Transport Coefficients of Poly(diisopropyl fumarate) in Dilute Solution

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The intrinsic viscosity $[\eta]$ was determined for 13 samples of poly(diisopropyl fumarate), each with the fraction of racemo diads $f_r = 0.22$, in the range of weight-average molecular weight M_w from 4.02×10^4 to 8.59×10^5 in tetrahydrofuran at 30.0 °C. The translational diffusion coefficient D was also determined from dynamic light scattering measurements for 12 of them in the range of M_w from 4.95×10^4 to 8.59×10^5 under the same solvent condition. The data so obtained were analyzed on the basis of the corresponding transport theories for the unperturbed Kratky–Porod (KP) wormlike cylinder model combined with the quasi-two-parameter theory for the intramolecular excluded-volume effect. It is shown that the experimental values are in quantitative agreement with the perturbed KP theory ones by the use of the model parameter values consistent with those determined previously from analyses of the mean-square radius of gyration $\langle S^2 \rangle$ and second virial coefficient A_2 . An examination was also made of behavior of the Flory–Fox factor Φ and reduced hydrodynamic radius ρ^{-1} as functions of M_w .

KEY WORDS: Poly(diisopropyl fumarate) / Intrinsic Viscosity / Translational Diffusion Coefficient / Kratky–Porod Wormlike Chain Model / Excluded-Volume Effect / Quasi-Two-Parameter Theory /

In a previous paper,¹ we have reported experimental results for the mean-square radius of gyration $\langle S^2 \rangle$ and second virial coefficient A_2 of poly(diisopropyl fumarate) (PDiPF) with the fraction of racemo diads $f_r = 0.22$ in tetrahydrofuran (THF) at 30.0 °C (good solvent). From analyses of the results on the basis of the Kratky–Porod (KP) wormlike chain model^{2,3} with the intra- and intermolecular excluded-volume effects,³ it has then been shown that the unperturbed KP theory⁴ of $\langle S^2 \rangle$ combined with the quasi-two-parameter (QTP) theory^{3,5–7} and the Yamakawa theory⁸ of A_2 may quantitatively reproduce those results if the parameter values $113 \text{ \AA}$, $89 \text{ \AA}^{-1}$, and 0.097 are used for the stiffness parameter λ^{-1} , the shift factor M_L as defined as the molecular weight per unit contour length of the KP chain, and the reduced excluded-volume strength λB , respectively. We note that the M_L value $89 \text{ \AA}^{-1}$ so determined is consistent with the value $80.3\text{--}84.7 \text{ \AA}^{-1}$ estimated on the basis of reasonable local chain conformations of PDiPF.¹

Because of steric hindrance to internal rotations caused by bulky substituents, *i.e.*, ester isopropyl groups, on every main-chain carbon atom, the PDiPF chain was expected to be stiff. Its λ^{-1} is, however, not so large as that for a typical semiflexible polymer such as poly(*n*-hexyl isocyanate) (PHIC) ($\lambda^{-1} = 840 \text{ \AA}$),⁹ although it is, of course, remarkably larger than that for a typical flexible polymer such as atactic polystyrene (a-PS) ($\lambda^{-1} = 20.6 \text{ \AA}$).^{3,10} The main assertion made in the previous paper¹ is that the excluded-volume effects must be taken into account in analyses of dilute solution properties of PDiPF (having moderate chain stiffness) in THF at 30.0 °C. As a continuation of the previous paper,¹ we here determine the intrinsic viscosity $[\eta]$ and translational diffusion coefficient D (or the hydrodynamic radius R_H defined from D)

from viscosity and dynamic light scattering (DLS) measurements, respectively, for PDiPF in the same solvent condition as that in the previous paper,¹ and confirm the assertion by analyzing the results so obtained on the basis of corresponding theories for the unperturbed KP wormlike cylinder combined with the QTP theory.³

In addition to the above-mentioned main purpose of the present paper, we also examine behavior of the Flory–Fox factor Φ and also of the reduced hydrodynamic radius ρ^{-1} , which may be calculated from $[\eta]$ and $\langle S^2 \rangle$ and from R_H and $\langle S^2 \rangle$, respectively. It is well known that both Φ and ρ^{-1} are sensitive to chain stiffness,³ so that the examination may be a fair judge of whether the previous estimation of λ^{-1} is reasonable or not.

EXPERIMENTAL

Materials

All the PDiPF samples used in this study are the same as those used in the previous study¹ of $\langle S^2 \rangle$ and A_2 , *i.e.*, fractions separated by fractional precipitation from the original samples prepared by radical polymerization following the procedure of Otsu *et al.*^{11,12} and Matsumoto and Nakagawa.¹³ The values of the weight-average molecular weight M_w , the ratio M_w/M_n of M_w to the number-average molecular weight M_n , and f_r are given in Table I, which have been reproduced from Table I of ref 1. The samples were freeze-dried from their benzene solutions after filtration through a Teflon membrane of pore size 1.0 μm prior to use.

The solvent THF used for viscosity and DLS measurements was purified by distillation after refluxing over sodium.

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Table I. Values of M_w , M_w/M_n , and f_r for Poly(diisopropyl fumarate)

sample	M_w	M_w/M_n	f_r
PDiPF4 ^a	4.02×10^4		
PDiPF5	4.95×10^4	1.10	0.22
PDiPF6	6.31×10^4	1.05	
PDiPF8	8.00×10^4	1.10	
PDiPF9	9.17×10^4	1.07	
PDiPF15	1.53×10^5	1.08	
PDiPF18	1.83×10^5	1.08	0.22
PDiPF22	2.18×10^5	1.09	
PDiPF34	3.37×10^5	1.07	
PDiPF44	4.37×10^5	1.07	
PDiPF50	5.00×10^5	1.05	0.22
PDiPF62	6.20×10^5	1.05	
PDiPF86	8.59×10^5		

^aAll values of M_w had been determined from light scattering in THF at 30.0 °C, all values of M_w/M_n from analytical gel permeation chromatography, and all values of f_r from ¹³C NMR.¹

Viscosity

Viscosity measurements were carried out for all the samples listed in Table I in THF at 30.0 °C. For the measurements, we used conventional capillary and four-bulb spiral capillary viscometers 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 30.0 °C within ± 0.005 °C during the measurements.

The test solutions were prepared gravimetrically and made homogeneous by continuous stirring in the dark at room temperature for 2 d. The polymer mass concentrations c were calculated from the weight fractions with the densities of the solutions. The density of each solution was calculated with the partial specific volume v_2 of the polymer and the density ρ_0 of the solvent. The quantities v_2 and ρ_0 were measured with a pycnometer of the Lipkin–Davison type having a volume of 3 cm³. The values of v_2 so determined in THF at 30.0 °C are 0.873 cm³/g for all the samples independently of M_w . The value of ρ_0 of THF at 30.0 °C is 0.8751 g/cm³. 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 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' .

Dynamic Light Scattering

DLS measurements were carried out to determine D for all the samples except PDiPF4 in THF at 30.0 °C by the use of a Brookhaven Instruments model BI-200SM light scattering goniometer with vertically polarized incident light of wavelength $\lambda_0 = 532$ nm (in a vacuum) from a Spectra-Physics model Millennia Pro 2s Nd:YVO₄ laser. The photomultiplier tube used was EMI 9893B/350, the output from which was processed by a Brookhaven Instruments model BI-9000AT Digital Correlator. (An electric shutter was attached to the original detector alignment in order to monitor the dark count

automatically.) The normalized autocorrelation function $g^{(2)}(t)$ of scattered light intensity $I(t)$ at time t was measured at 3–5 concentrations and at scattering angles θ ranging from 22 to 46°. The most concentrated solution of each sample was prepared in the same manner as in the case of the viscosity measurements. It was optically purified by filtration through a Teflon membrane of pore size 0.45 or 0.10 μ m. 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.

From the data for $g^{(2)}(t)$ so determined at finite concentrations c , we determined D at an infinitely long time at infinite dilution in the same manner as that used in the previous studies.^{14,15} At small c , the plot of $(1/2) \ln[g^{(2)}(t) - 1]$ against t in general follows a straight line represented by

$$(1/2) \ln[g^{(2)}(t) - 1] = \text{const} - At \quad (1)$$

with A the slope for such large t that all the internal motions of solute polymer chains have relaxed away.

With the slope A evaluated from the plot, we may determine the apparent diffusion coefficient $D^{(LS)}(c)$ at finite c from

$$D^{(LS)}(c) = \lim_{k \rightarrow 0} A/k^2 \quad (2)$$

where k is the scattering vector and is given by

$$k = (4\pi n_0/\lambda_0) \sin(\theta/2) \quad (3)$$

with n_0 the refractive index of the solvent. At very small c , $D^{(LS)}(c)$ may be expanded as

$$D^{(LS)}(c) = D^{(LS)}(0)(1 + k_D^{(LS)}c + \dots) \quad (4)$$

so that the desired $D = D(\infty)$ (at an infinitely long time) may be determined by an extrapolation of $D^{(LS)}(c)$ to $c = 0$ as

$$D = D^{(LS)}(0) \quad (5)$$

The values of n_0 at $\lambda_0 = 532$ nm and of the viscosity coefficient η_0 for THF at 30.0 °C are 1.404₅ and 0.439₇ cP, respectively. The former value was estimated by a linear interpolation of the plot of n_0 against λ_0^{-2} with the values 1.410₈ and 1.403₈ of n_0 at $\lambda_0 = 436$ and 546 nm, respectively, measured by the use of an Abbe refractometer (ERMA OPTICAL WORKS).

RESULTS

Intrinsic Viscosity $[\eta]$

Intrinsic viscosity data for all the PDiPF samples in THF at 30.0 °C are summarized in Table II along with the values of the Huggins coefficient k' . It is seen that k' is almost independent of M_w and its value *ca.* 0.4 is somewhat larger than that for typical flexible chains having large M_w in good solvents.^{16–20}

Figure 1 shows double-logarithmic plots of $[\eta]$ (in dL/g) against M_w for PDiPF in THF at 30.0 °C. The unfilled circles represent the present experimental values. The present data points are seen to form a curve slightly convex upward, its slope being *ca.* 0.86 for $M_w \lesssim 2 \times 10^5$ and *ca.* 0.73 for $M_w \gtrsim 3 \times 10^5$. The rather steep slope in the range of $M_w \lesssim 2 \times 10^5$ may be due to effects of chain stiffness, as in the case

Table II. Results of Viscosity Measurements for Poly(diisopropyl fumarate) in THF at 30.0 °C

sample	$[\eta]$ (dL/g)	k'
PDiPF4	0.308	0.41
PDiPF5	0.349	0.44
PDiPF6	0.455	0.42
PDiPF8	0.541	0.44
PDiPF9	0.589	0.42
PDiPF15	0.874	0.43
PDiPF18	1.01	0.42
PDiPF22	1.13	0.42
PDiPF34	1.65	0.42
PDiPF44	1.98	0.36
PDiPF50	2.38	0.42
PDiPF62	2.62	0.40
PDiPF86	3.27	0.42

Figure 1. Double-logarithmic plots of $[\eta]$ (in dL/g) against M_w for PDiPF in THF at 30.0 °C: (○) present data; (●) data by Matsumoto and Nakagawa.¹³ The solid and dashed curves represent the best-fit KP theory values with and without excluded volume, respectively (see the text).

of $\langle S^2 \rangle$.¹ In the figure, the solid and dashed curves represent the KP theory values with and without excluded volume, respectively, which are discussed in the next (DISCUSSION) section.

The figure also includes literature data for the same polymer–solvent system reported by Matsumoto and Nakagawa¹³ (filled circles). The literature and present values are rather in good agreement in the range of $M_w \gtrsim 2 \times 10^5$, while the former deviate downward from the latter for $M_w \lesssim 2 \times 10^5$. The reason for this deviation is not clear.

Translational Diffusion Coefficient D and Hydrodynamic Radius R_H

The data points $(1/2)\ln[g^{(2)}(t) - 1]$ as a function of t directly obtained from the DLS measurements for each test solution at each scattering angle θ were found to follow a straight line, so that the slope A on the right-hand side in eq 1 could be unambiguously determined. Further, in the range of k (or θ) where the DLS measurements were carried out, the ratio

Figure 2. Plots of $D^{(LS)}(c)$ against c for the indicated PDiPF samples in THF at 30.0 °C.**Table III.** Results of DLS Measurements for Poly(diisopropyl fumarate) in THF at 30.0 °C

sample	$10^7 D$ (cm ² /s)	$k_D^{(LS)}$ (cm ³ /g)	R_H (Å)
PDiPF5	8.48	11	59.6
PDiPF6	7.40	9.4	68.2
PDiPF8	6.84	7.1	73.8
PDiPF9	5.63	13	89.7
PDiPF15	5.01	20	101
PDiPF18	3.76	41	134
PDiPF22	3.50	45	144
PDiPF34	2.57	78	196
PDiPF44	2.37	60	213
PDiPF50	2.16	59	233
PDiPF62	1.89	69	267
PDiPF86	1.55	74	327

A/k^2 was independent of k within experimental error for all the test solutions, although we do not show the results here. Then $D^{(LS)}(c)$ for each solution was determined as a mean of the observed values of A/k^2 over k .

Figure 2 shows plots of $D^{(LS)}(c)$ so obtained against c for the indicated PDiPF samples in THF at 30.0 °C. The data points for each sample are seen to follow a straight line, and therefore $D^{(LS)}(0)$ ($= D$) and $k_D^{(LS)}$ on the right-hand side in eq 4 may be accurately determined from its ordinate intercept and slope, respectively. The values of D and $k_D^{(LS)}$ so obtained for PDiPF in THF at 30.0 °C are given in Table III. The estimated error in D is $\pm 3\%$ at most. In the last column of the Table are also given the values of the hydrodynamic radius R_H calculated from the defining equation

$$R_H = k_B T / 6\pi\eta_0 D \quad (6)$$

Figure 3. Double-logarithmic plots of R_H (in Å) against M_w for PDiPF in THF at 30.0°C. The solid and dashed curves represent the best-fit KP theory values with and without excluded volume, respectively (see the text).

where k_B is the Boltzmann constant, T is the absolute temperature, and η_0 is the viscosity coefficient of the solvent. The quantity $k_D^{(LS)}$ is positive for all the samples examined and increases with increasing M_w , as in the cases of typical flexible polymers having large M_w in good solvents.^{19–23}

In Figure 3, R_H (in Å) calculated from eq 6 with the present experimental values of D given in the second column of Table III are double-logarithmically plotted against M_w . The data points (○) are seen to form a curve slightly convex upward, its slope being *ca.* 0.62 for $M_w \lesssim 2 \times 10^5$ and *ca.* 0.58 for $M_w \gtrsim 3 \times 10^5$. We note that the error bounds to each value of R_H do not exceed the radius of the symbols in the figure. The rather steep slope in the range of $M_w \lesssim 2 \times 10^5$ may be due to the effect of chain stiffness of PDiPF, as in the cases of $[\eta]$ shown in Figure 1 and also of $\langle S^2 \rangle$.¹ In the figure, the solid and dashed curves represent the KP theory values with and without excluded volume, which are discussed in the next (DISCUSSION) section.

DISCUSSION

Analysis of $[\eta]$ on the Basis of the KP Model

We first analyze the data for $[\eta]$ on the basis of the unperturbed KP cylinder model^{3,24,25} combined with the QTP theory.^{3,5–7} We note that the KP chain model having only a bending energy is a special case of the helical wormlike (HW) chain model having both bending and torsional energies³ and that the QTP theory has been constructed on the basis of the latter model.

For the unperturbed KP cylinder model of total contour length L and diameter d , $[\eta]_0$ may be written in the form,

$$[\eta]_0 = \frac{1}{\lambda^2 M_L} f_{\eta, KP}(\lambda L; \lambda d) \quad (7)$$

where the subscript 0 on $[\eta]$ denotes the unperturbed value and $f_{\eta, KP}$ as a function of the reduced contour length λL and

reduced diameter λd is defined by

$$f_{\eta, KP}(\lambda L; \lambda d) = \lambda^{-1} M_L [\eta]_{KP} \quad (8)$$

with $[\eta]_{KP}$ being given by eq 6.89 with eq 6.90 of ref 3 (or eq 23 with eq 24 of ref 25) for $\lambda L \geq 2.278$ and by eq 6.91 with eqs 6.92 and 6.94 of ref 3 (or eq 25 with eqs 26 and 32 of ref 25) for $\lambda L < 2.278$. We note that $[\eta]_{KP}$ in refs 3 and 25 is written in units of $(\lambda^{-1})^3$ and the quantities L and d in those references mean the reduced quantities λL and λd , respectively. In the limit of $\lambda L \rightarrow \infty$, $f_{\eta, KP}$ satisfies the following asymptotic relation,

$$\lim_{\lambda L \rightarrow \infty} \frac{f_{\eta, KP}(\lambda L; \lambda d)}{(\lambda L)^{1/2}} = \Phi_\infty \quad (9)$$

where Φ_∞ denotes the (theoretical) coil-limiting value $2.87 \times 10^{23} \text{ mol}^{-1}$ of the Flory–Fox factor $\Phi = M[\eta]/(6\langle S^2 \rangle)^{3/2}$ with M the molecular weight (for the unperturbed chain in the limit of $\lambda L \rightarrow \infty$). We note that Φ is the reduced hydrodynamic volume³ defined as the ratio of the hydrodynamic (molar) volume V_H to $\langle S^2 \rangle^{3/2}$,

$$\Phi = V_H / \langle S^2 \rangle^{3/2} \quad (10)$$

with V_H defined from $[\eta]$ as

$$V_H = 6^{-3/2} M [\eta] \quad (11)$$

In a comparison of theory with experiment, L may be related to M by

$$L = M / M_L \quad (12)$$

For the perturbed KP cylinder model, $[\eta]$ may conventionally be expressed as a product of $[\eta]_0$ given by eq 7 and the cube of the viscosity-radius expansion factor α_η ,

$$[\eta] = [\eta]_0 \alpha_\eta^3 \quad (13)$$

In the framework of the QTP scheme or the Yamakawa–Stockmayer–Shimada theory,^{3,5–7} all the expansion factors, including α_η , are functions only of the scaled intramolecular excluded-volume parameter $\tilde{z}$ defined by

$$\tilde{z} = \frac{3}{4} K(\lambda L) z \quad (14)$$

where z is the (conventional) excluded-volume parameter z appearing in the two-parameter (TP) theory²⁶ and is defined by

$$z = (3/2\pi)^{3/2} (\lambda B)(\lambda L)^{1/2} \quad (15)$$

with B the excluded-volume strength. We note that in the case of the KP chain, B may be written in terms of the binary-cluster integral β between beads (or statistical segments) and their spacing a . We omit here the explicit expression for B , since it is unnecessary for the following discussion. In eq 14, the coefficient $K(L)$ as a function of reduced L is given by

$$\begin{aligned} K(L) &= \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} \quad \text{for } L > 6 \\ &= L^{-1/2} \exp(-6.611L^{-1} + 0.9198 + 0.03516L) \quad \text{for } L \leq 6 \end{aligned} \quad (16)$$

It is seen from eq 14 with eq 16 that $\tilde{z} = z$ in the limit of $\lambda L \rightarrow \infty$ (random-coil limit), so that the QTP theory becomes identical with the TP theory in this limit. We note that the function $K(L)$ represents the effects of chain stiffness on the intramolecular excluded-volume effect. As usual,³ we adopt the Barrett equation²⁷ for α_η ,

$$\alpha_\eta = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.1} \quad (17)$$

From eq 13 with eqs 7, 12, and 14–17, it is seen that the perturbed KP theory value of $[\eta]$ may be calculated as a function of M for a given set of values of the four parameters λ^{-1} , M_L , λB , and d . In other words, we can in principle determine the four parameters for PDiPF from a comparison of theory with experiment. Unfortunately, however, the plot of $[\eta]$ against M_w for PDiPF shown in Figure 1 has no salient feature such as a S-shaped curve observed for PHIC,⁹ so that it is difficult to determine all of them from the comparison. We therefore assume here the values 113 Å and 0.097 of λ^{-1} and λB , respectively, determined previously¹ from the analyses of $\langle S^2 \rangle$ and A_2 and then determine the remaining two parameters M_L and d .

In Figure 1, the solid curve associated with the present data points (○) represents the best-fit perturbed KP theory values calculated from eq 13 with eqs 7, 12, and 14–17 with the values 92 Å⁻¹ and 15 Å of M_L and d , respectively. Although the M_L value 92 Å⁻¹ so determined is slightly (*ca.* 3%) larger than 89 Å⁻¹ determined previously¹ from $\langle S^2 \rangle$ and A_2 , the quantitative agreement between theory and experiment confirms the previous assertion.¹ The d value 15 Å is consistent with *ca.* 13 Å estimated from reasonable local chain conformations of PDiPF (see Figure 3 in ref 1).

In Figure 1, the dashed curve represents the unperturbed KP theory values calculated from eq 7 with eq 12 with the above-mentioned values of λ^{-1} , M_L , and d . It is seen that the experimental value (○) and also the perturbed KP theory one (solid curve) agree with the unperturbed KP theory value for $M_w \lesssim 10^5$ but deviate upward progressively from the latter with increasing M_w for $M_w \gtrsim 10^5$ due to the intramolecular excluded-volume effect, as in the case of $\langle S^2 \rangle$.¹

Analysis of D on the Basis of the KP Model

For the unperturbed KP cylinder model of total contour length L and diameter d , D_0 may be written in the form,^{3,28,29}

$$D_0 = \left(\frac{k_B T}{3\pi\eta_0 L} \right) f_{D,KP}(\lambda L; \lambda d) \quad (18)$$

where the subscript 0 on D denotes the unperturbed value and $f_{D,KP}$ as a function of λL and λd is given by eqs 6.41–6.43 with eqs 6.22 and 6.23 of ref 3. We note that the quantity $3\pi\eta_0 L/\Xi$ given by eqs 49 and 51 in ref 28 or by eq 14 in ref 29 with $c_\infty = 1$ corresponds to $f_{D,KP}$ and that in refs 3, 28 and 29, the quantities L and d mean the reduced quantities λL and λd , respectively. Then the hydrodynamic radius $R_{H,0}$ of the unperturbed KP chain may be written in terms of $f_{D,KP}$ as

$$R_{H,0} = \frac{L}{2f_{D,KP}(\lambda L; \lambda d)} \quad (19)$$

In the limit of $\lambda L \rightarrow \infty$, $f_{D,KP}$ satisfies the following asymptotic relation,

$$\lim_{\lambda L \rightarrow \infty} \frac{f_{D,KP}(\lambda L; \lambda d)}{(\lambda L)^{1/2}} = \frac{\sqrt{6}}{2} \rho_\infty \quad (20)$$

where ρ_∞ denotes the (Kirkwood theoretical) coil-limiting value 1.505 of the ratio ρ of $\langle S^2 \rangle^{1/2}$ to R_H (for the unperturbed chain in the limit of $\lambda L \rightarrow \infty$). We note that the inverse ρ^{-1} of ρ is called the reduced hydrodynamic radius³ defined as the ratio of R_H to $\langle S^2 \rangle^{1/2}$,

$$\rho^{-1} = R_H / \langle S^2 \rangle^{1/2} \quad (21)$$

For the perturbed KP cylinder model, R_H may be expressed as a product of $R_{H,0}$ and the hydrodynamic-radius expansion factor α_H ,

$$R_H = R_{H,0} \alpha_H \quad (22)$$

In the framework of the QTP scheme,^{3,5–7} α_H is also a function only of $\tilde{z}$ and may be written in the form,^{3,30}

$$\alpha_H = \alpha_H^{(0)} h_H \quad (23)$$

where we use the Barrett equation³¹ for $\alpha_H^{(0)}$,

$$\alpha_H^{(0)} = (1 + 5.93\tilde{z} + 3.59\tilde{z}^2)^{0.1} \quad (24)$$

and h_H , which represents a possible effect of fluctuating hydrodynamic interaction on α_H ,³⁰ is given by

$$h_H = \frac{0.88}{1 - 0.12\alpha_S^{-0.43}} \quad (25)$$

In eq 25, we use the Domb-Barrett equation³² for the gyration-radius expansion factor α_S ,

$$\alpha_S^2 = [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} \times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \quad (26)$$

We note that in eq 24 the coefficient 5.93 of $\tilde{z}$ has been adopted in place of the coefficient 6.09 originally adopted by Barrett.³

From eq 22 with eqs 12, 19, and 23–26, it is seen that R_H may also be calculated as a function of M for a given set of values of the four parameters λ^{-1} , M_L , λB , and d . As in the case of $[\eta]$, we assume the values 113 Å and 0.097 of λ^{-1} and λB , respectively, and determine M_L and d from a comparison of theory with experiment. In Figure 3, the solid curve represents the best-fit perturbed KP theory values calculated from eq 22 with eqs 12, 19, and 23–26 with the values 81 Å⁻¹ and 16 Å of M_L and d , respectively. It is seen from the figure that the theory may quantitatively explain the behavior of the experimental results. The M_L value 81 Å⁻¹ so determined from D is somewhat smaller than 92 Å⁻¹ determined above from $[\eta]$ and 89 Å⁻¹ determined previously¹ from $\langle S^2 \rangle$ and A_2 . This tendency is the same as that in the cases of flexible polymers in the Θ solvents previously³ studied (see Tables 5.1 and 6.3 of ref 3). As often mentioned,^{3,14} it may be regarded as arising from the disagreement between the theoretical and experimental values of Φ_∞ and ρ_∞ .^{3,14} Note that their theoretical values have been obtained for Gaussian chain without consideration of the fluctuation in hydrodynamic interaction.³ Considering this

fact, it may be concluded that the unperturbed KP theory combined with the QTP theory may give a consistent explanation of the results for the three properties $\langle S^2 \rangle$, $[\eta]$, and R_H for PDiPF.

In Figure 3, the dashed curve represents the unperturbed KP theory values calculated from eq 19 with eq 12 with the above-mentioned values of λ^{-1} , M_L , and d . It is seen that the experimental value ($\circ$) and also the perturbed KP theory one (solid curve) agree with the unperturbed KP theory value in the range of $M_w \lesssim 10^5$ but deviate upward progressively from the latter with increasing M_w for $M_w \gtrsim 10^5$ due to the intramolecular excluded-volume effect, as in the cases of $[\eta]$ shown in Figure 1 and also of $\langle S^2 \rangle$.¹

Behavior of Φ and ρ

Finally, we examine behavior of the reduced hydrodynamic volume Φ and radius ρ^{-1} as functions of M_w . In Table IV are given the values of Φ and ρ^{-1} (and also ρ) for PDiPF in THF at 30.0 °C calculated from the present results for $[\eta]$ (Table II) and R_H (Table III) along with the previous results for $\langle S^2 \rangle$ (Table I of ref 1).

Figure 4 shows double-logarithmic plots of Φ (in mol⁻¹) and ρ^{-1} against M_w for PDiPF in THF at 30.0 °C ($\circ$), a-PS ($f_r = 0.59$) in cyclohexane at 34.5 °C (Θ) (Δ),^{14–16,33–35} and PHIC in *n*-hexane at 25.0 °C ($\square$).⁹ Both Φ and ρ^{-1} for a-PS first decrease for $M_w \lesssim 10^4$ and then become independent of M_w for $M_w \gtrsim 10^4$. This tendency is common to unperturbed flexible polymers.^{3,36} The quantities Φ and ρ^{-1} are remarkably smaller for PHIC than for a-PS in the range of M_w displayed in this figure, indicating that they decrease with increasing chain stiffness (λ^{-1}).³ The data points for PDiPF lie between those for a-PS and PHIC, which is consistent with the fact that the chain stiffness of PDiPF ($\lambda^{-1} = 113 \text{ \AA}$) is intermediate between those for a-PS ($\lambda^{-1} = 20.6 \text{ \AA}$) and PHIC ($\lambda^{-1} = 840 \text{ \AA}$).

It should be noted here that Φ and ρ^{-1} become small if the intramolecular excluded-volume effect becomes large. For PDiPF in THF at 30.0 °C, however, the effect is not so large in the range of M_w examined (see Figures 1 and 3) that Φ and ρ^{-1} become appreciably smaller than respective unperturbed values. Further, the effect is negligibly small, if any, for PHIC

Figure 4. Double-logarithmic plots of Φ (in mol⁻¹) and ρ^{-1} against M_w : ($\circ$) PDiPF in THF at 30.0 °C; (Δ) a-PS in cyclohexane at 34.5 °C (Θ);^{14–16,33–35} ($\square$) PHIC in *n*-hexane at 25.0 °C.⁹ The solid curves represent the KP or HW theory values of Φ and ρ^{-1} (see the text).

in *n*-hexane at 25.0 °C in the range of M_w displayed in Figure 4. Then the above-mentioned characteristic features in the behavior of Φ and ρ^{-1} of PDiPF and PHIC may be considered to arise only from their chain stiffness.

In Figure 4, the solid curves associated with the data points for PDiPF represent the perturbed KP theoretical values for Φ and ρ^{-1} calculated from eq 10 with eq 11 and from eq 21, respectively, with the perturbed KP theory values for $[\eta]$, R_H , and $\langle S^2 \rangle$, where the three sets of the values of the KP model parameters determined from $[\eta]$ and R_H in the present paper and from $\langle S^2 \rangle$ and A_2 in the previous one¹ have been used in the calculation of $[\eta]$, R_H , and $\langle S^2 \rangle$, respectively. The solid curves associated with the data points for a-PS and PHIC represent the unperturbed HW and KP theoretical values, respectively, which have been reproduced from Figure 6.12 of ref 3. It is seen that the KP and HW theories well explain the difference in the behavior of Φ and ρ^{-1} between the three polymers.

CONCLUSION

We have determined $[\eta]$ and D (and R_H) for PDiPF with $f_r = 0.22$ in THF at 30.0 °C in the range of M_w from 4.02×10^4 to 8.59×10^5 . The data so obtained were analyzed on the basis of the corresponding theories for the KP cylinder model combined with the QTP theory for the intramolecular excluded-volume effect. It was shown that the experimental values are in quantitative agreement with the perturbed KP theory ones by the use of the model parameter values consistent with those determined previously¹ from $\langle S^2 \rangle$ and A_2 . The result confirms the previous assertion that the excluded-volume effects must be taken into account in analyses of dilute solution properties of PDiPF in the above-mentioned range of M_w in THF at 30.0 °C. It was also shown that the data points of Φ and ρ^{-1} for PDiPF lie between those for a-PS (typical flexible polymer) and PHIC (typical semiflexible polymer), reconfirming the validity of the evaluation of the chain stiffness of PDiPF which is intermediate between those of a-PS and PHIC.

Table IV. Values of Φ , ρ^{-1} , and ρ for Poly(diisopropyl fumarate) in THF at 30.0 °C

sample	$10^{-23}\Phi$ (mol ⁻¹)	ρ^{-1}	ρ
PDiPF8	1.74	0.621	1.61
PDiPF9	1.53	0.671	1.49
PDiPF15	1.59	0.565	1.77
PDiPF18	1.62	0.676	1.48
PDiPF22	1.49	0.641	1.56
PDiPF34	1.69	0.694	1.44
PDiPF44	1.65	0.654	1.53
PDiPF50	2.01	0.680	1.47
PDiPF62	1.84	0.685	1.46
PDiPF86	1.99	0.714	1.40

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