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Conformational characteristics of poly(ethylene oxide) (PEO) in methanol

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Abstract

The conformational characteristics of poly(ethylene oxide) (PEO) in methanol at 25 °C were investigated by static light scattering and viscometry for high molar mass (M_w) PEO fractions covering $M_w = 3.42 \times 10^5$–5.05×10^6 g mol^{-1}. No trace of downturn in the plot of angular dependence of Kc/R_θ at low angle was found. Experimental scaling laws for the second virial coefficient (A_2), the third virial coefficient (A_3), the radius of gyration ($\langle R_G^2 \rangle^{1/2}$) and the intrinsic viscosity ($[\eta]$) were determined. The exponents characterizing these scaling laws confirmed that the PEO chain in methanol has a flexible conformation with relatively large excluded volume, but methanol is not as good solvent as water. On the other hand, the low value of interpenetration function (Ψ) and the relatively higher order of the dimensionless parameter Π are considered to be an indication of local chain stiffness. All the results obtained in this study allow us to conclude that the overall chain conformation of PEO assumed in methanol is basically a random coil, but is intermittently mixed with helical structure.

Keywords: Poly(ethylene oxide); Conformational characteristics; Third virial coefficient

1. Introduction

Poly(ethylene oxide) (PEO) has been one of the most extensively studied synthetic polymers, because of not only its unique behaviors in solution but also its wide applications [1,2]. For decades, the peculiar behaviors of PEO aggregation in various solvents including water have been the major concern in many PEO studies [3–7]. Many studies have been focused on whether the PEO aggregation is an inherent property or not. Kinugasa et al. [7], and Devanand and Selser [8] have shown that if proper care is taken in preparing the solution, molecular dispersion of PEO molecules in water or methanol can be attained without aggregation. Thus, no more plausible reasons that the aggregation is an inherent property of PEO/water or PEO/methanol systems can be found. However, there was not enough experimental evidence in dilute solution properties to conclude the conformational characteristics of PEO at present.

Kawaguchi et al. [9] analyzed the data of the radius of gyration ($\langle R_G^2 \rangle^{1/2}$) and the intrinsic viscosity ($[\eta]$) for PEO, having molar mass (M_w) range from 62 to 1.1×10^7 g mol^{-1}, in salt-free water and benzene, and also evaluated those helical wormlike chain parameters to describe the chain expansion behavior in water. By analogy, Devanand and Selser [3] have proposed that PEO chain has a flexible coil structure taking larger volume in water than in methanol, by observing the dynamic scattering behavior in the dilute regime. Their assertion, however, on the chain expansion is simply based on an earlier study suggesting the local helicity in PEO coil when water is used as the solvent [10], or the greater compacting effect of polymer in water than any other solvents. Indeed, there have been earlier spectral studies on local phenomena in PEO solutions using NMR [11,12], IR [11], and Raman spectroscopies [13], which have shown the evidences of locally helical structure of PEO chains in water.

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In their data analysis on the Peterlin parameter ε and Mark–Houwink exponent α of dilute aqueous PEO solutions, Eshuis and Mijnlieff [14] announced that a helix formation or local crystallization can be occurred among the PEO molecules in aqueous medium, and this might promote local associations. If polymers were not too low in M_ws, they insist that this will not affect the coil character of the dissolved polymer molecules, and their intrinsic viscosity will obey the Mark–Houwink relation with an α of about 0.5. On the other hand, Vandermiers et al. [15] determined experimentally those scaling laws for $\langle R_G^2\rangle^{1/2}$, the second virial coefficient (A_2), and the hydrodynamic radius (R_H) of the dilute PEO/methanol solution, and suggested that the methanol is a good solvent for PEO molecules without occurring aggregations. Nevertheless, according to the scaling law they established, $\langle R_G^2\rangle^{1/2}$ is varied with $M_w^{0.5\pm0.1}$, which is an indication that the polymer may be under or near the θ-state, and hence, in this condition, the chain expansion of the polymer coil due to excluded volume effect can hardly be anticipated. Despite these considerable works on dilute solution properties of PEO have been conducted, a full understanding of the accurate chain conformation of PEO molecules in solution still leaves much to be desired.

In light of the conformational ambiguities of PEO molecules in solution, whether they have originated from aggregation phenomena or inaccurate determinations of conformational parameters, particularly in their local conformation, it seems worthwhile to reexamine the conformational characteristics of this potential polymer in a more congenial solvent like methanol. In this study, five PEO samples covering M_w range from 3.42×10^5 to 5.05×10^6 g mol^{-1} were examined by static light scattering and viscometry. For more accurate determinations of M_w and A_2, the third virial coefficient (A_3) was taken into account. Scaling laws of some important molecular parameters were established and discussed in terms of the solvent quality and possible chain conformation. All those conformational parameters so far obtained experimentally, allowed us to propose cautiously that the PEO in methanol at 25 °C retains the expanded random coil structure.

2. Experimental

2.1. Materials and solution preparation

Five commercial PEO samples were purchased from Aldrich (PEO1) and Scientific Polymer Products Inc. (PEO2–PEO5). Spectral grade methanol (Aldrich) was used.

All the stock solutions were prepared gravimetrically. Firstly, the polymer was dissolved in methanol at 30–40 °C until the solution be transparent, and the solution temperature was raised to 50 °C with stirring for about 1 h after sealing the solution vial tightly. After cooling to room temperature, the final solution was filtered directly into light scattering cells using 0.2 μm pore size poly(tetrafluoroethylene) filter for the optical clarification. The concentration range of the final solutions varies from 0.024 to 5.050 mg cm^{-3}.

2.2. Size exclusion chromatography

The polydispersities of individual PEO samples were determined by size exclusion chromatography system equipped with Waters 510 pump, 410 differential refractometer and four Waters styragel columns (10^6, 10^5, 10^4 and 10^3 Å). Tetrahydrofuran was used as a mobile phase (flow rate : 1.0 cm^{3}min^{-1}, column temperature : 40 °C).

2.3. Static light scattering

Scattering intensities were measured at 25 °C for all the PEO/methanol solutions on Brookhaven BI200SM goniometer in angular range from 20° to 150°. Vertically polarized incident light of 633 nm wavelength from a 35 mW He–Ne laser was used. Pure benzene at 25 °C was used to calibrate the photometer. Its Rayleigh ratio was taken to be 11.84×10^{-6} cm^{-1} for 633 nm. For specific refractive index increment (dn/dc), the value of 0.142 cm^3 g^{-1} determined by Kinugasa et al. [7] under the same condition was used.

2.4. Viscometry

Viscosities of PEO/methanol solutions were measured by using the capillary viscometer of Ubbelohde type having flow times of about 200 s for the solvent. The Huggins' and Kreamer's plots were constructed to determine $[\eta]$ and Huggins' constant (k_H).

3. Results

3.1. Zimm plot and determination of $\langle R_G^2\rangle^{1/2}$

All the scattered intensity data were analyzed with the Zimm method. The values of Kc/R_θ were plotted against $\sin^2(\theta/2)+50c$ according to the following relation:

$$\frac{Kc}{R_\theta}=\left(\frac{1}{M_w}+2A_2c+3A_3c^2+\cdots\right)\left(1+\frac{q^2\langle R_G^2\rangle}{3}+\cdots\right) \qquad (1)$$

Where R_θ denotes the reduced scattering intensity at a scattering angle θ, and the optical constant (K) is defined by $K=4\pi^2n_o^2(\mathrm{d}n/\mathrm{d}c)/N_A\lambda_o^4$ with the Avogadro's number N_A, the refractive index of solvent n_o, and the wavelength of incident beam under vacuum λ_o. The scattering vector q is also defined by $q=(4\pi n_o/\lambda_o)\sin(\theta/2)$.

A representative Zimm plot for the methanol solutions at six different concentrations ($c=0.063$–4.329 mg cm^{-3}) of PEO2 sample at 25 °C is shown in Fig. 1. Evidently, Fig. 1 demonstrates that the plotted points follow a straight line, particularly at the low angle region, indicating no aggregation or association exists. The $\langle R_G^2\rangle^{1/2}$s of PEO samples in methanol at 25 °C calculated from the angular dependences of $(Kc/R_\theta)_{c=0}$ in respective Zimm plots. They are summarized in Table 1.

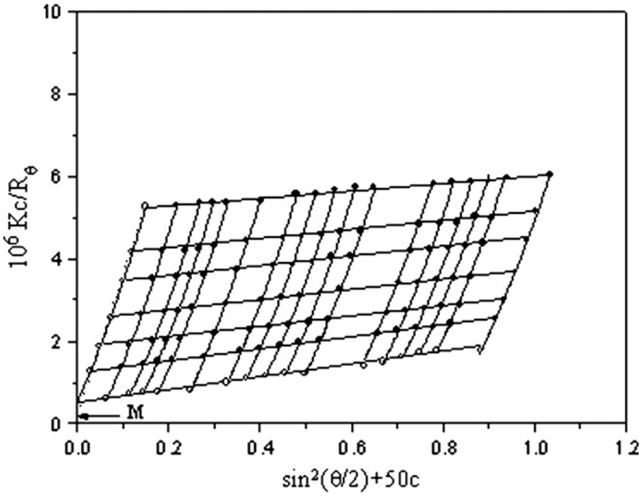

Fig. 1. Representative Zimm plot for PEO2 sample in methanol at 25 °C (M; the value of Kc/R_θ proposed by the PEO manufacturer).

3.2. Determination of A_2 and A_3

Also, Fig. 1 shows that the curves fitting the data points of the concentration dependence of Kc/R_θ bend upward. This phenomenon emphasizes the importance of A_3 term in evaluating accurate A_2 or M_w because the A_3 contributes significantly to the value of $(Kc/R_\theta)_{\theta=0}$. Generally, it has been known that any Bawn's plots do not show discernible curvature, which is suggestive that the second and third virial terms dominate $[(Kc/R_\theta)_{\theta=0} - (1/M_w)]$ over a wider range of concentrations in the methanol. Therefore, Bawn's plot [16] has been attempted instead of employing Kniewske and Kulicke curve-fitting method [17] to determine A_2 and A_3 in this study. The scattering intensities at zero-scattering angle, $(Kc/R_\theta)_{\theta=0}$ for different concentrations were calculated by the following expression:

$$S(c_1,c_2) = \frac{\left(\dfrac{Kc}{R_\theta}\right)_{\theta=0,\, c=c_2} - \left(\dfrac{Kc}{R_\theta}\right)_{\theta=0,\, c=c_1}}{c_2 - c_1} = 2A_2 + 3A_3(c_1+c_2) + \cdots \qquad (2)$$

where c_1 and c_2 are different polymer mass concentrations. The intercept and slope of the plot of $S(c_1,c_2)$ vs. $c_1 + c_2$ should give accurate values of A_2 and A_3, respectively. As shown in Fig. 2, the data points for each sample can be fitted by a straight line. All the values of A_2 and A_3 are summarized in Table 1.

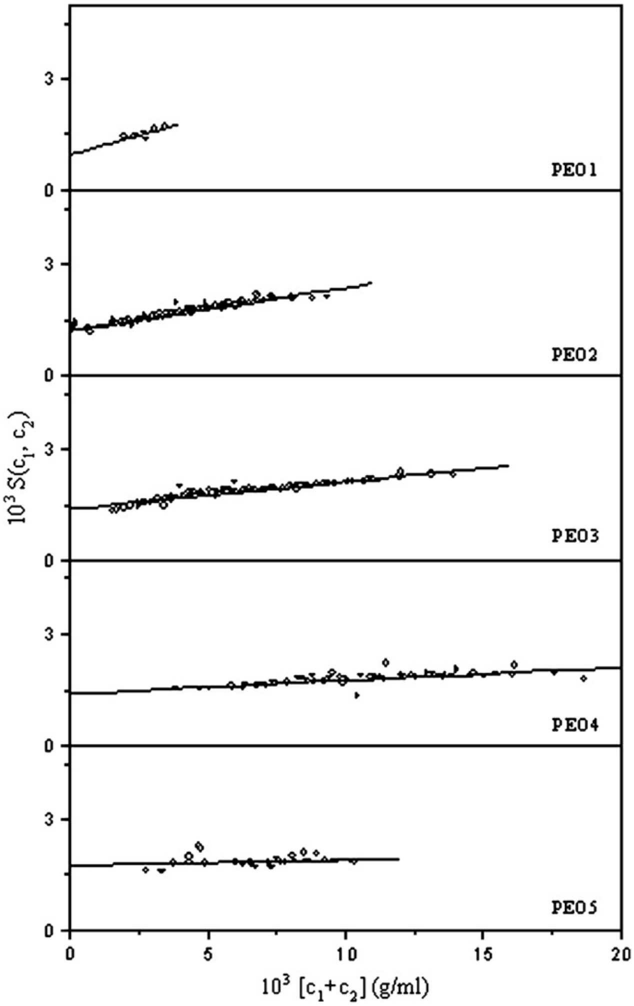

Fig. 2. Bawn's plots for indicated PEO samples in methanol at 25 °C.

3.3. Determination of M_w

In Fig. 1, the intercept marked by M on the axis of ordinate corresponds to the value of Kc/R_θ at $\theta = 0$ proposed by the PEO manufacturer, which has yielded quite different value of M_w from that we found. This may come from their overlooking of A_3 term in the calculation of M_w.

In order to obtain unambiguous M_w, it has been made to estimate apparent molar mass (M_{app}) with A_2 and A_3 evaluated

Table 1
Laser light scattering results and molecular parameters of PEO in methanol at 25 °C

Samples	$M_w \times 10^{-6}$ (g mol^{-1})	$A_2 \times 10^4$ (cm^3 mol g^{-2})	$A_3 \times 10^2$ (cm^6 mol g^{-3})	$\langle R_G^2 \rangle^{1/2}$ (nm)	g	Ψ	M_w/M_n[a]
PEO1	5.050	4.828	6.95	187.6	0.059	0.139	
PEO2	1.970	5.995	3.86	111.8	0.055	0.124	
PEO3	0.855	6.920	2.44	65.3	0.060	0.135	1.17
PEO4	0.693	7.090	2.14	57.2	0.061	0.136	1.16
PEO5	0.342	8.021	1.42	38.2	0.064	0.126	1.12

[a] Determined by size exclusion chromatography.

for a given PEO samples. Calculation was based on the following definition [18]:

$$M_{\mathrm{app}} = \left[\left(\frac{Kc}{R_\theta} \right)_{\theta=0} - 2A_2c - 3A_3c^2 \right]^{-1} \tag{3}$$

With A_2 and A_3 determined by Bawn's plot (Fig. 2), M_{app} was calculated as a function of concentration for each sample. Fig. 3 shows that the plots of M_{app} vs c constructed for all the PEO samples are essentially horizontal, whose intercepts give M_{w} for the respective PEO. A comparison of M_{w}s obtained from M_{app} and Zimm plot has made it clear that the latter takes slightly higher value within ±4.4% range. All the M_{w}s determined in this study are also summarized in Table 1.

3.4. Determination of [η]

The Huggins' and Kreamer's plots constructed for all the PEO samples in MeOH at 25 °C are shown in Fig. 4, and the [η] values and Huggins' constant k_{H}s obtained from the intercepts and slopes of the straight lines are summarized in Table 2.

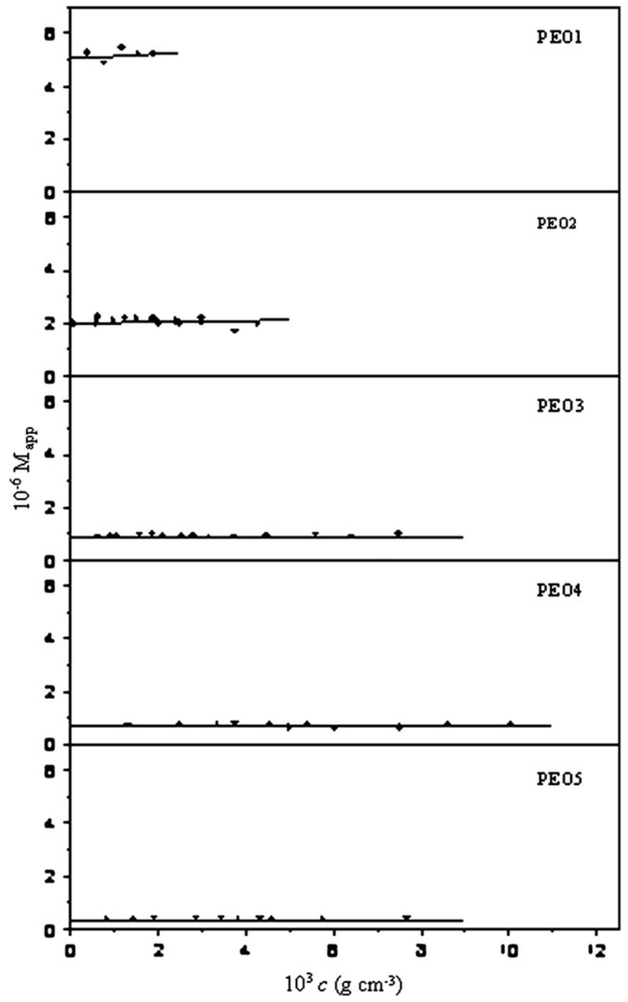

Fig. 3. Concentration dependence of M_{app} for indicated PEO samples in methanol at 25 °C.

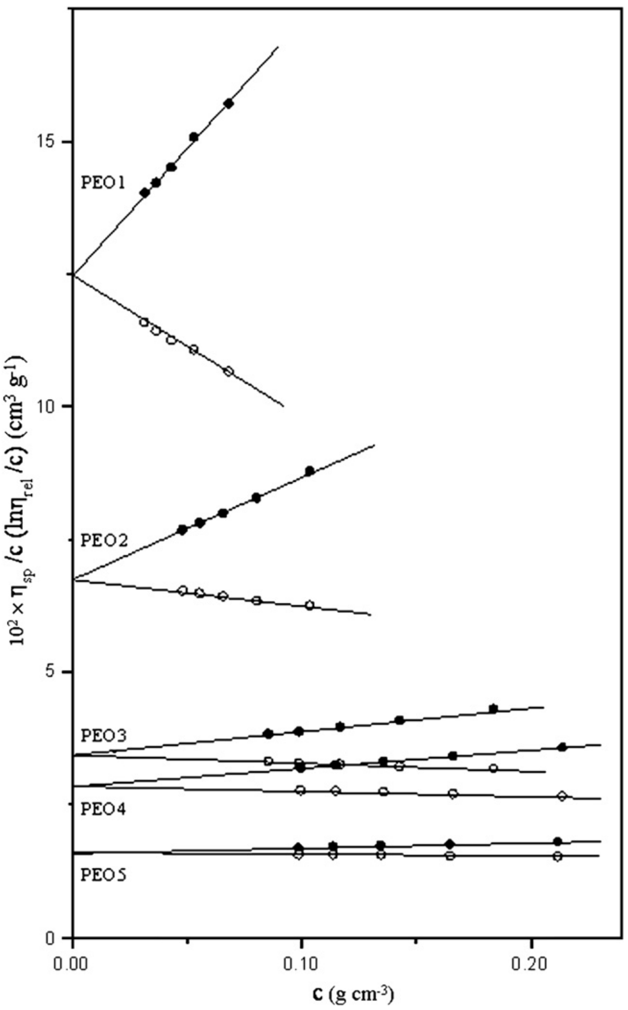

Fig. 4. Huggins' and Kreamer's plots constructed for indicated PEO samples in MeOH at 25 °C.

4. Discussion

4.1. The M_w dependence of A_2

The A_2 of a polymer solution has been the subject of the theoretical study for decades, but little is, as yet, explored on the molar mass dependence of A_2 in good solvent systems [19]. At present, however, many experimental works yielded a power law established by $A_2 \propto M_{\mathrm{w}}^{-\delta}$ with δ usually found in

Table 2
Viscometry results and molecular parameters of PEO in methanol at 25 °C

Samples	[η] × 10^{-3} (cm^3 g^{-1})	k_{H}	Π
PEO1	1.238	0.324	1.97
PEO2	0.668	0.447	1.77
PEO3	0.339	0.417	1.75
PEO4	0.284	0.411	1.73
PEO5	0.158	0.395	1.74

the range 0.2–0.3 and its asymptotic limit is inferred to be in the range of 0.20–0.22, regardless of the kind of solvent.

With the A_2 data from the Bawn's plot, following linear relationship between A_2 and M_w for PEO in methanol at 25 °C, shown in Fig. 5, can be obtained:

$$A_2 = 9.64 \times 10^{-3} M_w^{-0.193} \left(\mathrm{cm^3\,mol\,g^{-2}}\right) \tag{4}$$

The plots in the Fig. 5 include the data of Kinugasa et al. [7] evaluated from the PEO samples measured in the same solvent and temperature, but the slope is quite steeper (-0.28 ± 0.06) than -0.193 of this study. Nevertheless, the value -0.193 of this study is not only agreed very well with -0.19 ± 0.02, being estimated by Kawaguchi et al. [9] for those fractions having higher M_w than 10^5 in salt-free aqueous solution at 25 °C, but also consistent with the theoretical predictions for asymptotic good solvent region [20]. In particular, the exponent found is comparable to what is usually observed for flexible polymer but having somewhat larger excluded volume effect in good solvents [7,21–24].

4.2. The M_w dependence of A_3

Theoretically, A_3 reflects the excess interaction of ternary bead clusters, and its knowledge is important for accurate determination of A_2 in analyzing light scattering, osmotic pressure, and sedimentation equilibrium data. However, accurate measurement of A_3 is not a simple task, and the available data are, as yet, neither abundant nor systematic [19]. Besides, it has been reported that A_3 should depend on solvent quality and temperature, as well as M_w [25].

Fig. 6 illustrates the double logarithmic plot of A_3 against M_w, which gives the following scaling relation:

$$A_3 = 8.04 \times 10^{-6} M_w^{0.586} \left(\mathrm{cm^6\,mol\,g^{-3}}\right) \tag{5}$$

This relationship for the high molar mass PEO in methanol is probably the first finding. The exponent 0.586 in Eq. (5) is in excellent agreement with the relation, i.e., $A_3 \propto M_w^{0.59}$, which has been estimated by Kniewske and Kulicke [17] and Sato et al. [18] for polystyrene in toluene and benzene, respectively. Concurrently, the two-parameter theory [26] predicts that the A_3 of linear flexible polymer in good solvents can be asymptotically fitted by:

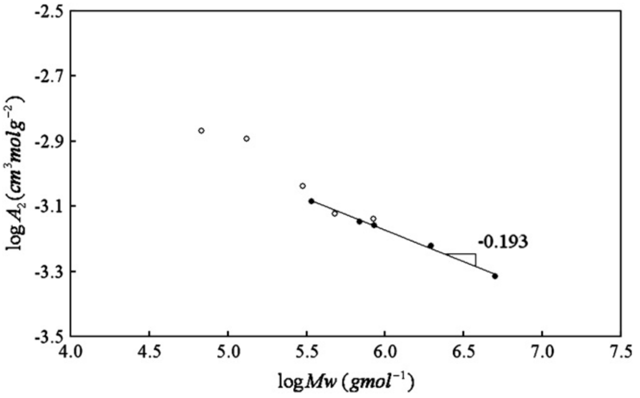

Fig. 5. Molecular weight dependence of second virial coefficient for PEO in methanol at 25 °C (filled circle, this work; open circle, Kinugasa et al. work [7]).

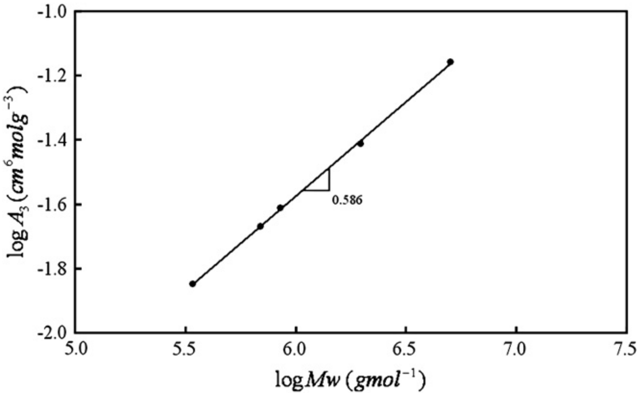

Fig. 6. Molecular weight dependence of third virial coefficient for PEO in methanol at 25 °C.

$$A_3 \propto M_w^{0.6} \left(\mathrm{cm^6\,mol\,g^{-2}}\right) \tag{6}$$

Hence, the consequence of M_w dependence of A_3 of this study conforms fairly well to Eq. (6). This experimental finding that the exponents derived from the power laws for A_2 and A_3 are happened to be close to the theoretical values allows us to suggest that the PEO chain in methanol at 25 °C is a flexible coil with somewhat expanded volume.

4.3. Reduced third virial coefficient

Two-parameter theory often uses a dimensionless quantity g, the reduced third virial coefficient, defined by $g = A_3/(A_2^2 M_w)$, in discussing those effects of chain stiffness and ternary cluster interactions on g. According to the theory, g is to converge to a finite value at the limit of large excluded volume variable z. However, the experimental findings on the M_w dependence of g so far found were contradictory, i.e., Kniewske and Kulicke [17] found a constant g value of 0.33 for PS, while Sato et al. [18] reported an increasing trend of g with M_w.

Fig. 7 shows the M_w dependence of g value of PEO in methanol, along with the data obtained by Nakamura et al. [25] for the PS/benzene system. Evidently, the obtained g values show not only M_w independent, which may lead to a asymptotic value, but also very low g values, which may come from the relatively large value of A_2 of the PEO molecule. At any rate, with this g value only, no decisive explanation on the chain conformation of the given polymer can be made at present, except for that the effect of three-segment interaction on g is insignificant, particularly in such a system having relatively large radius of expansion factor (α_s) [27].

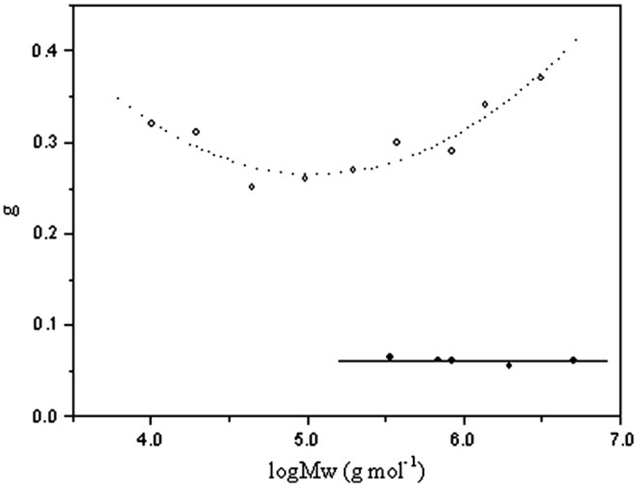

Fig. 7. Molecular weight dependence of reduced third virial coefficient (filled circle, this work; open circle, Nakamura et al. work for polystyrene in benzene at 25 °C [25]).

4.4. The M_w dependence of $\langle R_G^2\rangle^{1/2}$

As is generally known, $\langle R_G^2\rangle^{1/2}$ of those linear flexible polymers in good solvents usually increase with M_w, following the relation $\langle R_G^2\rangle \propto M_w^{2\nu}$. The M_w dependence of $\langle R_G^2\rangle^{1/2}$ for PEO in methanol at 25 °C is depicted in Fig. 8, along with the data of Kinugasa et al. [7] in methanol and the data of Kawaguchi et al. [9] in water for a comparison. The linear variation observed in the log–log plot corresponds to the following power law:

$$\langle R_G^2\rangle^{1/2} = 1.87 \times 10^{-2} M_w^{0.598}\ (\text{nm}) \tag{7}$$

The exponent 0.598 is in good agreement with the 3/5 in Flory's mean-field theory and 0.588 in the renormalization group theory. This power law indicates that the PEO molecule in methanol assumes flexible conformation, and such an unusual phenomenon like molecular association has not been taken place under the given conditions.

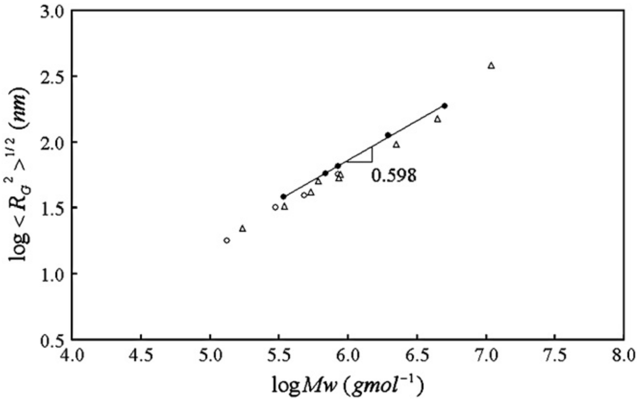

Fig. 8. Molecular weight dependence of radius of gyration for PEO (filled circle, this work in methanol at 25 °C; open circle, Kinugasa et al. work in methanol at 25 °C [7]; open triangle, Kawaguchi et al. work in water at 25 °C [9]).

4.5. Interpenetration function

The interpenetration function Ψ, a measure for the degree of excluded volume effect, is defined by:

$$\Psi = \frac{A_2 M_w^2}{4\pi^{3/2} N_A \langle R_G^2\rangle^{3/2}} \tag{8}$$

In the framework of the two-parameter theory [26], Ψ is an increasing function of excluded volume variables z and it contains excluded volume effects on chain dimensions as well as on A_2. As shown in Eq. (8), Ψ vanishes at $A_2 = 0$. This implies that a chain can be completely interpenetrated under θ-condition, while chain in very good solvents can be regarded as thermodynamically noninterpenetrating sphere. Thus, the value of function Ψ reflects the degree of interpenetration of polymer molecules in dilute solution. However, there exists a discrepancy [19] between two-parameter theory and experimental findings, that is, as radius of expansion factor decreases, experimental Ψ in a good solvent increases from the asymptotic value, while theoretical Ψ decreases toward zero. Recently, this contradictory phenomenon was explained by Yamakawa as due to those effects of chain stiffness on A_2 and radius of expansion factor [28].

Using the values listed in Table 1, Ψ values can be calculated by inserting A_2, M_w, and $\langle R_G^2\rangle^{1/2}$ into Eq. (8). The average value of 0.132 is appeared as slightly smaller than the asymptotic value 0.22 for PS [29] but is quite larger than 0.09 for PEO in water [9]. It indicates that PEO has higher degree of excluded volume effect. This behavior is in good agreement with the experimental result that a relatively large value of A_2 has been obtained by the PEO in methanol. Unfortunately, it is impossible to discuss Ψ value further because the correct M_w dependence of the unperturbed radius of gyration has not yet been clarified. However, based on the Yamakawa's theory, function Ψ represents the degree of interpenetration of polymer molecules and becomes smaller when those molecules are interpenetrable. Accordingly, the somewhat low value of Ψ in this study can be regarded as the consequence of the chain stiffening effect, which in turn leads to a local change of conformation.

4.6. The M_w dependence of $[\eta]$

The M_w dependence of $[\eta]$ is shown in Fig. 9 together with the data obtained by Kawaguchi et al. [9] for PEO samples in water at 25 °C. The present $[\eta]$ values in Fig. 9 are fitted by a straight line with slope 0.768. A direct power law fit to the data yields the following relation:

$$[\eta] = 9.235 \times 10^{-5} M_w^{0.768}\ (\text{cm}^3\ \text{g}^{-1}) \tag{9}$$

The Huggins' coefficients, listed in Table 2, are quite consistent with a mean value of $k_H = 0.399$, which is typical for linear, flexible polymers in good solvents. Moreover, the summation of k_H and Kraemer constant k_k (not shown) was

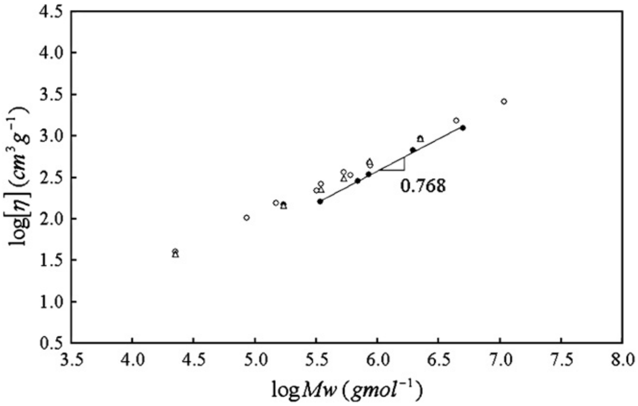

Fig. 9. Molecular weight dependence of intrinsic viscosity for PEO (filled circle, this work in methanol at 25 °C; open circle, Kawaguch et al. work in water at 25 °C [9]; open triangle, Kawaguchi et al. work in benzene at 25 °C [9]).

very close to 0.5, reflecting no aggregation during the viscosity measurements.

Fig. 9 also displays that the $[\eta]$ values for the PEO in water and benzene at 25 °C (data of Kawaguchi et al. [9]) were higher than those found in methanol at a given molar mass, while their slopes appeared were 0.679 and 0.699, which is somewhat smaller than 0.768 of the present study. This comparison makes it clear that the hydrodynamic shape of PEO molecule in water, benzene and methanol is different in their degree of coil expansion caused by excluded volume.

On the other hand, the mean-field theory predicted a relation of $a = 3\nu - 1$, where a is the Mark–Houwink exponent and ν is the Flory's exponent in the power relation $\langle R_G^2 \rangle^{1/2} = K_s M^{\nu}$. In the meantime, the renormalization theory predicts $\nu = 0.588$ ($a = 0.764$) for the perturbed coils. The exponent 0.768 of this study yields 0.589 as ν which is well agreed with both the theoretical value of 0.588 and the experimental finding of 0.598 in this study. However, the a value of the present study approaches to the limiting value of 0.8 with which a flexible chain can be assumed, is considered to be responsible for the local change of conformation due possibly to the chain stiffening effect of local segments. This large value of Mark–Houwink exponent also allows us to conclude that the PEO molecule in methanol at 25 °C adopts the global shape of a random coil while local segments remain probably helical structure [30].

4.7. Parameter Π

The dimensionless parameter Π is often used to assess the degree of excluded volume effect or the interrelationship between the coil draining and excluded volume effects [26,31]. This parameter is defined by:

$$\Pi = \frac{V_{A_2}}{V_\eta} = \frac{MA_2}{[\eta]} \tag{10}$$

where both the V_η and V_{A_2} are coil volumes which can be expressed, respectively, by $M_w[\eta]/N_A$ and $M_w^2 A_2/N_A$. The Π values listed in Table 2 are exhibiting an increasing trend with M_w and give a mean value of 1.79, which is quite larger than that for those conventional linear, flexible polymers in good solvent ($\Pi = 1.0$–1.2) [26] and 1.10 predicted theoretically for nondraining coil [32], but smaller than 1.88 for the PEO in aqueous system [33]. Moreover, Miyaki et al. [23] and Einaga et al. [34] have reported a mean value of $\Pi = 1.20$ for high molar mass PS fractions ($M_w = 8.8$–57×10^6) in benzene at 25 °C through the experimental findings of $A_2 \propto M_w^{-0.2}$ and $[\eta] \propto M_w^{0.75}$. Their Π value found is far below than 1.79 of this work. The higher Π value for PEO is presumably ascribed to the extensive excluded volume swelling, leading to the higher order of A_2, but the small $[\eta]$ is due to the coil draining, producing a relatively small hydrodynamic radii.

5. Conclusion

The major conclusions, being drawn from the work on the conformational characteristics of PEO molecules in methanol at 25 °C evaluated by static light scattering and viscosity measurements, can be summarized as follows. Firstly, the molar mass dependences of $\langle R_G^2 \rangle^{1/2}$, A_2, A_3 and $[\eta]$ in this work gives evidence for flexible chain conformation with high degree of intramolecular excluded volume effect. Secondly, however, the lower value of interpenetration function Ψ than those conventional flexible, linear polymer, the large value of dimensionless parameter Π, and particularly the sigmoidal shape of the curve plotted by the data of $\langle R_G^2 \rangle / x_w$ against $\log x_w$, reflect the unusual feature that is unable to be expected from a flexible chain. Thus, the overall conclusion for the present study is that though the global conformation of the PEO chains in methanol at 25 °C is random coil, the chain may assumes a certain helical conformation locally.

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