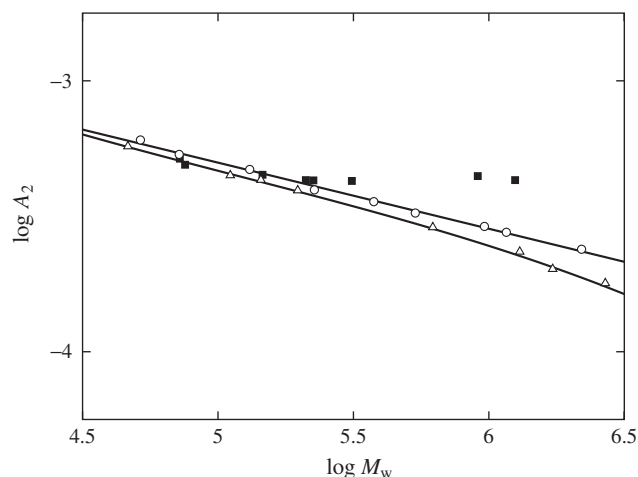


Figure 2. Double-logarithmic plots of A_2 (in $\text{cm}^3 \text{mol/g}^2$) against M_w for PNIPA in methanol at 25.0°C : (■) literature data by Chiantore *et al.*⁸ The unfilled symbols and curves have the same meaning as those in Figure 1.

number of branch points is, the smaller the average chain dimension is. Further, the difference in the number of branch points between the two kinds of samples seems to increase with increasing M_w .

Second Virial Coefficient

Figure 2 shows double-logarithmic plots of A_2 (in $\text{cm}^3 \text{mol/g}^2$) against M_w for PNIPA in methanol at 25.0°C . The unfilled symbols and the solid curves have the same meaning as those in Figure 1. As in the case of $\langle S^2 \rangle$ shown in Figure 1, the data points for the samples synthesized in benzene deviate downward from those synthesized in *tert*-butanol in the whole range of M_w examined, and the deviation increases with increasing M_w . It indicates that the effective volume V_E excluded to one polymer chain by the presence of another, which may be defined by

$$A_2 = 4N_A V_E / M_w^2 \quad (1)$$

with N_A the Avogadro constant, is smaller for the former samples. The slopes of the data points in the range of $M_w \gtrsim 10^6$ are -0.2_3 and -0.3_3 for the samples synthesized in *tert*-butanol and benzene, respectively, which are somewhat less than -0.2 for linear flexible polymers with very large M_w in good solvents, implying that the distribution of segments constituting a single polymer chain is more compact for the present PNIPA, especially for that synthesized in benzene, than for linear flexible polymers in good solvents.

For comparison, in Figure 2 are also plotted the literature data for PNIPA in methanol at 25.0°C reported by Chiantore *et al.*⁸ (■) by the use of samples synthesized in methanol at temperatures ranging from 50 to 70°C with AIBN as an initiator. Although their values of A_2 are rather in good agreement with ours in the range of $M_w \lesssim 10^5$, the former values deviate upward from ours and seem almost independent of M_w . Such behavior of A_2 is usually observed for very stiff chains and is unusual for flexible polymers with very large M_w in good solvents.

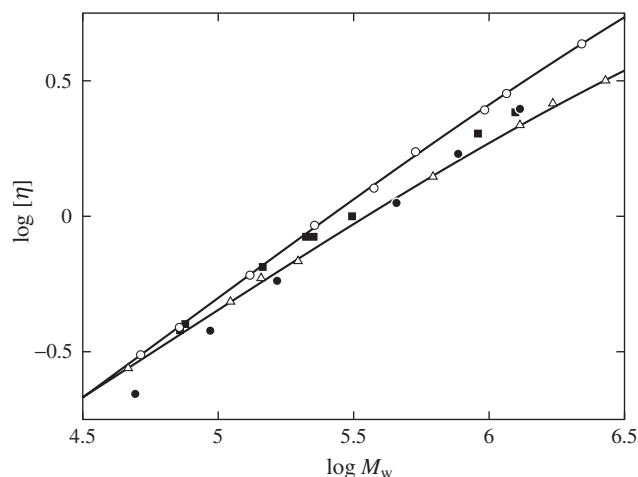


Figure 3. Double-logarithmic plots of $[\eta]$ (in dL/g) against M_w for PNIPA in methanol at 25.0°C : (■) literature data by Chiantore *et al.*⁸ (●) literature data by Zeng *et al.*⁹ The unfilled symbols and curves have the same meaning as those in Figure 1.

Intrinsic Viscosity

Figure 3 shows double-logarithmic plots of $[\eta]$ (in dL/g) against M_w for PNIPA in methanol at 25.0°C . The unfilled symbols and the solid curves have the same meaning as those in Figure 1. As in the cases of $\langle S^2 \rangle$ and A_2 shown in Figures 1 and 2, respectively, the data points for the samples synthesized in benzene deviate downward from those synthesized in *tert*-butanol in the whole range of M_w examined, and the deviation increases with increasing M_w . It indicates that the effective hydrodynamic (molar) volume, which may be defined by

$$V_H = 6^{-3/2} M_w [\eta] \quad (2)$$

is smaller for the former samples. The slopes of the data points in the range of $M_w \gtrsim 10^6$ are 0.6_7 and 0.5_1 for the samples synthesized in *tert*-butanol and benzene, respectively, which are smaller than 0.8 for linear flexible polymers with very large M_w in good solvents.

For comparison, in Figure 3 are also plotted the literature data for PNIPA in methanol at 25.0°C reported by Chiantore *et al.*⁸ (■) by the use of the same samples as those shown in Figure 2 and by Zeng *et al.*⁹ (●) by the use of samples synthesized in *tert*-butanol at 55°C with AIBN as an initiator. The data points by Chiantore *et al.* follow a straight line with a slope of 0.6_1 in the range of $M_w \gtrsim 10^5$, implying that their PNIPA should be flexible. Such behavior is inconsistent with that of A_2 . The data points by Zeng *et al.* deviate downward from the present ones for the samples synthesized in *tert*-butanol (○). The reason for this difference is not clear.

Interpenetration Function

All the present experimental results for $\langle S^2 \rangle$, A_2 , and $[\eta]$ shown above imply that the number of branch points in the PNIPA samples synthesized in benzene is larger than that in the samples synthesized in *tert*-butanol. The interpenetration function Ψ defined by

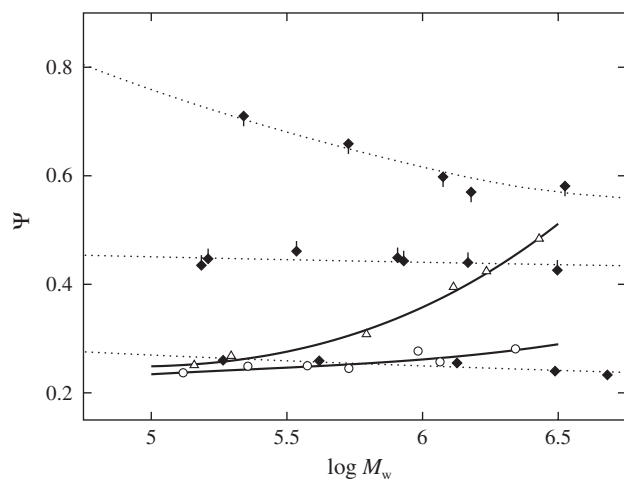


Figure 4. Plots of Ψ against $\log M_w$. The unfilled symbols and solid curves have the same meaning as those in Figure 1. The filled symbols represent the literature data for PS in benzene at 25.0 °C: (◆) linear PS;^{10,11} (◆) 4-arm star PS;¹² (◆) 6-arm star PS.¹³ The dotted curve connects smoothly the data points for each kind of PS.

$$\Psi = \frac{V_E}{\pi^{3/2} \langle S^2 \rangle^{3/2}} \quad (3)$$

is known to be a quantity sensitive to the primary structure of a polymer chain,^{6,7} which takes a value *ca.* 0.24 for linear flexible polymer chains with very large M in good solvents and takes a larger value if the segment density of the polymer chain under consideration in dilute solution is larger than that of the linear flexible chain. It is therefore interesting to examine the behavior of Ψ .

In the seventh column of Table II are given the values of Ψ calculated from eq 3 with eq 1 along with the values of M_w , $\langle S^2 \rangle$, and A_2 given in the second through fourth columns, respectively, of the table. Figure 4 shows plots of Ψ against $\log M_w$ for PNIPA in methanol at 25.0 °C. The unfilled symbols and the solid curves have the same meaning as those in Figure 1. It is seen that Ψ for the samples synthesized in benzene remarkably increases with increasing M_w .

For comparison, in Figure 4 are also plotted the literature data for linear polystyrene (PS) (◆),^{10,11} regular four-arm star PS (◆),¹² regular six-arm star PS (◆),¹³ all measured in benzene at 25.0 °C. The dotted curve connects smoothly the data points for each kind of PS. It is seen that Ψ increases with increasing number of the arms. Note that the linear PS corresponds to the regular 2-arm star PS. For the PNIPA samples synthesized in benzene, Ψ is close to that for the linear PS in the range of $M_w \lesssim 3 \times 10^5$, but deviates upward from the latter as M_w is increased, and becomes even larger than that for the regular four-arm star PS. In contrast to this, Ψ for the PNIPA samples synthesized in *tert*-butanol becomes slightly larger than that for the linear PS as M_w is increased. The difference in the behavior of Ψ between the two kinds of samples confirms the above implication that the number of branch points in the PNIPA samples synthesized in benzene is larger than that in the samples synthesized in *tert*-butanol.

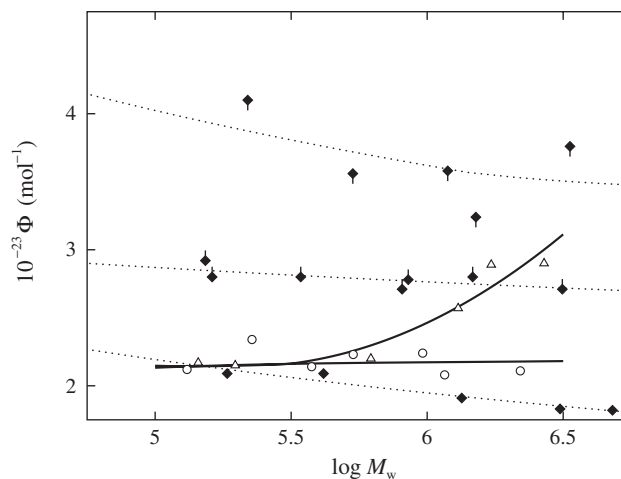


Figure 5. Plots of Φ (in mol⁻¹) against $\log M_w$. The unfilled symbols and solid curves have the same meaning as those in Figure 1. The filled symbols and dotted curves have the same meaning as those in Figure 4.

Flory–Fox Factor

The Flory–Fox factor Φ defined by

$$\Phi = \frac{V_H}{\langle S^2 \rangle^{3/2}} \quad (4)$$

is also sensitive to the primary structure of a given polymer chain, which takes a value *ca.* 2×10^{23} mol⁻¹ for linear flexible polymer chains with very large M in good solvents and takes a larger value if the segment density of the polymer chain under consideration in dilute solution is larger than that of the linear flexible chain. In the eighth column of Table II are given the values of Φ calculated from eq 4 with eq 2 along with the values of M_w , $\langle S^2 \rangle$, and $[\eta]$ given in the second, third, and fifth columns, respectively, of the table.

Figure 5 shows plots of Φ (in mol⁻¹) against $\log M_w$ for PNIPA in methanol at 25.0 °C. All the symbols and curves in the figure have the same meaning as those in Figure 4. The difference in behavior of Φ between the two kinds of PNIPA samples is the same as that in the behavior of Ψ .

Finally, we make brief mention of the number of branch points in the PNIPA samples. Existence of branch points could not be detected by ¹H NMR even for the samples synthesized in benzene,¹ which are considered to have not a few branch points, while, as expected, it has been clearly verified in the present study of the average chain dimension. Probability that a given proton belongs to one of the branch points in PNIPA chains should be smaller than 1%, *i.e.*, detectability of ¹H NMR spectroscopy.

CONCLUSION

We have determined $\langle S^2 \rangle$, A_2 , and $[\eta]$ in methanol at 25.0 °C for the two kinds of PNIPA samples synthesized by radical polymerization in *tert*-butanol and benzene by the use of AIBN as an initiator. For all the three quantities, it has been found that

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the observed value for the latter PNIPA is smaller than that for the former and the difference increases with increasing M_w , indicating that the average chain dimension of the latter PNIPA is smaller than that of the former. Since the two kinds of PNIPA have the same stereochemical composition (and also the same chain end group), the difference in the average chain dimension may be regarded as arising from the difference in the primary structure, *i.e.*, the number of branch points. The average dimension of a given polymer chain in general decreases with increasing the number of branch points. It may then be concluded that the number of the branch points is larger in the latter PNIPA than in the former. It has also been found that the values of Ψ and Φ for the latter PNIPA are remarkably larger than the corresponding values for the linear PS, confirming the conclusion. Increase in the number of branch points is necessarily accompanied by increase in the number of hydrophobic end groups, which might be the reason for the difference in the cloud point between the two kinds of PNIPA.¹

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