

Dilute Solution Properties
of Poly(*n*-hexyl isocyanate) and
Poly(diisopropyl fumarate)

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1 Introduction

1.1 Background

In the study of physical properties of semiflexible or stiff polymers in solutions, the Kratky–Porod (KP) wormlike chain model^{1–3} plays a unique and important role, especially in the molecular characterization, *i.e.*, estimation of the stiffness parameter λ^{-1} , which has the dimension of length and is a measure of chain stiffness; the stiffer the chain, the larger the parameter λ^{-1} . The model was first proposed by Kratky and Porod¹ in order to explain the behavior of the scattering function determined for synthesized flexible polymers from small angle X-ray scattering measurements, which reflects local chain conformations. Contrary to their expectations, the model was shown not to be valid for common flexible polymers which usually take locally curved conformations.³ This is due to the fact that the model assumes that the polymer chain contour prefers to take locally a straight line and thermally fluctuates around it isotropically.^{2–4} Subsequently, the model was shown to be very useful and powerful in the description of the dilute solution behavior of another class of polymers — semiflexible or stiff polymers such as DNA, α -helical polypeptides, poly(*n*-alkyl isocyanate)s, and polysaccharides, all of which have firm helical structures and are cylindrically symmetry about their respective helix axes. We note that the helical wormlike chain model proposed by Yamakawa^{3,5} is suitable for the description of the dilute solution behavior of the common flexible polymers.

Since the mid-1970s experimental studies have been extensively made of equilibrium

conformational and transport properties of typical stiff chains.⁶ Above all, accurate measurements of the mean-square radius of gyration $\langle S^2 \rangle$, intrinsic viscosity $[\eta]$, and sedimentation coefficients s were carried out for poly(*n*-hexyl isocyanate) (PHIC),⁶ which is a typical example of semiflexible or stiff polymers. Dependence of those quantities on the molecular weight M was shown to be well explained by the corresponding KP theories with the model parameters λ^{-1} and M_L determined unambiguously,^{3,6} where M_L is the shift factor as defined as the molecular weight per unit contour length of the KP chain. The results for PHIC along with those for DNA, schizophyllan, and so forth⁶ have shown the KP chain to be a well-established model for semiflexible or stiff polymers.

Although an understanding of the dilute solution behavior of semiflexible or stiff polymers on the basis of KP chain at the present time is rather satisfactory, as mentioned above, there still remain some problems to be addressed in order to ensure the understanding. The solution properties studied so far are not many, so that an extended study of a variety of other properties including dynamical ones is desirable in order to confirm the validity of the KP chain for typical semiflexible polymers. Further, there seems to be required an intensive investigation into the intramolecular excluded-volume effect on $\langle S^2 \rangle$ and $[\eta]$ of semiflexible polymers with moderate chain stiffness. Since the probability of contact between repeat units in a polymer chain, *i.e.*, the ring-closure probability, increases with decreasing λ^{-1} , the effect is gradually enhanced as λ^{-1} is decreased and it is therefore necessary to take the effect into account in an evaluation of λ^{-1} of moderately semiflexible polymers. In this thesis, we study the two problems taking PHIC as a typical semiflexible polymer and poly(diisopropyl fumarate) (PDiPF) as a moderately semiflexible one.

For PHIC, we study the mean-square optical anisotropy $\langle \Gamma^2 \rangle$ as a static property and

the spin-lattice relaxation time T_1 , spin-spin relaxation time T_2 , and nuclear Overhauser enhancement NOE for ^{13}C nuclei, as dynamical properties. The quantity $\langle\Gamma^2\rangle$ reflects the strength of the correlation between the orientations of the optical polarizability tensors of adjacent repeat units on a polymer chain and belongs to a class of static properties different from that of $\langle S^2\rangle$, $[\eta]$, and s which are concerned with the average chain dimension. In our laboratory, experimental studies were made of $\langle\Gamma^2\rangle$ for typical flexible polymers, *e.g.*, atactic polystyrene (a-PS)^{3,7} and atactic poly(methyl methacrylate) (a-PMMA)^{3,8}, and the results so obtained gave us useful information about their local chain conformations. Although $\langle\Gamma^2\rangle$ of PHIC is not sufficiently large⁹ to make a precise examination of its behavior as a function of M , we address this problem in order to confirm the validity of the KP chain model for all kinds of static properties.

The quantities T_1 , T_2 , and NOE for ^{13}C nuclei give us information about local chain motions, which is different from the one about global chain motions given by the dynamic structure factor studied previously in our laboratory.¹⁰ Experimental studies were also made in our laboratory of the quantities for a-PS^{3,11} and a-PMMA,^{3,12} as typical examples of flexible polymers. It was then shown for the flexible polymers that T_1 , T_2 , and NOE becomes independent of M for $M \gtrsim 10^3$, since the tumbling motion of repeat units becomes independent of the entire motion of the polymer chain. For semiflexible polymers, however, the situation is different, since the tumbling motion may be coupled to the entire one even for rather large M , and therefore T_1 , T_2 , and NOE depend on M in the range of large M , as shown by Budd *et al.*¹³ for poly(γ -benzyl L-glutamate). Although DuPré and Wang¹⁴ made a nuclear magnetic relaxation study of PHIC, measurements were carried out only for one sample with the weight-average molecular weight $M_w = 3.3_9 \times 10^4$. We therefore intend to examine the dependence of T_1 , T_2 , and NOE on M and clarify whether

the KP chain model may well explain the result or not.

PDiPF is such vinyl polymer that high bulky substituents, isopropyl fumarate group, are joined to every main-chain carbon atom. Because of steric hindrances to internal rotations brought by those substituents, PDiPF is considered to be stiffer than common vinyl polymer which has no such effect. Indeed, stiffness parameter λ^{-1} of PDiPF was determined to be 220 Å by Matsumoto and Nakagawa¹⁵ from the analysis of the M dependence of $\langle S^2 \rangle$ and $[\eta]$ using the KP wormlike chain model without the intramolecular excluded-volume effect. However, Kasabo *et al.* showed that the intramolecular excluded-volume effect is not negligible for cellulose tris(phenyl carbamate) (CTC)¹⁶ with $\lambda^{-1} = 210$ Å. This indicates that it is necessary to take into account the intramolecular excluded-volume effect for analysis of dilute solution properties of PDiPF.

The intramolecular excluded-volume effect can be ignored for a typical semiflexible polymer if its λ^{-1} is very large and its M is not very large. In the case of PHIC with $\lambda^{-1} = 840$ Å¹⁷, the intramolecular excluded-volume effect can be ignored, if its M_w is not very large, which is in the range of $M_w \lesssim 3 \times 10^6$. Considering that the λ^{-1} value of PDiPF is not so large as that of PHIC and following the CTC result, it is required to make an analysis of dilute solution properties of PDiPF with the intramolecular excluded-volume effect so as to evaluate λ^{-1} for PDiPF accurately. When the intramolecular excluded-volume effect can be ignored, we can evaluate λ^{-1} for PDiPF from an analysis only of $\langle S^2 \rangle$ as a function of M_w by the use of the method proposed by Murakami *et al.*¹⁷, but the method is not effective in this case. $\langle S^2 \rangle$ with the intramolecular excluded-volume effect is larger than without that effect, and a difference of $\langle S^2 \rangle$ between with and without intramolecular excluded-volume effect increases as the chain length increases. Consequently, the probability of contact between polymer chains, *i.e.*, the intermolecular excluded-volume

effect, increases with enhancing the intramolecular excluded-volume effect. If we analyze $\langle S^2 \rangle$ with the intramolecular excluded-volume effect, it is necessary to analyze the second virial coefficient A_2 with the intermolecular excluded-volume effect, simultaneously. We have yet determined λ^{-1} for flexible polymers, *e.g.*, a-PS^{3,18} and a-PMMA^{3,19}, along with the method and we apply this approach to make an analysis for PDiPF and try to evaluate λ^{-1} for PDiPF accurately.

First, we then make an attempt to analyze $\langle S^2 \rangle$ and A_2 on the basis of the quasi-two-parameter (QTP) theory of the intramolecular excluded-volume effect and the Yamakawa theory of A_2 ^{3,20}, which is taken intermolecular excluded-volume effect into account. We confirm the validity of this approach, and from the values of λ^{-1} and M_L , which we can determine on this approach, we verify that PDiPF is stiffer than common flexible polymers from the value of λ^{-1} and M_L is consistent with that value estimated on the basis of the chain conformations of PDiPF.

Next, we show the necessity to take intramolecular excluded-volume effect into consideration for analysis of $[\eta]$ and the translational diffusion coefficient D . From the dependence of the Flory-Fox factor Φ and the reduced hydrodynamic radius ρ^{-1} on M , we also inspect whether the previous estimation of λ^{-1} is rational or not.

1.2 Outline

The plan of this thesis is as follows.

In Chap. 2, $\langle \Gamma^2 \rangle$ was determined from anisotropic light scattering measurements for 9 samples of PHIC in the range of weight-average molecular weight from 1.65×10^4 to 1.04×10^5 in *n*-hexane at 25.0 °C. It was found that the behavior of the ratio $\langle \Gamma^2 \rangle / x_w$ as a function of x_w may be satisfactorily explained by the corresponding theory on the basis of

the KP wormlike chain model with the respective values $\lambda^{-1}=840 \text{ \AA}$ and $M_L=71.5 \text{ \AA}^{-1}$ of the basic model parameters, and also with the assigned value $1.1_2 \text{ \AA}^2$ of the difference $\Delta\alpha$ between the polarizabilities, per unit contour length, parallel and perpendicular to the chain contour. From a comparison of the present results for PHIC with previous ones for typical flexible polymers, it is seen that the difference in the behavior of $\langle\Gamma^2\rangle/x_w$ between them arises from that in chain stiffness.

In Chap. 3, T_1 , T_2 , and NOE were determined from nuclear magnetic relaxation measurements on five well-fractionated samples of PHIC in the range of weight-average molecular weight M_w from 1.65×10^4 to 5.71×10^4 in *n*-hexane at 25 °C. It is found that T_1 increases and T_2 decreases monotonically with increasing M_w in the range of M_w examined, while NOE is almost independent of M_w . Such behavior may be regarded as arising from effects of chain stiffness. A comparison is then made of the present data for T_1 , T_2 , and NOE with the theory developed for the generalized KP wormlike chain as a special case of the helical wormlike chain, and it is shown that the theory may almost quantitatively explain the data, using the established values of the KP model parameters.

In Chap. 4, $\langle S^2 \rangle$ and A_2 were determined from light scattering measurements for 13 samples of PDiPF in the range of weight-average molecular weight M_w from 4.02×10^4 to 8.59×10^5 in THF at 30.0 °C. The model parameters of the KP wormlike chain for PDiPF are then determined by analyzing the data for $\langle S^2 \rangle$ and A_2 , simultaneously, by the use of the KP theories with the excluded-volume effect. From the analyses, it is confirmed that the PDiPF chain has an intermediate chain stiffness between typical flexible polymers such as atactic polystyrene and typical semiflexible polymers such as poly(*n*-hexyl isocyanate). With the model parameter values so determined, it is shown that the intramolecular excluded-volume effect for this polymer-solvent system is negligibly small

for the reduced contour length (or the Kuhn statistical segment number) $\lambda L \lesssim 10$ and becomes appreciable for $\lambda L \gtrsim 10$.

In Chap. 5, $[\eta]$ was determined for 13 samples of PDiPF in the range of weight-average molecular weight M_w from 4.02×10^4 to 8.59×10^5 in THF at 30.0 °C. D was also determined from dynamic light-scattering measurements for 12 samples of PDiPF 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 are analyzed on the basis of the KP wormlike chain theories combined with the quasi-two-parameter scheme for the excluded-volume effects. The intramolecular excluded-volume effects on $[\eta]$ and the hydrodynamic radius R_H for PDiPF are negligibly small for $M_w \lesssim 10^5$ and become appreciable for $M_w \gtrsim 10^5$. However, on the whole, the intramolecular excluded-volume effects for this system are rather small in the range of M_w studied due to the effect of the chain stiffness. The behavior of the two quantities $[\eta]$ and R_H may be well explained by the corresponding KP theories by the use of the model parameters consistent with those previously determined from $\langle S^2 \rangle$ and A_2 , confirming the previous conclusion derived from $\langle S^2 \rangle$ and A_2 that the PDiPF chain has an intermediate chain stiffness between typical flexible polymers such as a-PS and typical semiflexible polymers such as PHIC. A comparison is also made of the reduced hydrodynamic volume Φ and radius ρ^{-1} for PDiPF with those for a-PS and PHIC.

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2 Mean-Square Optical Anisotropy of Poly(*n*-hexyl isocyanate)

2.1 Introduction

As mentioned Chap. 1, $\langle \Gamma^2 \rangle$ as well as the mean-square radius of gyration $\langle S^2 \rangle$ as a function of the degree of polymerization x may provide useful information about polymer chain stiffness and local chain conformations.¹ All our studies made so far are restricted to typical flexible polymers (atactic polystyrene(a-PS),^{1,2} atactic poly(methyl methacrylate) (a-PMMA),^{1,3} and isotactic (i-) PMMA,^{1,4}), so that it is desirable to obtain data for $\langle \Gamma^2 \rangle$ for typical semiflexible polymers and then to compare them with the theory and also with the data for the above typical flexible polymers.

Although there have been a number of experimental studies of the optical anisotropy of semiflexible polymers in dilute solution,⁵ none of them have dealt with poly(*n*-hexyl isocyanate) (PHIC), a typical example of semiflexible polymers whose dilute solution properties have been almost thoroughly investigated. This may probably be due to the fact that its optical anisotropy is not sufficiently large to determine $\langle \Gamma^2 \rangle$ precisely, as seen from the data obtained by Jinbo et al.⁶ in moderately concentrated solution. In this work, we tackle the problem to determine $\langle \Gamma^2 \rangle$ for PHIC in dilute solution (in *n*-hexane at 25.0 °C) despite the rather difficult experimental condition in order to investigate its dependence on x .

Now it is well known that the PHIC chain in *n*-hexane preserves the Schmueli–Traub–

Rosenheck⁷ 8_3 helices^{8–10} and that the equilibrium conformational behavior of its helix axis may be well represented by the Kratky-Porod (KP) wormlike chain.^{1,11} All the local physical quantities such as the local polarizability tensor affixed to the chain may therefore be considered to be cylindrically symmetric around the axis. Then the parameters necessary for the theoretical calculation of $\langle \Gamma^2 \rangle$ are the difference $\Delta\alpha$ between the polarizabilities parallel and perpendicular to the axis and the two basic KP model parameters: the static stiffness parameter λ^{-1} and the shift factor M_L as defined as the molecular weight per unit contour (or helix axis in this case) length. While the values of these KP model parameters have already been determined rather unambiguously,⁹ the parameter $\Delta\alpha$ remains unknown. In this paper, we regard $\Delta\alpha$ as an adjustable parameter to determine so that the experimental and theoretical values of $\langle \Gamma^2 \rangle$ are in good agreement with each other, and then compare the determined value of $\Delta\alpha$ with that estimated from the bond polarizabilities on the basis of the chemical structure of PHIC.

For the present anisotropic LS measurements, we adopt an improved data acquisition procedure different from that used for our usual isotropic LS measurements in order to increase reliability.

2.2 Experimental Section

2.2.1 Materials

As in the previous study of the dynamic structure factor of PHIC,¹² the original PHIC samples were prepared following the procedure of Aharoni.¹³ The polymerization was carried out in a toluene/*N,N*-dimethylformamide (1:1) mixture at -78°C with sodium cyanide as an initiator and methanol as a terminator. All the test samples except the one with the highest molecular weight are fractions separated from the original samples

by fractional precipitation using benzene as a solvent and methanol as a precipitant. The highest molecular weight sample PHIC10 is the same as that used in the previous study.¹²

The solvent *n*-hexane used for all measurements was purified according to a standard procedure prior to use.

2.2.2 Light Scattering

LS measurements were carried out to determine the weight-average molecular weight M_w and $\langle \Gamma^2 \rangle$ for all the samples, and also $\langle S^2 \rangle$ for the samples with $M_w \gtrsim 4 \times 10^4$ in *n*-hexane at 25.0 °C. A Fica 50 light-scattering photometer was used for all the measurements with vertically (v) polarized incident light of wavelength $\lambda_0 = 436$ nm.

Before proceeding to give a description of the experimental procedure, it is pertinent to refer here to modifications made in our photometer. Since it had been having trouble with its circuits, we replaced all of them except the chopper one by a couple of programmable digital voltmeters (YOKOGAWA model 7551) controlled by a personal computer. In the photometer so modified, the outputs from the chopper circuit, i.e., the incident and scattered light intensities converted into voltage, were independently measured by the voltmeters, each with an integration time of 100 ms. The two kinds of voltage were alternately recorded on the computer at intervals of ca. 150 ms, and then each scattered intensity was divided by a mean of its preceding and following incident light intensities to determine the corrected scattered intensity, which does not suffer from fluctuations in the incident light intensity (brightness of a mercury lamp). For the unpolarized (Uv) component of the scattered intensity, 20 successive corrected intensities were averaged to obtain a final observed value, as done so far. For the depolarized (Hv) component, which is very weak compared to the Uv one, more than 60 successive reduced intensities were

accumulated to determine the average value in order to reduce experimental error. In addition to the above modifications of the circuits, a pair of pieces of Polaroid with an extinction ratio of ca. 10^{-2} originally used as a polarizer and an analyzer were replaced by Gran–Thompson prisms with an extinction ratio smaller than 10^{-5} , as previously¹⁴ mentioned.

For a calibration of the apparatus, the Uv and Hv components of the intensity of light scattered from pure benzene were measured at 25.0 °C at a scattering angle θ of 90° without and with the analyzer, respectively. The apparatus constants in the cases of the Uv and Hv measurements were estimated from the experimental values of the respective intensities so determined and also from the values of the Uv and Hv components of the reduced intensity absolutely determined. The latter absolute values were calculated from the literature value¹⁵ $46.5 \times 10^{-6} \text{ cm}^{-1}$ of the Rayleigh ratio $R_{\text{Uu}}(90^\circ)$ and the experimental value 0.41 ± 0.01 of the depolarization ratio ρ_{u} of pure benzene at 25.0 °C.

Thus the Uv and Hv components of the scattered intensity were measured for all the samples at four or five different concentrations and at θ ranging from 30 to 142.5° in *n*-hexane at 25.0 °C. We used the literature value⁹ $0.134 \text{ cm}^3/\text{g}$ of the refractive index increment for PHIC in *n*-hexane at 25.0 °C along with the value 1.380 of the refractive index n_0 of *n*-hexane at 25.0 °C, both at $\lambda_0 = 436 \text{ nm}$.

The most concentrated solution of each sample was prepared gravimetrically and made homogeneous by continuous stirring at ca. 50 °C for 1 or 2 days. It was optically purified by filtration through a Teflon membrane of pore size 0.45 or 1.0 μm . The solutions of lower concentrations were obtained by successive dilution, adding the solvent optically purified by filtration through a Teflon membrane of pore size 0.1 μm . The weight concentrations of the test solutions were converted to the polymer mass concentrations c by the use of

the densities of the solutions.

**Table 2.1. Results of LS Measurements for
Poly(*n*-hexyl isocyanate) in *n*-Hexane at 25.0 °C**

sample	$10^{-4}M_w$	x_w	$10^3\delta$	$10^{-4}\langle S^2 \rangle, \quad 10^{-4}\langle \Gamma^2 \rangle, \quad 10^{-2}\langle \Gamma^2 \rangle/x_w,$			M_w/M_n^b
				$\text{\AA}^2$	$\text{\AA}^6$	$\text{\AA}^6$	
PHIC1	1.65	130	2.2 ₇		3.9 ₄	3.0 ₃	1.10
PHIC2a	2.18	172	1.9 ₇		5.9 ₅	3.4 ₆	1.10
PHIC2b	2.66	209	1.8 ₁		8.1 ₇	3.9 ₁	1.07
PHIC3	2.90	228	1.8 ₅		9.8 ₉	4.3 ₄	1.10
PHIC4	4.71	371	1.2 ₅	3.1 ₈	17.7	4.7 ₇	1.04
PHIC5	5.71	450	1.1 ₃	4.3 ₆	23.4	5.2 ₀	1.05
PHIC7	7.67	604	0.90 ₈	6.8 ₁	34.0	5.6 ₃	1.06
PHIC8	8.42	663	0.85 ₉	7.7 ₂	38.8	5.8 ₅	1.03
PHIC10	10.4 ^a	819	0.82 ₄	10.2 ^a	48.2	5.8 ₉	1.03

^a Reproduced from ref 12. ^b Determined by analytical GPC.

2.3 Results

2.3.1 Characterization

According to the theories on the basis of the Gaussian chain model¹⁶ and also the KP¹⁷ and HW¹⁸ chain models, the excess unpolarized (Uv) and depolarized (Hv) components, ΔR_{Uv} and ΔR_{Hv} , of the reduced scattered intensity determined from LS measurements with vertically polarized incident light may be related to M_w in the limit of $c \rightarrow 0$ and $\theta \rightarrow 0$ by the equations,

$$\lim_{c, \theta \rightarrow 0} \frac{\Delta R_{Uv}}{2Kc} = (1 + 7\delta)M_w \quad (2.1)$$

$$\lim_{c, \theta \rightarrow 0} \frac{\Delta R_{Hv}}{2Kc} = 3\delta M_w \quad (2.2)$$

where K is the optical constant and δ is a parameter representing the anisotropy of the local polarizability tensor affixed to the statistical segment or the chain contour. Then the values of M_w and δ for a given sample may be simultaneously determined from the experimental values of $(\Delta R_{Uv}/2Kc)_{c=0, \theta=0}$ and $(\Delta R_{Hv}/2Kc)_{c=0, \theta=0}$.

The value of $(\Delta R_{Uv}/2Kc)_{c=0, \theta=0}$ may readily be determined from the Berry square-root plot.¹⁹ However, the determination of $(\Delta R_{Hv}/2Kc)_{c=0, \theta=0}$ requires some comments. The theoretical ΔR_{Hv} is independent of θ for the Gaussian chain model,¹⁶ but in general depends on θ for the KP¹⁷ and HW¹⁸ chain models. Strictly, therefore, the values of $\Delta R_{Hv}/2Kc$ determined at finite θ (and also at very low but finite c) should be extrapolated to $\theta = 0$ by the use of an appropriate theoretical curve, for instance, the KP theory values at infinite dilution. In fact, however, for the KP chains corresponding to the present PHIC samples the variations of the theoretical values of ΔR_{Hv} around the respective mean values over the range of θ measured are within $\pm 3\%$. Thus we simply adopted as the experimental value of $(\Delta R_{Hv}/2Kc)_{\theta=0}$ (at finite c) a mean of values of $\Delta R_{Hv}/2Kc$

determined at different θ . A possible error arising from this rather simplified procedure may be considered not to exceed an experimental error in $\Delta R_{\text{Hv}}/2Kc$, which is appreciably larger than that in $\Delta R_{\text{Uv}}/2Kc$.

As an example, plots of $\Delta R_{\text{Hv}}/c$ against $\sin^2(\theta/2)$ for the sample PHIC5 in *n*-hexane at 25.0 °C are shown in Figure 2.1 for the indicated values of c . At any c , an appreciable dependence of $\Delta R_{\text{Hv}}/c$ on $\sin^2(\theta/2)$ cannot be observed in the range of θ studied, being buried in the scatter of data points. The horizontal straight line associated with the data points at each c represents the mean value. The standard deviations of the experimental values shown in the figure are 2% at the highest concentration and 7% at the lowest concentration. The values of $(\Delta R_{\text{Hv}}/c)_{\theta=0}$ so determined are plotted against c in Figure 2.2 for all the samples in *n*-hexane at 25.0 °C. The vertical line segments attached to the data points indicate the error bounds estimated from the standard deviations. The data points for each sample were extrapolated to infinite dilution by the straight line shown in the figure in order to determine $(\Delta R_{\text{Hv}}/c)_{c=0,\theta=0}$.

In the fourth column of Table 2.1 are given the values of δ for all the samples in *n*-hexane at 25.0 °C calculated from eqs 2.1 and 2.2 with the values of $(\Delta R_{\text{Uv}}/2Kc)_{c=0,\theta=0}$ and $(\Delta R_{\text{Hv}}/2Kc)_{c=0,\theta=0}$ determined above. It is seen from these values that the value of the ratio $(\Delta R_{\text{Hv}}/\Delta R_{\text{Uv}})_{c=0,\theta=0} \simeq 3\delta$ are even smaller than 10^{-2} . It is then reconfirmed that the optical anisotropy of PHIC is very small. For this polymer, therefore, no corrections of the optical anisotropy to M_w and $\langle S^2 \rangle$ have been made, and M_w and $\langle S^2 \rangle$ have been determined by the use of the Berry plot of $(2Kc/\Delta R_{\text{Uv}})^{1/2}$ against c and/or $\sin^2(\theta/2)$.^{6,9,12} As is well known, the molecular weight determined from this plot is not M_w but the apparent weight-average molecular weight $M_{w,\text{ap}} = M_w(1 + 7\delta)$ if δ cannot be neglected (see eq 2.1). We made corrections to M_w for those samples whose 7δ are

larger than 10^{-2} , i.e., for the samples PHIC1 through PHIC3. We note that the difference between M_w and $M_{w,ap}$ does not exceed 1.6%. In the determination of M_w for the samples PHIC4 through PHIC10, we neglected the term 7δ in eq 2.1. In the second and third columns of Table 2.1 are given the values of M_w so determined and also those of the weight-average degree of polymerization x_w calculated from the M_w values with the value 127 of the molecular weight of the repeat unit.

In the fifth column of Table 2.1 are given the values of $\langle S^2 \rangle$ determined for the samples PHIC4 through PHIC10 in *n*-hexane at 25.0 °C without consideration of the effect of the optical anisotropy. This effect on $\langle S^2 \rangle$ for these samples may be considered to be negligibly small as in the case of M_w . For the samples PHIC1 through PHIC3, $\langle S^2 \rangle$ could not be accurately determined. The values of the ratio of M_w to the number-average molecular weight M_n determined by analytical GPC for all the samples are also given in the last column of Table 2.1.

Figure 2.3 shows double-logarithmic plots of $\langle S^2 \rangle / M_w$ against M_w for PHIC in *n*-hexane at 25.0 °C. The large unfilled circles represent the experimental values obtained in the present work, and the three small ones represent those previously obtained in the study of the dynamic structure factor of PHIC in the same solvent condition.¹² Of the latter three samples, the one with the lowest M_w (PHIC10) was also used in the present study of $\langle \Gamma^2 \rangle$. The filled circles represent the experimental values obtained by Murakami et al.⁹ The solid curve represents the KP theory values calculated from^{1,20}

$$\langle S^2 \rangle = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1}{8\lambda^4 L^2} (1 - e^{-2\lambda L}) \quad (2.3)$$

where L is the total contour length and is related to the molecular weight M by

$$L = M/M_L \quad (2.4)$$

with $\lambda^{-1} = 840 \text{ \AA}$ and $M_L = 71.5 \text{ \AA}^{-1}$.⁹ As seen from the figure, our present and previous¹² data are consistent with those by Murakami et al.⁹ within experimental error, and the data of the two groups are rather well fitted by the theoretical curve in the range of $M_w \lesssim 3 \times 10^6$. Note that the excluded-volume effect becomes appreciably large for $M_w \gtrsim 3 \times 10^6$.

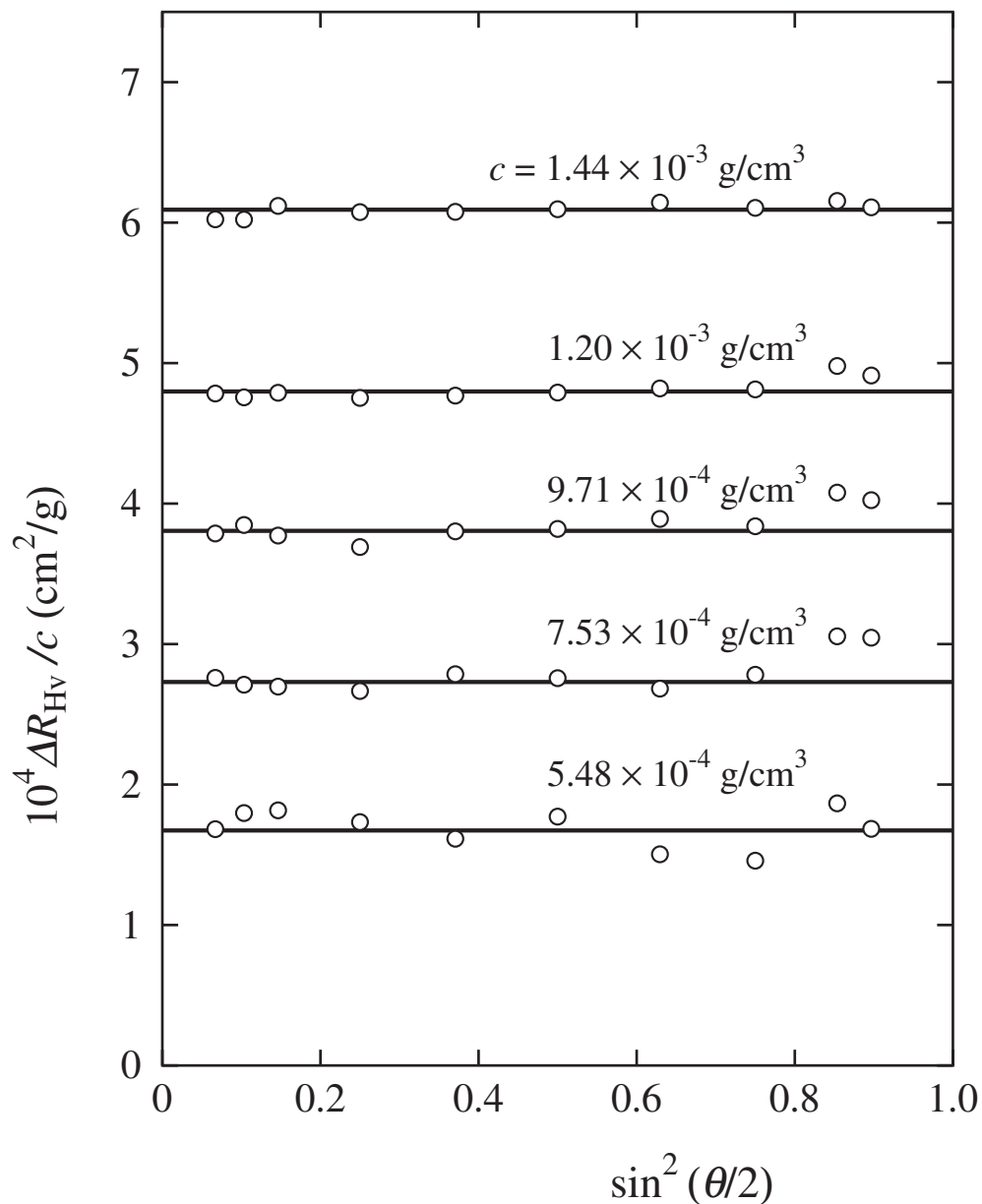


Fig. 2.1. Plots of $\Delta R_{\text{HV}}/c$ against $\sin^2(\theta/2)$ for the PHIC sample PHIC5 in *n*-hexane at 25.0 °C for the indicated value of c . The data points at $c = 7.53 \times 10^{-4}$, 9.71×10^{-4} , 1.20×10^{-3} , and 1.44×10^{-3} g/cm^3 are shifted upward by 1×10^{-4} , 2×10^{-4} , 3×10^{-4} , and 4×10^{-4} cm^2/g , respectively.

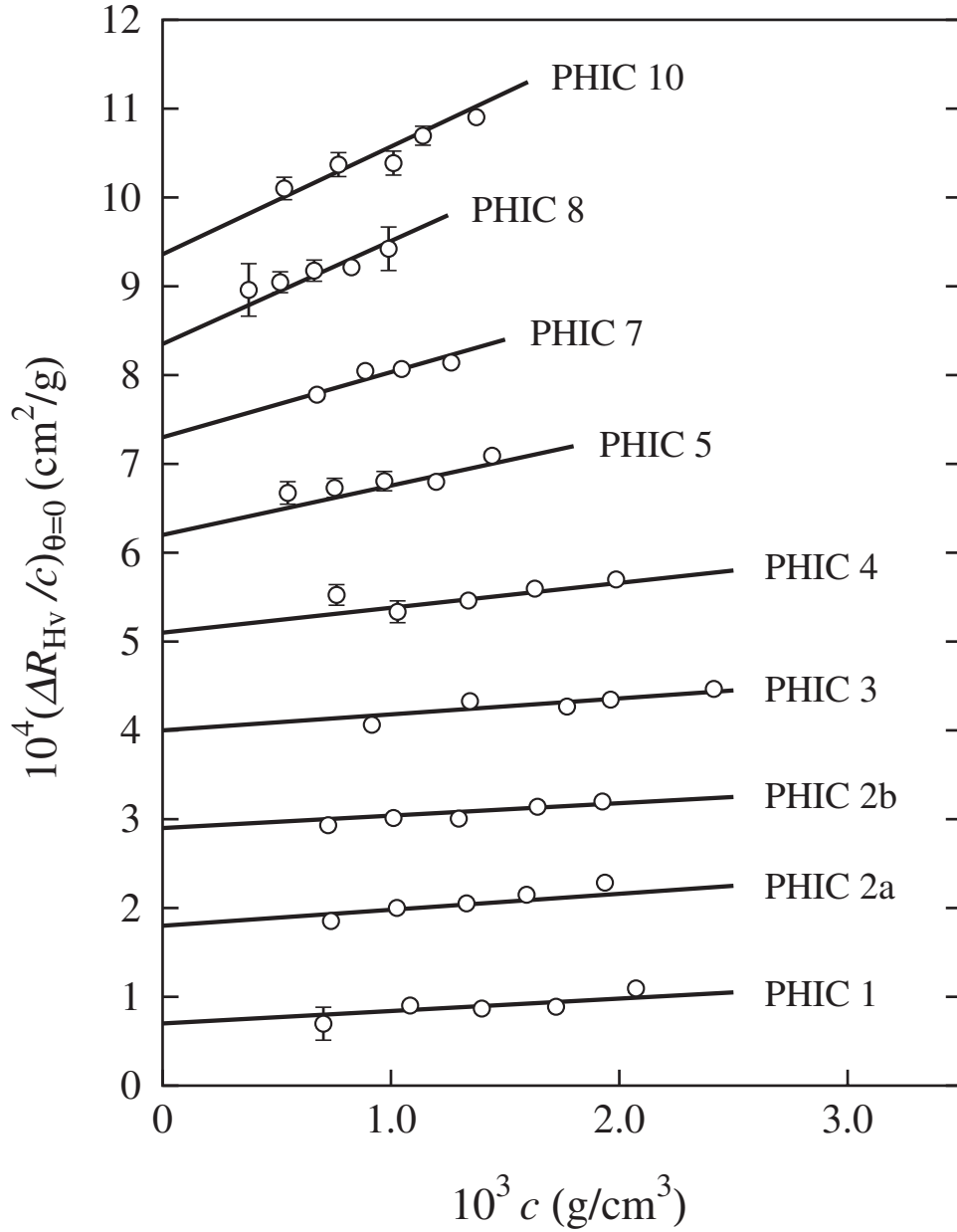


Fig. 2.2. Plots of $(\Delta R_{Hv}/c)_{\theta=0}$ against c for the PHIC samples indicated in *n*-hexane at 25.0 °C. The data points for the samples PHIC2a through PHIC10 are shifted upward by 1×10^{-4} , 2×10^{-4} , 3×10^{-4} , 4×10^{-4} , 5×10^{-4} , 6×10^{-4} , 7×10^{-4} , and 8×10^{-4} cm²/g, respectively. The vertical line segments attached to the data points indicate the error bounds.

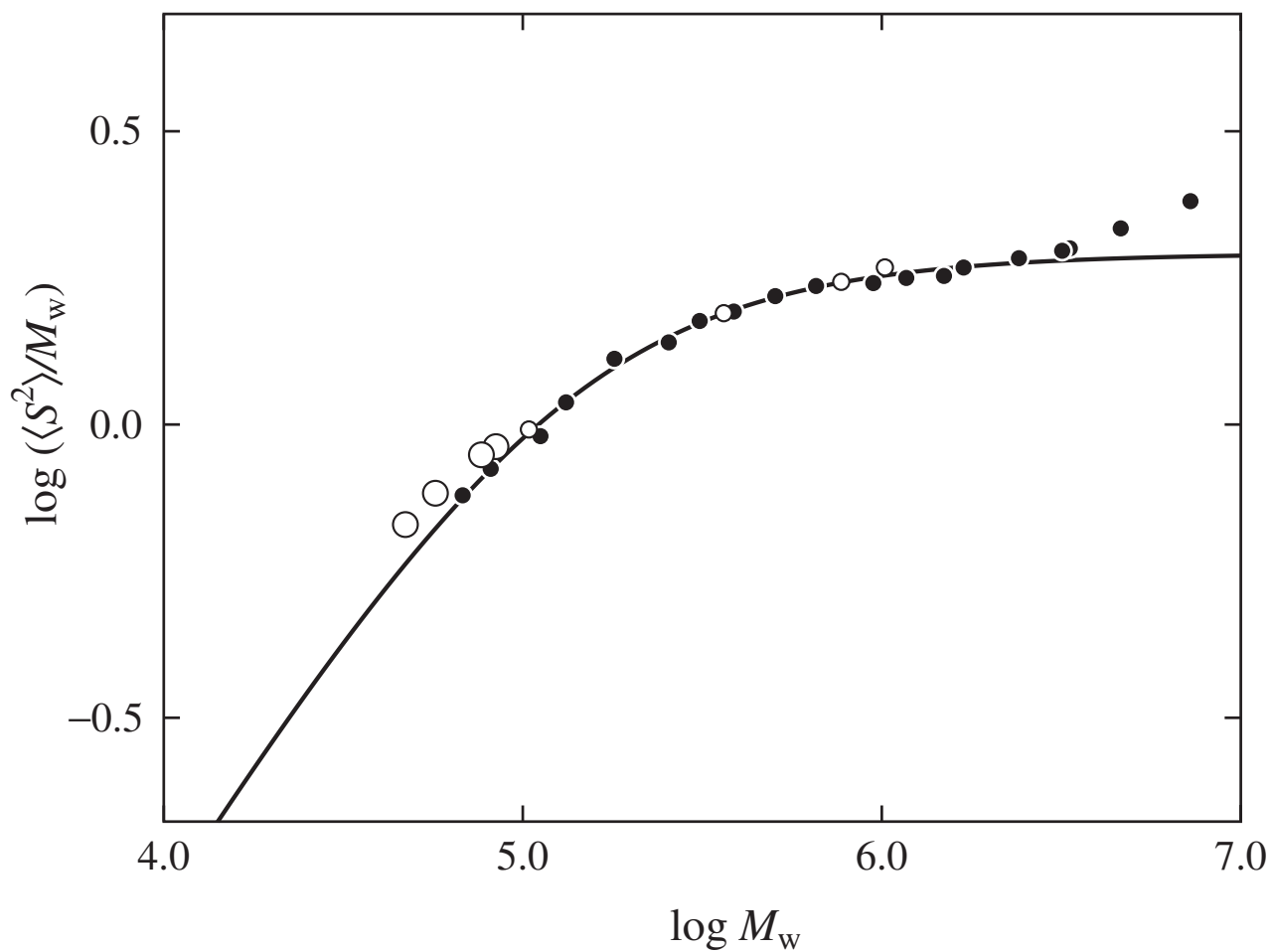


Fig. 2.3. Double-logarithmic plots of $\langle S^2 \rangle / M_w$ against M_w for PHIC in *n*-hexane at 25.0 °C: (O) present data; (◐) previous data;¹² (●) data by Murakami et al.⁹ The solid curve represents the KP theory values calculated from eq 3 with eq 4 with $\lambda^{-1} = 840 \text{ \AA}$ and $M_L = 71.5 \text{ \AA}^{-1}$.

2.3.2 Mean-Square Optical Anisotropy

If the effect of the internal electric field is taken into account by the use of the Lorentz–Lorenz equation and if the effect of collision-induced polarizabilities^{2,14} is ignored, the mean-square optical anisotropy $\langle \Gamma^2 \rangle$ may be calculated from

$$\langle \Gamma^2 \rangle = \frac{15\lambda_0^4}{16\pi^4} \frac{M_w}{N_A} \left(\frac{3}{n_0^2 + 2} \right)^2 \left(\frac{\Delta R_{Hv}}{c} \right)_{c=0, \theta=0} \quad (2.5)$$

with the experimental value of $(\Delta R_{Hv}/c)_{c=0, \theta=0}$ determined above, where λ_0 is the wavelength of the incident light in a vacuum and is equal to 436 nm, N_A is the Avogadro constant, and n_0 is the refractive index of the solvent. Equation 2.5 requires some comments. There are some objections to the use of the above second-power-type correction (Lorentz–Lorenz equation). However, we already discussed this point thoroughly in the previous study of $\langle \Gamma^2 \rangle$ of a-PMMA,³ and thus have adopted above the same correction as that previously^{2–4} used. Note that this adoption never affects the dependence itself of $\langle \Gamma^2 \rangle$ on x_w , but alters only the assigned value of $\Delta\alpha$. The neglect of collision-induced polarizabilities has a similar effect, and the effect is discussed in the next section. Thus the use of eq 2.5 does not injure a comparison of the present results with previous ones.

The values of $\langle \Gamma^2 \rangle$ calculated from eq 2.5 with the values of $(\Delta R_{Hv}/c)_{c=0, \theta=0}$ determined in the last subsection are given in the sixth column of Table 2.1. There are also given the values of $\langle \Gamma^2 \rangle/x_w$ in the seventh column. Figure 2.4 shows plots of $\langle \Gamma^2 \rangle/x_w$ against the logarithm of x_w for PHIC in *n*-hexane at 25.0 °C. The unfilled circles represent the present experimental values, where the vertical line segments attached to the data points indicate the error bounds. The filled circles represent the values estimated by extrapolation to infinite dilution from the results by Jinbo et al.⁶ for moderately concentrated solutions of PHIC in toluene at 25.0 °C. We note that $\lambda^{-1} = 740 \text{ \AA}$ and

$M_L = 74.0 \text{ \AA}^{-1}$ for PHIC in toluene at $25.0 \text{ }^\circ\text{C}$,²¹ so that the conformations of the PHIC chain in toluene and in *n*-hexane at $25.0 \text{ }^\circ\text{C}$ may be considered not to be very different. The present data are consistent with those by Jinbo et al.⁶ within experimental error. It is seen from the figure that $\langle \Gamma^2 \rangle / x_w$ increases monotonically with increasing x_w , and then approaches its asymptotic value. In the figure, the solid curve represents the KP theoretical values, which are mentioned in the next section.

2.4 Discussion

2.4.1 Comparison with Theory

The mean-square optical anisotropy $\langle \Gamma^2 \rangle$ for the KP chain is given by^{17,18,22}

$$\frac{\langle \Gamma^2 \rangle}{x} = \frac{\lambda^{-1} M_0}{3M_L} (\Delta\alpha)^2 \left[1 - \frac{1}{6\lambda L} (1 - e^{-6\lambda L}) \right] \quad (2.6)$$

where $\Delta\alpha$ is the difference between the polarizabilities, per unit contour length, parallel and perpendicular to the contour, which we denote by $\alpha_{\parallel}$ and $\alpha_{\perp}$, respectively, i.e.,

$$\Delta\alpha = |\alpha_{\parallel} - \alpha_{\perp}| \quad (2.7)$$

and L is related to x by

$$L = x M_0 / M_L \quad (2.8)$$

with M_0 the molecular weight of the repeat unit.

In Figure 2.4, the solid curve represents the best-fit KP theory values calculated from eq 2.6 with eq 2.8 with $M_0 = 127$, $\Delta\alpha = 1.12 \text{ \AA}$,² and the basic model parameter values, $\lambda^{-1} = 840 \text{ \AA}$ and $M_L = 71.5 \text{ \AA}^{-1}$.⁹ As mentioned in the Introduction, $\Delta\alpha$ has been treated as an adjustable parameter, and determined to give the above best-fit theoretical curve. It is seen that the theory may rather well explain the dependence of $\langle \Gamma^2 \rangle / x_w$ on x_w .

2.4.2 Local Polarizability Tensor

Now we estimate the value of $\Delta\alpha$ for PHIC by the use of literature values of the bond polarizability tensors. For this purpose, in Figures 2.5a and 2.5b are shown side and bottom views, respectively, of the skeleton of one turn of the (rigid) helix of PHIC with a localized Cartesian coordinate system (ξ, η, ζ) affixed to it. Here, we have assumed that the two kinds of rotation angles around the C–N bonds in the main chain take the values given by Troxell and Scheraga⁸ for poly(methyl isocyanate), and also that each *n*-hexyl group takes the all-*trans* conformation and is attached to the N atom with its axis of symmetry making a right angle with the helix axis (with the minimum energy), for simplicity. The same bottom view as that in Figure 2.5b is shown in Figure 2.5c, where all atoms are depicted by the spheres having the van der Waals radii, and the circle of diameter 16 Å determined from the intrinsic viscosity⁹ $[\eta]$ is also drawn. It is seen from Figure 2.5c that the above two assumptions are not so unrealistic.

In the evaluation of $\Delta\alpha$, we only need the bond polarizability tensors averaged over the rotation around the ζ axis, each of the resultant averaged tensors being cylindrically symmetric around the ζ axis, i.e., of the form of a 3×3 tensor with the $\xi\xi$ and $\eta\eta$ components being identical with each other. The absolute values of the angles between the ζ axis and the bonds necessary for the evaluation of the $\zeta\zeta$ ($\parallel$) and $\xi\xi$ (or $\eta\eta$) ($\perp$) components of the averaged tensors have been given by Troxell and Scheraga.⁸ We have used the literature values of the bond polarizability tensors for the C–H,²³ C–C,²³ C–N,²⁴ and C–O²³ bonds, which are summarized in ref 25. As for the C=O bond, we have estimated its polarizability tensor by the use of the literature value for methyl acetate^{25,26} along with the above values for C–H, C–C, and C–O bonds, assuming the additivity of bond polarizabilities. With the correction made by multiplying all the bond polarizability

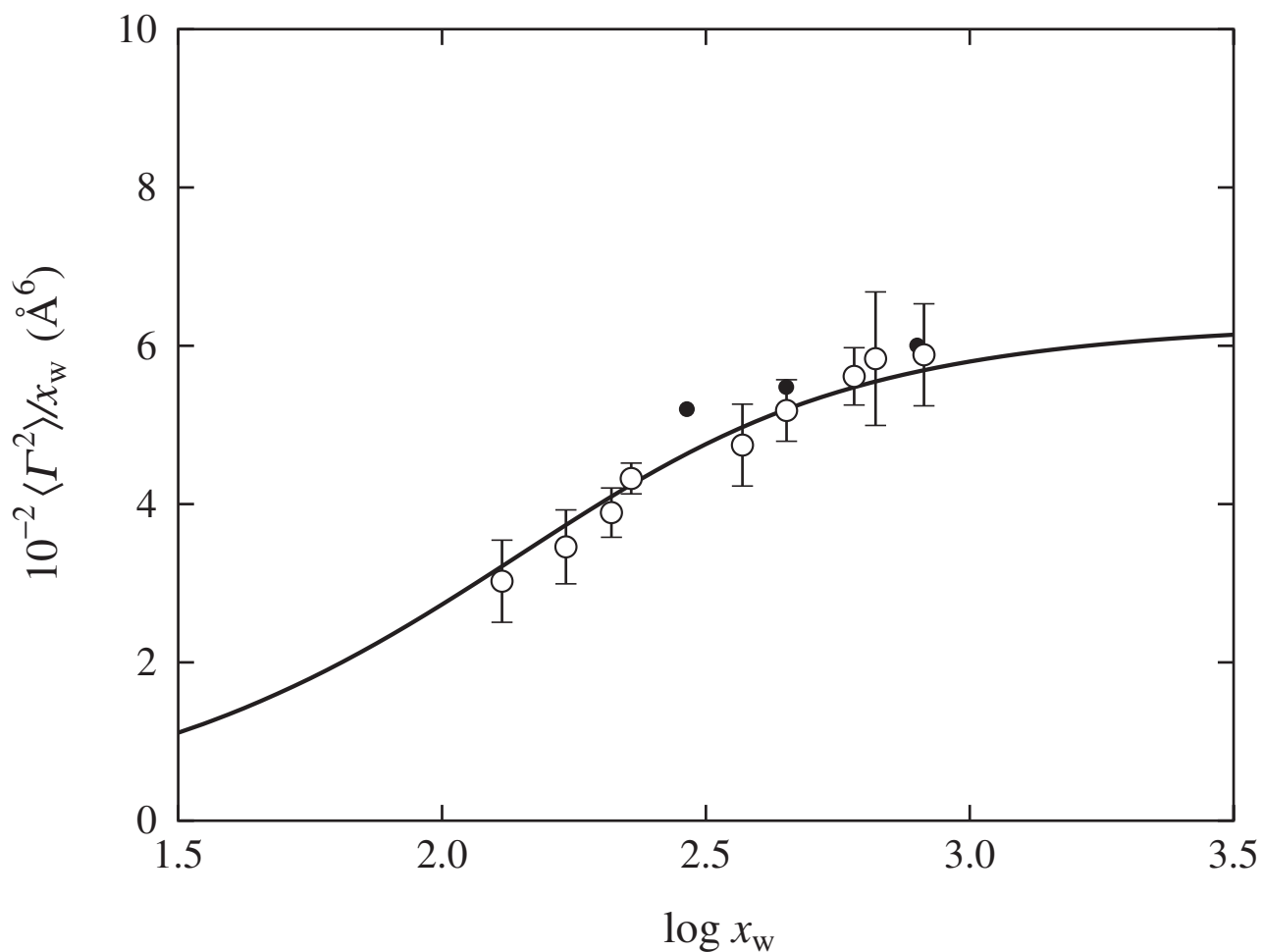


Fig. 2.4. Plots of $\langle \Gamma^2 \rangle / x_w$ against $\log x_w$ for PHIC; (○) present data in *n*-hexane at 25.0 °C; (●) data by Jinbo et al.⁶ in toluene at 25.0 °C. The vertical line segments attached to the present data points indicate the error bounds. The solid curve represents the best-fit KP theory values calculated from eq 6 with eq 8 with $M_0 = 127$, $\Delta\alpha = 1.12 \text{ \AA}^2$, $\lambda^{-1} = 840 \text{ \AA}$, and $M_L = 71.5 \text{ \AA}^{-1}$.

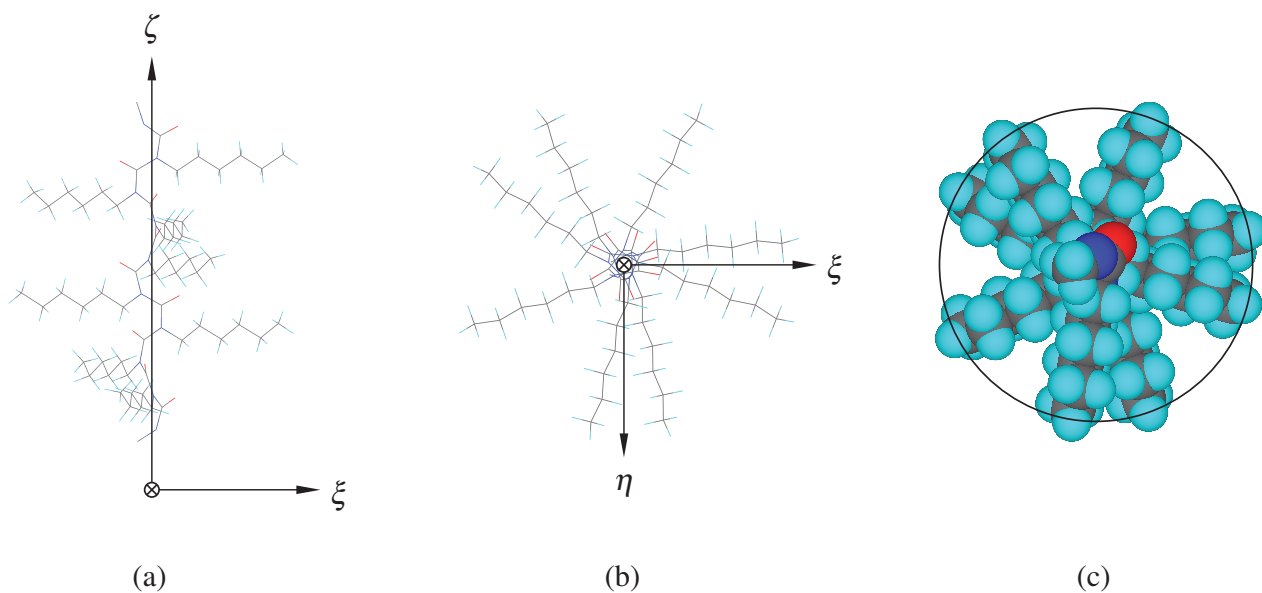


Fig. 2.5. Schematic drawing of the helix of PHIC with a localized Cartesian coordinate system affixed to it: (a) side view of its skeleton; (b) bottom view of its skeleton; (c) bottom view, where all atoms are depicted by the spheres (see the text). The circle in (c) has the diameter of 16 Å determined from $[\eta]$.⁹

tensors by the common factor $\sqrt{1.9_4}$,³ $\Delta\alpha$ is then estimated to be 0.5_3 Å^2 , which is appreciably smaller than the value 1.1_2 Å^2 determined above.

The above difference between the experimental and calculated values of $\Delta\alpha$ indicates that there exists definitely some additional scattered intensity arising from the effect of collision-induced polarizabilities, although the latter value of $\Delta\alpha$ may probably be somewhat underestimated. However, this does not affect the dependence itself of $\langle\Gamma^2\rangle$ on x_w , as already mentioned in the Results section.

2.4.3 Comparison with Other Polymers

For comparison, values of $\langle\Gamma^2\rangle/x_w$ for other polymers along with those for PHIC are double-logarithmically plotted against x_w in Figure 2.6. The unfilled and filled circles represent the present experimental values obtained for PHIC in *n*-hexane at 25.0 °C and

the literature ones⁶ for PHIC in toluene at 25.0 °C, respectively, both already shown in Figure 2.4. The unfilled squares, triangles, and inverted triangles represent the values previously obtained for a-PS in cyclohexane at 34.5 °C (Θ),^{2,3} a-PMMA in acetonitrile at 44.0 °C (Θ),³ and i-PMMA in acetonitrile at 28.0 °C (Θ),⁴ respectively. As an example of semiflexible polymers other than PHIC, there are also plotted the literature values obtained by Sakurai et al.²⁷ for poly(terephthalamide-*p*-benzohydrazide) (PPAH) in dimethyl sulfoxide at 25.0 °C (filled squares). The solid and dashed curves associated with the data points represent the KP and HW theory values for the semiflexible polymers PHIC and PPAH and for the flexible polymers a-PS, a-PMMA, and i-PMMA, respectively. The KP theory values for PPAH have been calculated from eq 6 with eq 8 with $M_0 = 281$, $\Delta\alpha = 2.2 \text{ \AA}^2$, $\lambda^{-1} = 224 \text{ \AA}$, and $M_L = 18.5 \text{ \AA}^{-1}$, where the value of $\Delta\alpha$ has been estimated from the value 2.1 of the parameter ϵ used by Sakurai et al. The HW theory values have been reproduced from the previous papers.^{3,4}

The asymptotic value of $\langle \Gamma^2 \rangle / x_w$ in the limit of $x_w \rightarrow \infty$ for PHIC is very large compared to those for the three flexible polymers, although $\Delta\alpha$ of PHIC is of the same order of magnitude as the polarizability tensors assigned to the three flexible chains. Furthermore, the value of x_w where $\langle \Gamma^2 \rangle / x_w$ reaches its asymptotic value is also remarkably larger for PHIC than for the flexible polymers. This is, of course, due to the fact that λ^{-1} of PHIC is very large compared to those of typical flexible polymers. PPAH has the largest asymptotic value of all the polymers shown in Figure 2.6. This is because its $\Delta\alpha$ is appreciably larger than those of the others.

Finally, we must note that the experimental errors in the values of $\langle \Gamma^2 \rangle$ previously determined for the flexible polymers may be considered to be smaller than those in the present values for PHIC despite the fact that $\langle \Gamma^2 \rangle$ is much smaller for the former than for

the latter. The reason for this is that the range of c adopted for the present measurements is far lower than those for the flexible polymers, which were from ca. 0.1 to ca. 0.3 g/cm³.

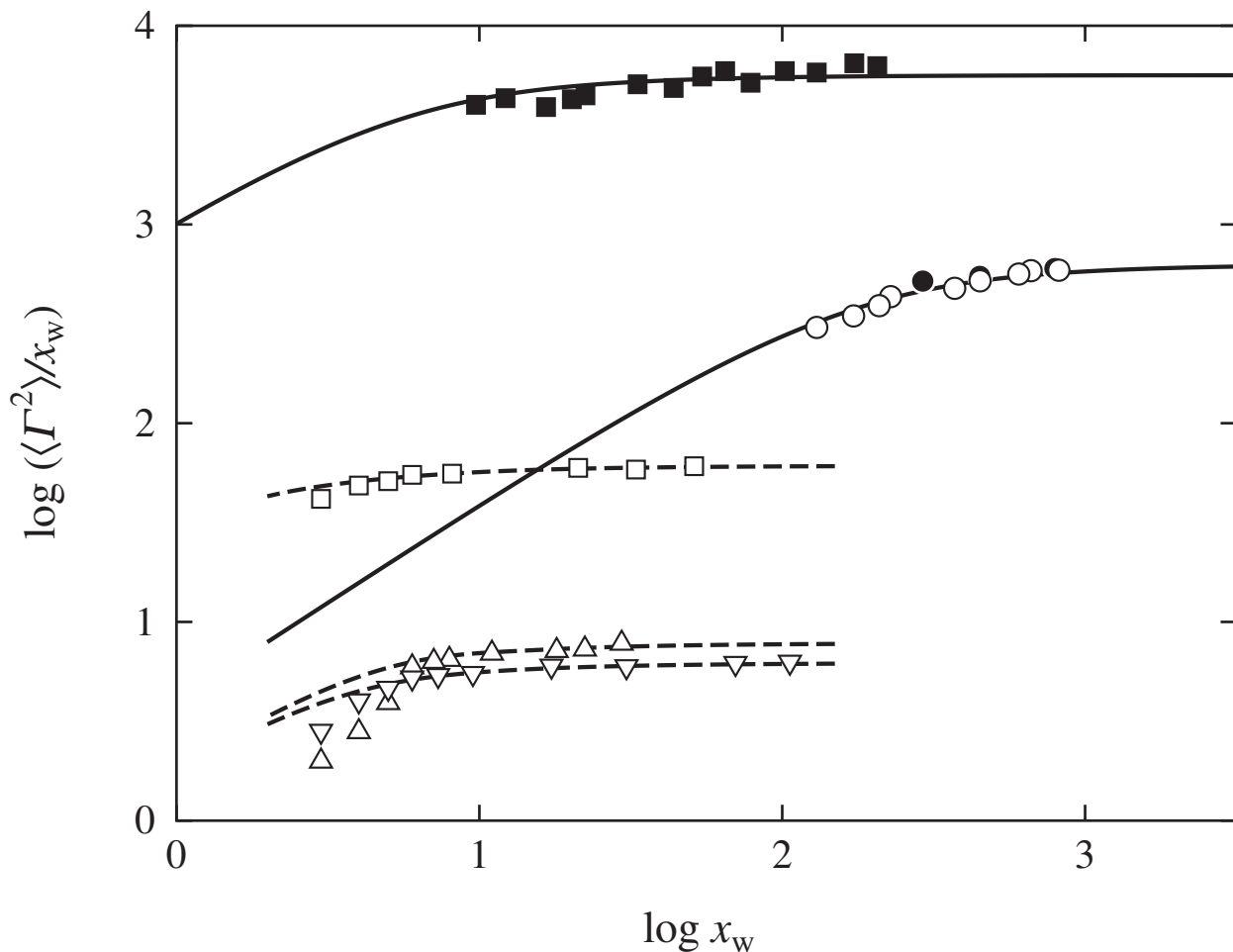


Fig. 2.6. Double-logarithmic plots of $\langle \Gamma^2 \rangle / x_w$ against x_w : (○) present data for PHIC in *n*-hexane at 25.0 °C; (●) data by Jinbo et al. for PHIC in toluene at 25.0 °C;⁶ (□) previous data for a-PS in cyclohexane at 34.5 °C (Θ);^{2,3} (△) previous data for a-PMMA in acetonitrile at 44.0 °C (Θ);³ (▽) previous data for i-PMMA in acetonitrile at 28.0 °C (Θ);⁴ (■) data by Sakurai et al. for PPAH in dimethyl sulfoxide at 25.0 °C.²⁷ The solid and dashed curves represent the KP and HW theory values, respectively (see the text).

2.5 Conclusion

We could determine the mean-square optical anisotropy $\langle \Gamma^2 \rangle$ for PHIC, whose optical anisotropy is very small, within permissible experimental error. It was then found that the dependence of $\langle \Gamma^2 \rangle / x_w$ on x_w may be satisfactorily explained by the corresponding theory on the basis of the KP chain model. The assigned value of $\Delta\alpha$ is appreciably larger than its value estimated from the bond polarizabilities, indicating that there exists definitely some additional scattered intensity arising from the effect of collision-induced polarizabilities. However, this does not affect the dependence itself of $\langle \Gamma^2 \rangle / x_w$ on x_w . From a comparison of the present results for PHIC with the previous ones for the typical flexible polymers, it is seen that the difference in the behavior of $\langle \Gamma^2 \rangle$ between them arises from that in chain stiffness as in the cases of $\langle S^2 \rangle$ and also the transport coefficients (intrinsic viscosity and translational diffusion coefficient).¹

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3 Nuclear Magnetic Relaxation of Poly(*n*-hexyl isocyanate)

3.1 Introduction

In Chap. 2, we have determined the mean-square optical anisotropy $\langle \Gamma^2 \rangle$ for poly(*n*-hexyl isocyanate) (PHIC), whose optical anisotropy is very small, within permissible experimental error. In this chapter, we characterize PHIC by the use of Nuclear Magnetic Relaxation. As is well known, the spin-lattice relaxation time T_1 , spin-spin relaxation time T_2 , and nuclear Overhauser enhancement NOE for ^{13}C nuclei may be expressed in terms of time-correlation functions of components of the dyadic of the internuclear vector $^{13}\text{C} \rightarrow ^1\text{H}$ from a ^{13}C nucleus to a bonded ^1H one if we simply assume that the nuclear magnetism of ^{13}C relaxes only due to the heteronuclear dipolar interaction.^{1,2}

As mentioned in Chap. 1, we have made so far experimental studies of T_1 and NOE for backbone ^{13}C of typical flexible polymers such as atactic polystyrene,³ atactic poly(methyl methacrylate),⁴ isotactic poly(methyl methacrylate),⁵ and atactic poly(α -methylstyrene).⁶ However, such literature data for typical semiflexible polymers are not available except those obtained by Budd *et al.*⁷ for T_1 and T_2 for poly(γ -benzyl L-glutamate) (PBLG). In the present paper, therefore, we examine experimentally the dependence on M of T_1 , T_2 , and also NOE for poly(*n*-hexyl isocyanate) (PHIC) as another example of semiflexible polymers. We note that DuPré and Wang⁸ have determined T_1 , T_2 , and NOE for a PHIC sample with the weight-average molecular weight $M_w = 3.39 \times 10^4$, and therefore have

not examined the dependence of these quantities on M_w .

PHIC is a typical semiflexible polymer whose molecular characterization has almost completely been done by an analysis of dilute solution properties on the basis of the Kratky–Porod (KP) wormlike chain model.^{9,10} Specifically, the KP model parameters for PHIC, i.e., the static stiffness parameters λ^{-1} , the shift factor M_L as defined as the molecular weight per unit contour length of the KP chain, and the hydrodynamic diameter d , have been determined rather unambiguously.¹¹ Thus, from a comparison of present experimental data with the theory previously¹² developed for the generalized KP chain [a special case of the helical wormlike (HW) chain],¹⁰ we may verify its validity. This is the main purpose of the present paper.

A remark should be made here on the ^{13}C atoms of PHIC under observation. In their study of PBLG, Budd *et al.*⁷ have observed signals from backbone $^{13}\text{C}^\alpha$ atoms in order to trace main-chain motions. In the present case of PHIC, however, the backbone carbon atoms are only carbonyl ones and their nuclear magnetism never relaxes due to the heteronuclear dipolar interaction, so that main-chain motions cannot then be directly traced. Thus, following DuPré and Wang,⁸ we assume that the bond vector from the *n*-hexyl (side-chain) C atom next to a (main-chain) nitrogen atom, which we designate by C1, to a bonded H atom is rigidly attached to the backbone, and make a comparison of experimental results for $^{13}\text{C}1$ with the theory.

3.2 Experimental Section

3.2.1 Materials

All the five PHIC samples PHIC1, PHIC2b, PHIC3, PHIC4, and PHIC5 used in this work are the same as those used in a previous study of the mean-square optical anisotropy

$\langle \Gamma^2 \rangle$.¹³ The original sample from which the five test samples were separated by fractional precipitation had been prepared following the procedure of Aharoni,¹⁴ i.e., polymerized in a toluene/*N,N*-dimethylformamide (1:1) mixture at -78°C with sodium cyanide as an initiator and methanol as a terminator. In Table 3.1 have been reproduced the values of M_w , the weight-average degree of polymerization x_w , and the ratio M_w/M_n of M_w to the number-average molecular weight M_n for the five samples from Table 1 of ref 13.

The solvent *n*-hexane used for nuclear magnetic relaxation measurements was purified according to a standard procedure prior to use.

3.2.2 Nuclear Magnetic Relaxation

T_1 and T_2 were determined for $^{13}\text{C}1$ of all the five samples by the inversion-recovery method with a pulse sequence $\pi-\tau-\pi/2$ on a JEOL JNM GX-400 spectrometer at 100.5 MHz. NOE for $^{13}\text{C}1$ for each sample was evaluated from the ratio of the integrated intensity of its peak obtained with complete noise decoupling of protons to that obtained with gated decoupling only during data acquisition. A pulse delay was taken to be longer than 1.5 s, so that it is ca. 8 times as long as T_1 for $^{13}\text{C}1$ under observation. Measurements were carried out on solutions in *n*-hexane at 25°C with a lock signal obtained from an external C_6D_{12} tube. The values of the polymer mass concentration c of the test solutions are 0.009₇, 0.020₁, 0.046₄, 0.058₄, and 0.051₀ g/cm³ for PHIC1, PHIC2b, PHIC3, PHIC4, and PHIC5, respectively, which were calculated from the weight fractions with the densities of the solutions. The solutions were not degassed since T_1 's of interest never exceeded 2 s, as shown in the next (RESULTS) section. We note that the resonance peak of $^{13}\text{C}1$ (48.8 ppm) is well separated from those of ^{13}C in the solvent *n*-hexane.

Table 3.1. Values of M_w , x_w , and M_w/M_n for
Poly(*n*-hexyl isocyanate)

sample	M_w	x_w	M_w/M_n
PHIC1	1.65×10^4	130	1.10
PHIC2b	2.66×10^4	209	1.07
PHIC3	2.90×10^4	228	1.10
PHIC4	4.71×10^4	371	1.04
PHIC5	5.71×10^4	450	1.05

Table 3.2. Values of T_1 , T_2 , and NOE for
Poly(*n*-hexyl isocyanate) in *n*-hexane at 25 °C

sample	T_1 , s	T_2 , s	NOE
PHIC1	0.16 ₇	0.012 ₉	1.0 ₈
PHIC2b	0.17 ₀	0.008 ₁	1.1 ₃
PHIC3	0.18 ₆	0.005 ₀	1.1 ₂
PHIC4	0.19 ₉	0.003 ₉	1.3 ₅
PHIC5	0.21 ₈	0.003 ₄	1.2 ₀

3.3 Results

In Table 3.2 are given the values of T_1 , T_2 , and NOE for $^{13}\text{C}1$ for the five PHIC samples PHIC1 (at $c = 0.009_7$ g/cm³), PHIC2b (at $c = 0.020_1$ g/cm³), PHIC3 (at $c = 0.046_4$ g/cm³), PHIC4 (at $c = 0.058_4$ g/cm³), and PHIC5 (at $c = 0.051_0$ g/cm³) in *n*-

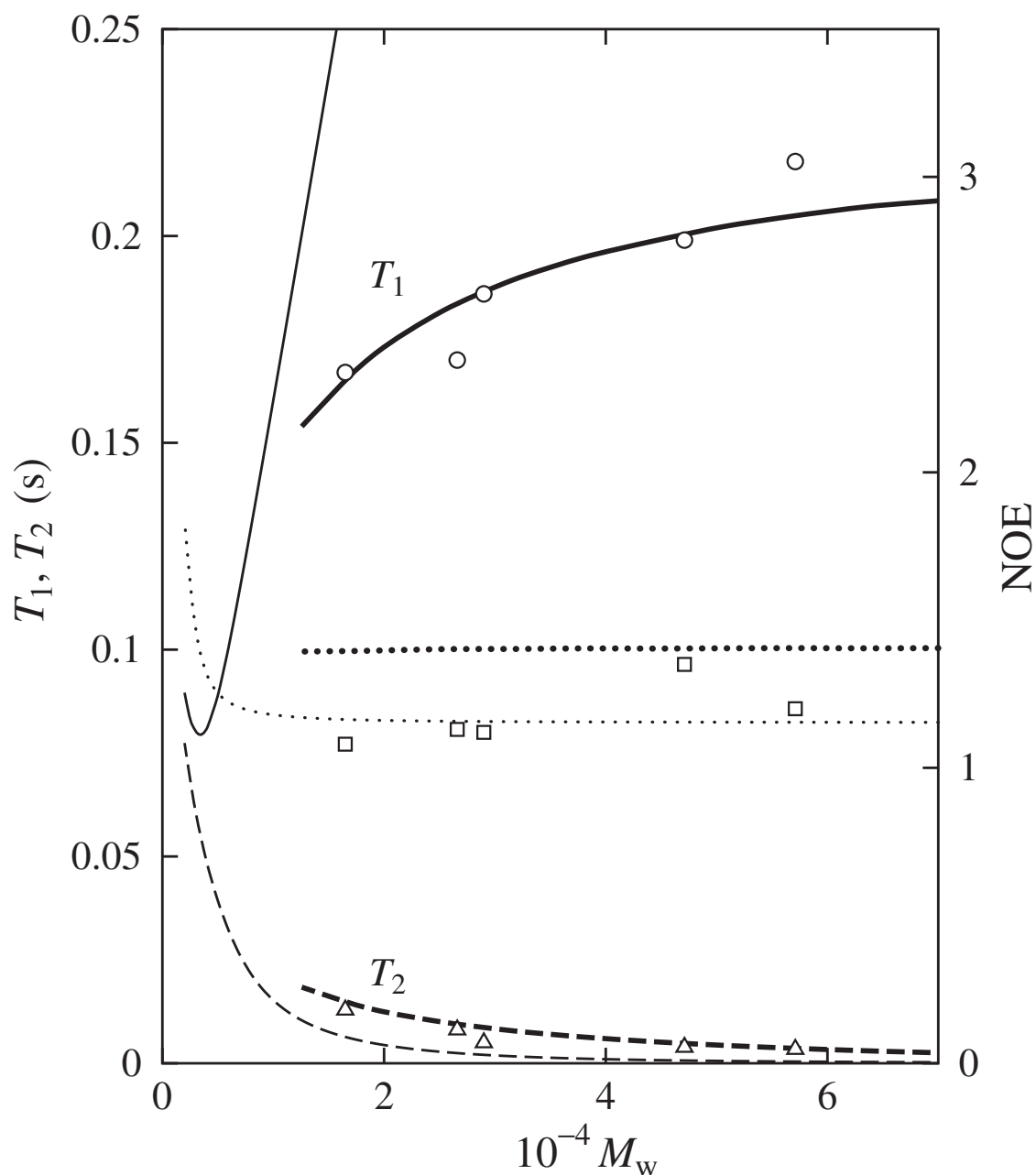


Fig. 3.1. Plots of T_1 , T_2 , and NOE against M_w for the $^{13}\text{C}1$ atoms for PHIC in n -hexane at 25 °C: (○) T_1 ; (△) T_2 ; (□) NOE. The heavy solid, dashed, and dotted curves represent the generalized KP theoretical values of T_1 , T_2 , and NOE, respectively, and the light curves represent the respective theoretical values for the rigid prolate spheroid (see the text).

hexane at 25 °C and at the Larmor frequency 100.5 MHz of ^{13}C . Figure 1 shows plots of T_1 , T_2 , and NOE for $^{13}\text{C}1$ so obtained against M_w . The circles, triangles, and squares represent the experimental values of T_1 , T_2 , and NOE, respectively. In the figure, the heavy solid, dashed, and dotted curves represent the generalized KP theoretical values of T_1 , T_2 , and NOE, respectively, and the light curves represent the respective theoretical values for the rigid prolate spheroid, which are obtained and discussed in the next (DISCUSSION) section.

It is clearly seen that T_1 increases and T_2 decreases monotonically with increasing M_w in the range of M_w examined as in the case of PBLG.⁷ Such behavior of T_1 and T_2 may be regarded as arising from effects of chain stiffness. As for NOE, it seems almost independent of M_w in the range of M_w examined.

DuPré and Wang⁸ have determined T_1 , T_2 , and NOE for $^{13}\text{C}1$ for the PHIC sample with $M_w = 3.39 \times 10^4$ in chloroform-*d* and in toluene at 30 °C and at the Larmor frequencies 75 and 126 MHz of ^{13}C . We note that the concentrations of their test solutions are ca. 0.06 g/cm³ and are nearly of the same order as ours. The values of T_1 , T_2 , and NOE obtained in chloroform-*d* are 0.145 s, 0.005 s, and 1.59, respectively, at 75 MHz and 0.290 s, 0.005 s, and 1.13, respectively, at 126 MHz, and those in toluene are 0.100 s, 0.005 s, and 1.63, respectively, at 75 MHz. As for the results in toluene at 126 MHz, they have reported only the values 0.342 s and 0.003 s of T_1 and T_2 , respectively. Since their solvent conditions and Larmor frequencies are different from those adopted in the present measurements, we cannot directly compare the present results with the above literature data. We only note that the present and literature data are not very inconsistent with each other, being of the same order of magnitude.

3.4 Discussion

3.4.1 HW Theory

Before proceeding to make a comparison of the present data for T_1 , T_2 , and NOE with the generalized KP chain theory,^{10,12} we briefly summarize its relevant results.

The generalized KP chain is a special case of the HW chain which is defined as an elastic wire.¹⁰ The equilibrium conformational behavior of the HW chain may in general be described by four parameters: the constant differential-geometrical curvature κ_0 and torsion τ_0 of the characteristic helix taken at minimum zero of its elastic energy and the bending and torsional force constants. In the particular case of $\kappa_0 = 0$, the characteristic helix becomes a straight line, and then the HW chain with $\kappa_0 = 0$ is referred to as the *generalized* KP chain. Further, for convenience, the generalized KP chain is classified into two types: one with $\tau_0 \neq 0$ (KP1) and the other with $\tau_0 = 0$ (KP2). In an application of the HW chain to flexible polymers, the bending and torsional force constants are set equal to each other (Poisson's ratio $\sigma = 0$), for simplicity, and these two parameters may then be reduced to the single (static stiffness) parameter λ^{-1} . Although the two force constants should not necessarily be set equal to each other in the case of the generalized KP chain, we do so as in the previous analysis¹² of the PBLG data.⁷ Then the model parameters describing the generalized KP chain in the present case are λ^{-1} and τ_0 . The basic equations necessary for the present analysis are in principle the same as those for the HW chain ($\sigma = 0$) used in the previous analyses^{3,4,5,6} of the data for the typical flexible polymers.

In order to apply the HW (or generalized KP) chain to an analysis of dynamic properties, we use its dynamic version, the *discrete* HW (or generalized KP) chain,¹⁰ which is composed of N identical rigid subbodies, each with the translational and rotatory friction

coefficients ζ_t and ζ_r . The subbodies are successively joined with bonds of fixed length a , and the potential energy as a function of the orientation of a subbody relative to the preceding one is properly chosen so that the equilibrium conformational behavior of the dynamic version may reproduce well that of the original one.

As mentioned in the INTRODUCTION, we assume that the nuclear magnetic spin (of ^{13}C atom in the present case) relaxes only due to the heteronuclear dipolar interaction between two unlike spins I and S with spin I observed and spin S irradiated (i.e., spins of ^{13}C and ^1H atoms, respectively, in the present case, so that $I = S = 1/2$) and with the internuclear distance r between them. Then T_1 , T_2 , and NOE for the single (discrete) generalized KP chain [i.e., the single (discrete) HW chain with $\kappa_0 = 0$] may be given by^{10,12}

$$T_1^{-1} = (1/20)K^2r^{-6}[J_0(\omega_S - \omega_I) + 3J_1(\omega_I) + 6J_2(\omega_S + \omega_I)] \quad (3.1)$$

$$T_2^{-1} = (1/40)K^2r^{-6}[4J_0(0) + J_0(\omega_S - \omega_I) + 3J_1(\omega_I) + 6J_1(\omega_S) + 6J_2(\omega_S + \omega_I)] \quad (3.2)$$

$$\text{NOE} = 1 + \frac{\gamma_S}{\gamma_I} \left[\frac{6J_2(\omega_S + \omega_I) - J_0(\omega_S - \omega_I)}{J_0(\omega_S - \omega_I) + 3J_1(\omega_I) + 6J_2(\omega_S + \omega_I)} \right] \quad (3.3)$$

with

$$K = \hbar\gamma_I\gamma_S \quad (3.4)$$

where γ_I and γ_S are the gyromagnetic ratios of spins I and S , respectively, ω_I and ω_S are the respective Larmor angular frequencies, $\hbar$ is Dirac's constant (Planck's constant divided by 2π), and $J_m(\omega)$ ($m = 0, 1, 2$) is the spectral density written in the form^{10,12}

$$J_m(\omega) = 2 \sum_{k=1}^N (Q_{pk}^0)^2 \sum_{j=-2}^2 \frac{A_{2,k}^j \tau_{2,k}^j}{1 + (\omega\tau_{2,k}^j)^2} \quad (3.5)$$

with p indicating the subbody number and with

$$Q_{pk}^0 = [2/(N+1)]^{1/2} \sin[\pi pk/(N+1)] \quad (3.6)$$

$$\tau_{2,k}^j = 1/\lambda_{2,k}^j \quad (3.7)$$

We note that J_m is independent of m . The quantities $\lambda_{2,k}^j$ in eq 3.7 are the eigenvalues of the matrix representation of the diffusion operator associated with the subspace 2(1) (of full Hilbert space) spanned by the basis set with the “total angular momentum quantum number” $L = 2$ and the number of “excited” subbodies $n = 1$, and the coefficients $A_{2,k}^j$ in eq 3.5 are given by eq 29 of ref 12. We use the eigenvalues $\lambda_{2,k}^j$ in the crude subspace approximation given by eq B5 of ref 15 as in the previous study¹² of nuclear magnetic relaxation of semiflexible polymers. Thus $\lambda_{2,k}^j$ may readily be calculated for given values of N and the five (discrete) generalized KP model parameters: λ^{-1} , τ_0 , a , ζ_t , and ζ_r . We note that the coefficient $A_{2,k}^j$ depends on the parameters λ^{-1} and τ_0 and also on the absolute value of the angle α between the C-H internuclear vector and the KP chain contour.

When two or more spins S contribute to the relaxation of spin I under consideration, the above formula 3.1—3.3 should be modified. If the internuclear distances of all spin pairs are the same, then T_1 , T_2 , and NOE are given by eqs 3.1—3.3, respectively, but with the sum of spectral densities $J_m^{(i)}$ over spin pair i in place of J_m .

3.4.2 Dependence of T_1 , T_2 , and NOE on M_w

As in the previous study of $\langle \Gamma^2 \rangle$,¹³ we assume that the two kinds of rotation angles around the C—N bonds in the main chain of PHIC take the values given by Troxell and Scheraga¹⁶ for poly(methyl isocyanate), and also that each n -hexyl group takes the all-*trans* conformation and is attached to the N atom with its axis of symmetry making a right angle with the helix axis (with the minimum energy), for simplicity. Then the backbone of PHIC takes the Schmueli–Traub–Rosenheck¹⁷ 8_3 helix,^{16,18,19,20} and the equilibrium

conformational behavior of its helix axis (without consideration of the torsion) may be well described by the (original⁹) KP chain with $\lambda^{-1} = 840 \text{ \AA}$ and $M_L = 71.5 \text{ \AA}^{-1}$.¹⁸ If we take the repeat unit of PHIC as the subbody composing the discrete model, the bond length a may then be calculated to be $1.78 \text{ \AA}$ from the relation $a \simeq M_0/M_L$ with the above value of M_L and the value 127 of the molecular weight M_0 of the repeat unit. Further, the localized Cartesian coordinate system (ξ, η, ζ) ¹⁰ affixed to each subbody with its ζ axis in the direction of the chain contour (the 8_3 helix axis in the present case) rotates around the helix axis with the pitch $h = 4.74 \text{ \AA}$ (of the present 8_3 helix), so that the KP1 torsion $\tau_0 (= 2\pi/h)$ becomes equal to $1.33 \text{ \AA}^{-1}$ (see also Fig. 4.4b of ref 10). The dimensionless parameters $r_1 \equiv \zeta_t/3\pi\eta_0a$ and $r_2 \equiv \zeta_r/a^2\zeta_t$ with η_0 the solvent viscosity are used in place of ζ_t and ζ_r themselves. The values of r_1 is set equal to 1, as usually done,^{3,4,5,6,12,21} and r_2 as an adjustable parameter is determined from a best fit of the theoretical values to the data for T_1 , as previously done.¹²

Each $^{13}\text{C1}$ atom of PHIC has two bonded ^1H atoms and the two angles α 's, each between one of the two internuclear vectors $^{13}\text{C1} \rightarrow ^1\text{H}$ and the chain contour (the 8_3 helix axis), are estimated to be 39° and 71° for the chain conformation mentioned above. Then the observed T_1 and T_2 must be compared with one half of the harmonic mean of the two theoretical values calculated from eqs 3.1 and 3.2 with eqs 3.4—3.7 with $\alpha = 39^\circ$ and 71° . As for NOE, we simply compare the observed value with the arithmetic mean of the two theoretical values calculated from eqs 3.3—3.7 with $\alpha = 39^\circ$ and 71° , which gives a good approximate value, as done by DuPré and Wang.⁸

In Figure 3.1, the heavy solid, dashed, and dotted curves represent the generalized KP theoretical values of T_1 , T_2 , and NOE, respectively, so calculated from eqs 3.1—3.7 with $r_2 = 320$ along with the above mentioned values of the parameters, where N has

been converted to M_w by $M_w = NM_0$, $(Q_{pk}^0)^2$ in eq 3.5 has been replaced by N^{-1} , and the value 0.299 cP has been used for η_0 for *n*-hexane at 25 °C. It is seen that the theory gives almost a quantitative explanation of the experimental results within experimental error. We then find the hydrodynamic diameter d of the KP cylinder having the same hydrodynamic volume as the discrete generalized KP chain to be equal to 19 Å. It has been calculated from eqs 35—38 of ref 21 with the above values of r_2 and a , assuming, as in the previous study,¹² that the subbody of the latter is an oblate spheroid having the rotation axis of length a and the diameter d_s . (We note that $d_s = 23$ Å.) This value of d is fairly consistent with the values 16 and 25 Å determined from the intrinsic viscosity and sedimentation coefficient,¹⁸ respectively.

It is pertinent to make here a remark on the assumption of $\sigma = 0$. In the case of duplex DNA, especially in the problem in which its torsion must be explicitly considered,^{10,22} σ is usually chosen to be a negative value (~ -0.3), the torsional constant being larger than the bending one. For single-helix chains such as PHIC and PBLG, the torsional constant may not be considered to be larger than the bending one, and therefore the assumption of $\sigma = 0$ seems rather reasonable.

For comparison, the light solid, dashed, and dotted curves in Figure 3.1 represent the theoretical values of T_1 , T_2 , and NOE, respectively, calculated from the equations of Woessner²³ for the equivalent, rigid prolate spheroid having the rotation axis of length $d_{\parallel}$ ($= M_w/M_L$) and the diameter $d_{\perp}$. We have set $d_{\perp} = (3/2)^{1/2}d$ so that the hydrodynamic volume of the spheroid is identical to that of the KP cylinder with $d = 19$ Å. His equations read eqs 3.1—3.3 with the spectral density given by

$$J_m(\omega) = \frac{(3\cos^2\alpha - 1)^2}{2} \frac{\tau_1}{1 + (\omega\tau_1)^2} + \frac{3\sin^2(2\alpha)}{2} \frac{\tau_2}{1 + (\omega\tau_2)^2} + \frac{3\sin^4\alpha}{2} \frac{\tau_3}{1 + (\omega\tau_3)^2} \quad (3.8)$$

where α ($= 39^\circ$ or 71°) is the angle between the internuclear vector and the rotation axis, and τ_i ($i = 1, 2, 3$) is the relaxation time defined by

$$\begin{aligned}\tau_1 &= (6D_\perp)^{-1} \\ \tau_2 &= (5D_\perp + D_\parallel)^{-1} \\ \tau_3 &= (2D_\perp + 4D_\parallel)^{-1}\end{aligned}\tag{3.9}$$

with $D_\parallel$ and $D_\perp$ the rotatory diffusion coefficients of the spheroid around the rotation and transverse axes, respectively, given by^{24,25}

$$\frac{\pi\eta_0 d_\perp^3 D_\parallel}{k_B T} = \frac{3}{2(\epsilon^2 - 1)}[\epsilon - F(\epsilon)]\tag{3.10}$$

$$\frac{\pi\eta_0 d_\perp^3 D_\perp}{k_B T} = \frac{3}{2(\epsilon^4 - 1)}[(2\epsilon^2 - 1)F(\epsilon) - \epsilon]\tag{3.11}$$

In eqs 3.10 and 3.11, k_B is the Boltzmann constant, T is the absolute temperature, and $F(\epsilon)$ is the function of the ratio $\epsilon = d_\parallel/d_\perp$ given by

$$F(\epsilon) = (\epsilon^2 - 1)^{-1/2} \cosh^{-1} \epsilon\tag{3.12}$$

for $\epsilon > 1$ (prolate spheroid). It is seen that the behavior of the present data for PHIC cannot be explained by the completely rigid spheroid as in the previous analysis of the PBLG data.¹²

Finally, we note that the values 39° and 71° adopted here for α in the calculation of the theoretical values for the generalized KP chain and the rigid spheroid are different from the values 81.3° and 118.6° used by DuPré and Wang,⁸ but that the theoretical values are not appreciably altered even if the latter values of α are used in place of the former.

3.5 Conclusion

The spin-lattice relaxation time T_1 , spin-spin relaxation time T_2 , and nuclear Overhauser enhancement NOE were determined for PHIC in *n*-hexane at 25 °C, probing the *n*-hexyl ^{13}C atoms bonded to the main-chain nitrogen atoms. It has been found that T_1 increases and T_2 decreases monotonically with increasing M_w in the range of M_w examined. Such behavior may be regarded as arising from effects of chain stiffness. It has then been shown that the generalized KP theory (a special case of the HW one) may almost quantitatively explain such behavior of the experimental data within experimental error.

3.6 Acknowledgment

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4 Chain Stiffness of Poly(diisopropyl fumarate)

4.1 Introduction

About 30 years ago, Bengough *et al.*¹ and Otsu *et al.*^{2–5} found that dialkyl fumarate (DRF) such as isopropyl fumarate can polymerize to yield poly(DRF) through radical polymerization. Because of steric hindrances to internal rotations caused by substituents on every main-chain carbon atom, poly(DRF) chains were considered to be stiffer than familiar vinyl polymer chains having substituents on every other main-chain carbon atom. After that Matsumoto and Nakagawa⁶ confirmed the conjecture by an analysis of experimental data for the mean-square radius of gyration $\langle S^2 \rangle$ and intrinsic viscosity of poly(diisopropyl fumarate) (PDiPF) in tetrahydrofuran (THF) at 30.0 °C on the basis of the Kratky–Porod (KP) wormlike chain model.⁷ The value of the stiffness parameter λ^{-1} for PDiPF has been determined to be 220 Å, which is appreciably larger than those for typical flexible polymers such as atactic polystyrene (a-PS) ($\lambda^{-1} = 20.6$ Å)^{8,9} or atactic poly(methyl methacrylate) (a-PMMA) ($\lambda^{-1} = 57.9$ Å)^{8,10}

In the above analysis, Matsumoto and Nakagawa assumed that the intramolecular excluded-volume effect was negligibly small if any, although THF is a good solvent for PDiPF. The effect may actually be ignored for a typical semiflexible polymer if its λ^{-1} is very large and its molecular weight M (chain length) is not very large, as in the case of poly(*n*-hexyl isocyanate) (PHIC) whose λ^{-1} is 840 Å.¹¹ The λ^{-1} value 220 Å determined

for PDiPF is, however, not so large as that for PHIC. Further, in a recent study of dilute solution properties of cellulose tris(phenyl carbamate) (CTC) made by Kasabo *et al.*,¹² it has been shown that the intramolecular excluded-volume effect cannot be ignored even for a polymer with $\lambda^{-1} = 210 \text{ \AA}$ in the ordinary range of M . In order to evaluate λ^{-1} accurately for PDiPF, therefore, it is desirable to make an analysis with due consideration for the excluded-volume effects. This is the purpose of the present paper.

The determination of λ^{-1} for PDiPF in a good solvent requires some comments. We could determine it from an analysis only of $\langle S^2 \rangle$ as a function of the weight-average molecular weight M_w by the use of the method proposed by Murakami *et al.*,¹¹ if experimental data were obtained for $\langle S^2 \rangle$ in an M_w range where the intramolecular excluded-volume effect might be ignored. In anticipation of results, we note that the effect on $\langle S^2 \rangle$ cannot be ignored in the whole range of M_w ($4.02 \times 10^4 \leq M_w \leq 8.59 \times 10^5$) investigated. Then we make a maiden attempt to analyze $\langle S^2 \rangle$ and the second virial coefficient A_2 simultaneously, both determined from light scattering (LS) measurements, on the basis of the quasi-two-parameter (QTP) theory^{8,13–15} of the intramolecular excluded-volume effect and also the Yamakawa theory^{8,16} of A_2 .

4.2 Experimental Section

4.2.1 Materials

Three original PDiPF samples were synthesized by radical polymerization, following the procedure of Otsu *et al.*^{4,5} and Matsumoto and Nakagawa.⁶ Polymerization was carried out in benzene by the use of dimethyl 2,2'-azobisisobutyrate as an initiator under dry nitrogen at 60 °C for *ca.* 120 h for two samples in the range of $M_w \lesssim 4 \times 10^5$ and under a high vacuum condition at 40 °C for *ca.* 240 h for the other sample having larger M_w .

It was terminated by pouring each polymerization mixture into a large amount of hexane to precipitate an original sample. Each original sample so synthesized was separated into fractions by fractional precipitation using benzene as a solvent and methanol as a precipitant. Thirteen test samples so obtained were freeze-dried from their benzene solutions after filtration through a Teflon membrane of pore size $1.0\ \mu\text{m}$.

The values of the ratio of M_w to the number-average molecular weight M_n for all the samples except the two having the smallest and largest M_w were determined from analytical gel permeation chromatography (GPC) using tetrahydrofuran as an eluent.

The solvent THF used for LS was purified by distillation after refluxing over sodium. The solvents THF and deuterated chloroform used for analytical GPC and ^{13}C NMR spectroscopy, respectively, were of reagent grade.

4.2.2 Light Scattering

LS measurements were carried out to determine M_w and A_2 for all the 13 samples and $\langle S^2 \rangle$ for 10 samples with $M_w \gtrsim 8 \times 10^4$, in THF at $30.0\ ^\circ\text{C}$. A Fica 50 light-scattering photometer was used for all the measurements with vertically polarized incident light of wavelength $\lambda_0 = 436\ \text{nm}$. For a calibration of the apparatus, the intensity of light scattered from pure benzene was measured at $25.0\ ^\circ\text{C}$ at a scattering angle of $90\ ^\circ$, where the Rayleigh ratio $R_{\text{Uu}}(90^\circ)$ of pure benzene was taken as $46.5 \times 10^{-6}\ \text{cm}^{-1}$.¹⁷ The depolarization ratio ρ_u of pure benzene at $25.0\ ^\circ\text{C}$ was determined to be 0.41 ± 0.01 . Scattered intensities were measured at six different concentrations and at scattering angles θ ranging from 30.0 to $142.5\ ^\circ$. The data obtained were treated by using the Berry square-root plot.¹⁸ For three samples with $M_w \lesssim 7 \times 10^4$, corrections for optical anisotropy were necessary to estimate the true M_w and A_2 . Therefore, the excess depolarized (Hv)

components ΔR_{HV} of the reduced scattered intensity for their solutions were measured in addition to the excess unpolarized (Uv) components ΔR_{UV} in order to make those necessary corrections. As for the other samples with $M_w \gtrsim 8 \times 10^4$, effects of optical anisotropy were negligibly small, so that the corrections were unnecessary and only ΔR_{UV} was measured for each solution.

The most concentrated solution of each sample was prepared gravimetrically and made homogeneous by continuous stirring in the dark at room temperature for 2 days. It was optically purified by filtration through a Teflon membrane of pore size 0.45 or 0.10 μm . The solutions of lower concentrations were obtained by successive dilution. The weight concentrations 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 THF. The quantities v_2 and ρ_0 were measured with a pycnometer of the Lipkin–Davison type having the volume of 3 cm^3 . The values of v_2 so determined in THF at 30.0 $^\circ\text{C}$ are 0.873 cm^3/g for all the samples independently of M_w . The value of ρ_0 of THF at 30.0 $^\circ\text{C}$ is 0.8751 g/cm^3 .

The refractive index increment $\partial n/\partial c$ was measured at wavelength of 436 nm by the use of a Shimadzu differential refractometer. The values of $\partial n/\partial c$ so determined in THF at 30.0 $^\circ\text{C}$ are 0.0623₃ cm^3/g for all the samples independently of M_w . The value of the refractive index n_0 of THF at 30.0 $^\circ\text{C}$ and at wavelength of 436 nm was determined to be 1.410₈ by the use of an Abbe refractometer (ERMA OPTICAL WORKS).

4.2.3 ^{13}C NMR

^{13}C NMR spectra for three of the 13 test samples and for the (unfractionated) three original samples were recorded on a JEOL JNM EX-400 spectrometer at 100.4 MHz. The

spectra were taken in deuterated chloroform at room temperature using an rf pulse angle of 90° with a pulse repetition time of 3 s. The relative chemical shifts δ_r of ^{13}C signals of a test sample referred to the ^{13}C signal of chloroform were measured and then converted to the chemical shifts in the tetramethylsilane scale $\delta = \delta_r + 77.00$ ppm.

Table 4.1. Experimental Results for Poly(diisopropyl fumarate)

sample	M_w	$10^{-2}\langle S^2 \rangle^{1/2}$		$10^4 A_2$		f_r
		$10^3 \delta$	(Å)	(cm ³ mol/g ²)	M_w/M_n	
PDiPF4	4.02×10^4	9.1 ₂		5.1 ₄		
PDiPF5	4.95×10^4	8.8 ₆		5.4 ₅	1.10	0.22
PDiPF6	6.31×10^4	5.2 ₀		4.9 ₃	1.05	
PDiPF8	8.00×10^4		1.1 ₉	4.2 ₅	1.10	
PDiPF9	9.17×10^4		1.3 ₄	4.0 ₇	1.07	
PDiPF15	1.53×10^5		1.7 ₉	4.0 ₀	1.08	
PDiPF18	1.83×10^5		1.9 ₈	3.5 ₁	1.08	0.22
PDiPF22	2.18×10^5		2.2 ₄	3.7 ₅	1.09	
PDiPF34	3.37×10^5		2.8 ₂	3.5 ₃	1.07	
PDiPF44	4.37×10^5		3.2 ₉	3.4 ₅	1.07	
PDiPF50	5.00×10^5		3.4 ₃	3.3 ₄	1.05	0.22
PDiPF62	6.20×10^5		3.9 ₁	2.9 ₁	1.05	
PDiPF86	8.59×10^5		4.5 ₈	2.9 ₉		

4.3 Results

As is well known, we cannot correctly evaluate M_w , $\langle S^2 \rangle$, and A_2 from the (standard) Berry square-root plot if the effects of optical anisotropy of polymer chains are not small,^{19–23} and must make an appropriate correction for the optical anisotropy. Following the standard procedure^{19–23} by the use of the reduced Hv component ΔR_{Hv} of the excess scattered intensity in addition to the Uv component ΔR_{Uv} used for the square-root plot, we may calculate M_w and the optical anisotropy factor δ from

$$\lim_{c, \theta \rightarrow 0} \frac{\Delta R_{Uv}}{2Kc} = M_{w,ap} = (1 + 7\delta)M_w \quad (4.1)$$

$$\lim_{c, \theta \rightarrow 0} \frac{\Delta R_{Hv}}{2Kc} = 3\delta M_w \quad (4.2)$$

with the values of $\Delta R_{Uv}/2Kc$ and $\Delta R_{Hv}/2Kc$ in the limit of the vanishing mass concentration c and scattering angle θ . In eqs 4.1 and 4.2, K is the optical constant and $M_{w,ap}$ is the the apparent weight-average molecular weight determined directly from the square-root plot. In the second and third columns of Table 4.1 are given the values of M_w and δ so determined for all the 13 samples. We note that the correction for the optical anisotropy is not necessary for the samples PDiPF8 through PDiPF86.

For the three samples PDiPF4, PDiPF5, and PDiPF6, the apparent mean-square radius of gyration $\langle S^2 \rangle_{ap}$ could not be evaluated directly from the square-root plot with sufficient accuracy to estimate (true) $\langle S^2 \rangle$, because the slopes of the plots are very small for these samples. As for the other 10 samples with larger M_w , for which correction for the optical anisotropy is unnecessary, $\langle S^2 \rangle$ for each sample may be equated to $\langle S^2 \rangle_{ap}$ evaluated directly from the slope of the plot. The values of $\langle S^2 \rangle$ so determined for the 10 samples are given in the fourth column of Table 4.1.

The correction for the optical anisotropy to A_2 may be given by^{19–21}

$$A_{2,\text{ap}} = A_2(1 + 7\delta)^{-2} \quad (4.3)$$

For the three samples PDiPF4, PDiPF5, and PDiPF6, the values of A_2 have been calculated from eq 4.3 with the values of δ given in the third column of Table 4.1 and also the values of the apparent second virial coefficient $A_{2,\text{ap}}$ determined directly from the square-root plot. As for the other 10 samples with larger M_w , for which the correction for the optical anisotropy is unnecessary, A_2 for each sample may be equated to $A_{2,\text{ap}}$. The values of A_2 so determined for all the samples are given in the fifth column of Table 4.1.

In the sixth column of Table 4.1 are also given the values of the ratio of M_w to M_n determined for all the samples except PDiPF4 and PDiPF86 by analytical GPC with the use of the values of M_w of all the samples given in the second column of the table. It is seen that the samples PDiPF5 through PDiPF62 are very narrow in molecular weight distribution. Although M_w/M_n could not be evaluated for the samples PDiPF4 and PDiPF86 with high accuracy because of lack of the calibration curve in the necessary range, their molecular weight distribution may be considered to be as narrow as that of the other samples.

From intensity of signals in the ^{13}C NMR spectra in a range of the chemical shift from 40.0 to 50.0 ppm, we have determined stereochemical compositions of the three samples PDiPF5, PDiPF18, and PDiPF50 and also of the (unfractionated) three original samples. Naturally, stereochemical terminology used for PDiPF composed of successive (pseudo-)asymmetric backbone carbon atoms is different from that for vinyl polymers in which every other backbone carbon atoms are asymmetric. Following the terminology proposed by Wang *et al.*,²⁴ we call a pair of adjacent backbone carbon atoms (diad) in a PDiPF chain *meso* if vicinal substituents joined to them are located on opposite sides of

a plane containing all the backbone carbon atoms of the PDiPF chain in the planar *trans* conformation, and *racemo* otherwise. According to Wang *et al.*²⁴ and Yoshioka *et al.*,²⁵ the signals in the above range of the chemical shift may then be assigned to the *meso* and *racemo* diads. The stereochemical compositions specified by fractions f_r of *racemo* diads for the test samples PDiPF5, PDiPF18, and PDiPF50 are given in the last column of Table I, which are consistent with the literature values^{24,25} 0.22-0.23. The values of f_r for the original samples are the same as those for the three test samples, indicating that all the PDiPF samples should have the same value 0.22 of f_r .

Figure 4.1 shows double-logarithmic plots of $\langle S^2 \rangle / M_w$ ($\langle S^2 \rangle$ in Å²) against M_w for PDiPF in THF at 30.0 °C. The unfilled circles represent the present experimental data. The solid and dashed curves represent the theoretical values for the KP chain with and without excluded volume, respectively, which are obtained and discussed in the next (Discussion) section. It is seen that $\langle S^2 \rangle / M_w$ increases monotonically with increasing M_w . It is also seen that the present data points form a curve convex upward, the slope of which is *ca.* 0.19 for $M_w \lesssim 2 \times 10^5$ and *ca.* 0.08 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 of PDiPF. For comparison, literature data for PDiPF in THF at 30.0 °C by Matsumoto and Nakagawa⁶ are also plotted in the figure (filled circles). Their values are scattered around ours in the range of $M_w \lesssim 3 \times 10^5$ but agree with ours within experimental error in the range of $M_w \gtrsim 3 \times 10^5$.

Figure 4.2 shows double-logarithmic plots of A_2 (in cm³mol/g²) against M_w for PDiPF in THF at 30.0 °C. All the symbols have the same meaning as those in Figure 4.1. The vertical line segment attached to each present data point (o) indicates its error bound. The solid curve represents the theoretical values for the KP chain without effects of chain

ends, which are obtained and discussed in the next (DISCUSSION) section. The present data points follow a straight line of slope *ca.* -0.13 , which is appreciably larger than *ca.* -0.2 for typical flexible polymers with large M_w in good solvents, implying that the PDiPF chain has rather large stiffness. The literature data obtained by Matsumoto and Nakagawa⁶ (filled circles) agree well with the present ones, although they are somewhat scattered in the range of $M_w \lesssim 1 \times 10^5$.

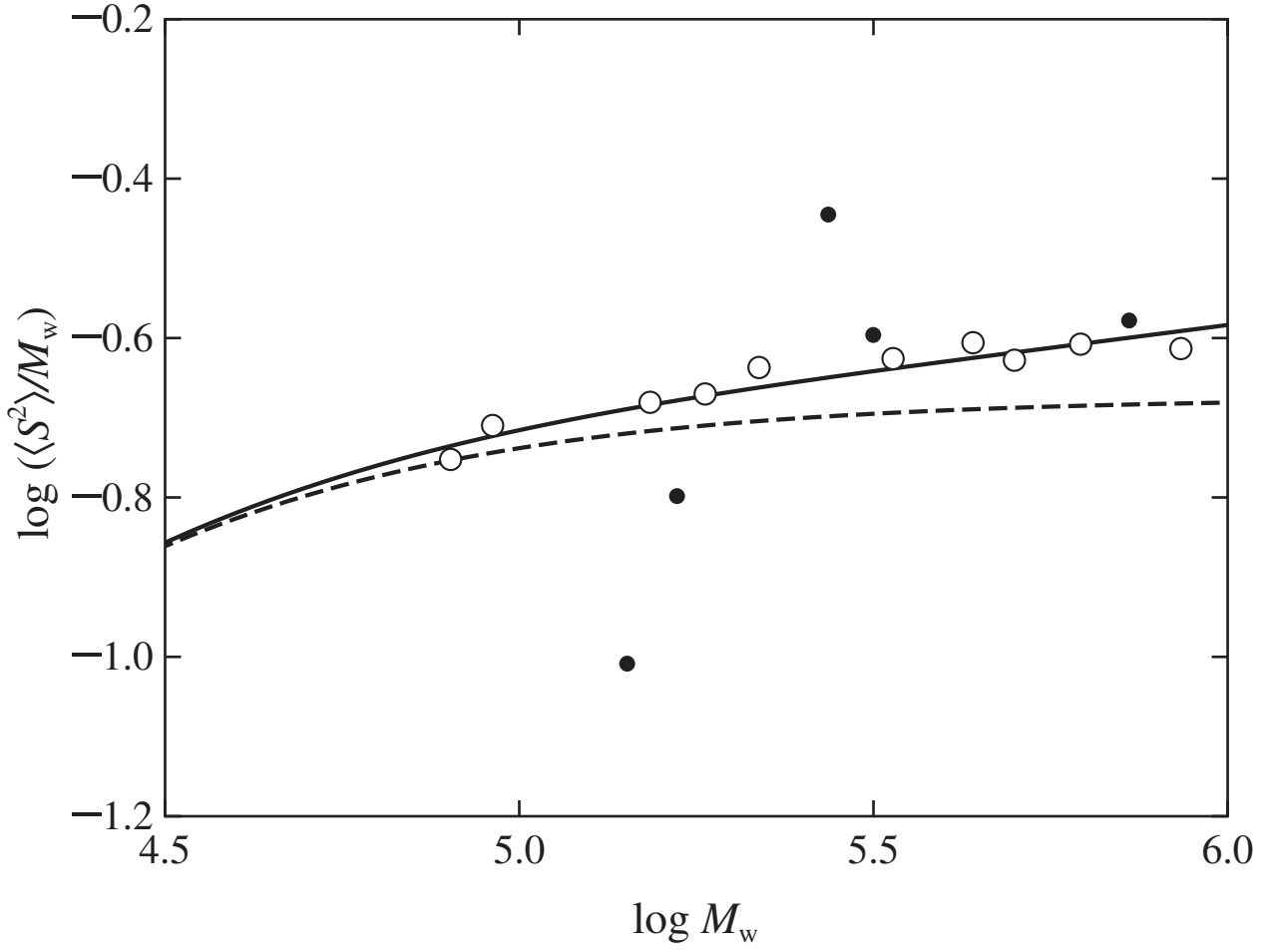


Fig. 4.1. Double-logarithmic plots of $\langle S^2 \rangle / M_w$ ($\langle S^2 \rangle$ in $\text{\AA}^2$) against M_w for PDiPF in THF at 30.0 °C: ($\circ$) present data; ($\bullet$) data by Matsumoto and Nakagawa.⁶ The solid and dashed curves represent the best-fit KP theory values for the perturbed and unperturbed chains, respectively.

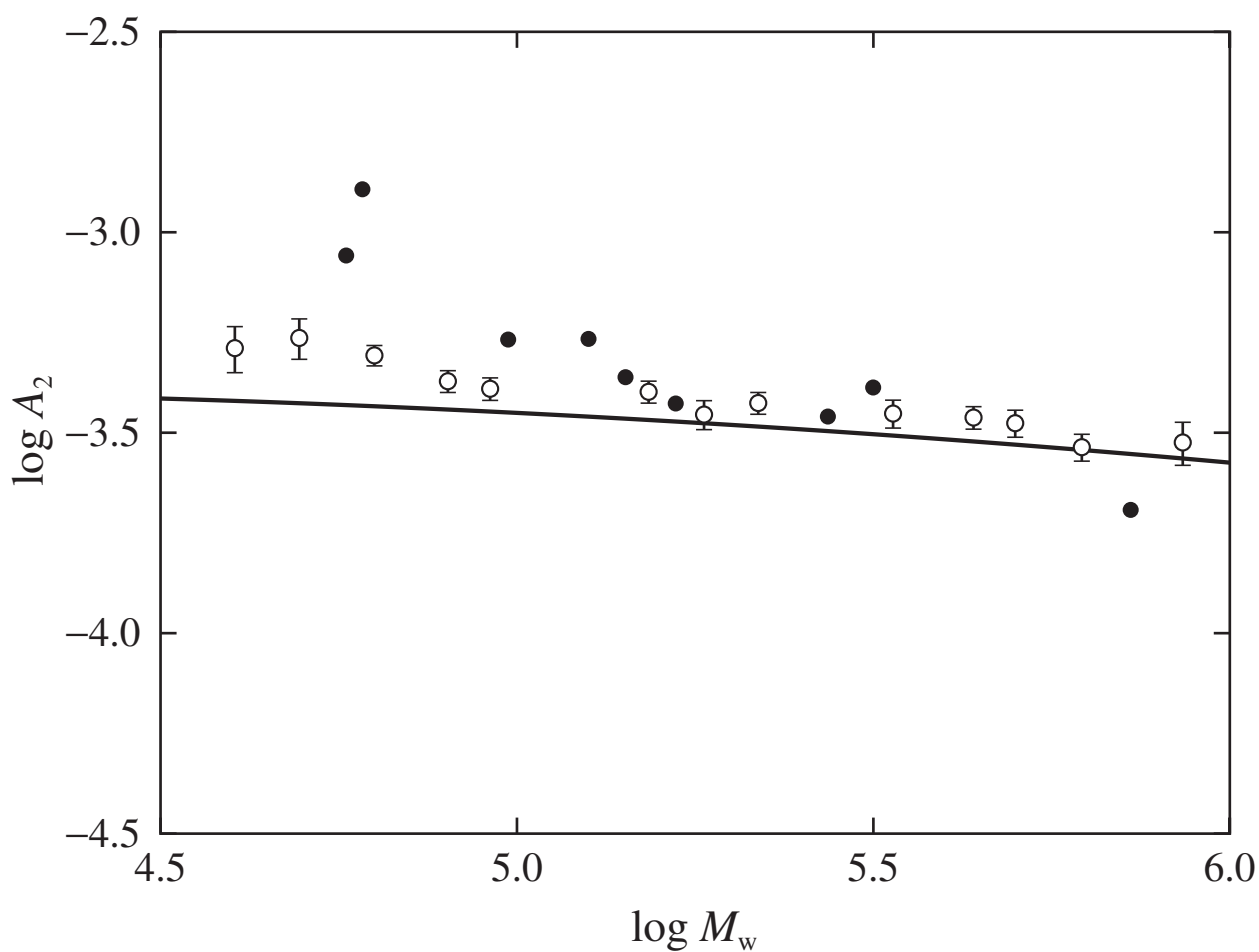


Fig. 4.2. Double-logarithmic plots of A_2 (in $\text{cm}^3\text{mol/g}^2$) against M_w for PDiPF in THF at 30.0 °C. All the symbols have the same meaning as those in Figure 4.1. The vertical line segments attached to the present data points ($\circ$) indicate the error bounds. The solid curve represents the theoretical values for the KP chain without the effects of chain ends (see the text).

4.4 Discussion

Now we proceed to analyze the present data for $\langle S^2 \rangle$ and A_2 for PDiPF given in the last section on the basis of the KP theory of the unperturbed mean-square radius of gyration^{8,26} $\langle S^2 \rangle_0$ along with the QTP scheme or the Yamakawa–Stockmayer–Shimada theory^{8,13–15} of the intramolecular excluded-volume effect and also of the Yamakawa theory^{8,16} of A_2 .

For the KP chain of total contour length L , $\langle S^2 \rangle$ may be written in the form,

$$\langle S^2 \rangle = \langle S^2 \rangle_0 \alpha_S^2 \quad (4.4)$$

where $\langle S^2 \rangle_0$ is given by^{8,26}

$$\langle S^2 \rangle_0 = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1}{8\lambda^4 L^2} (1 - e^{-2\lambda L}) \quad (4.5)$$

and the gyration-radius expansion factor α_S may be given by the Domb–Barrett equation,²⁷

$$\alpha_S^2 = [1 + 10\tilde{z} + (\frac{70\pi}{9} + \frac{10}{3})\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \quad (4.6)$$

In the QTP scheme, the (conventional) excluded-volume parameter z defined in the two-parameter (TP) scheme on the basis of the Gaussian chain model is replaced by the intramolecular scaled excluded-volume parameter $\tilde{z}$ defined by

$$\tilde{z} = \frac{3}{4} K(\lambda L) z \quad (4.7)$$

where the coefficient $K(\lambda L)$ as a function of the reduced contour length λL is given by

$$\begin{aligned} K(\lambda L) &= \frac{4}{3} - 2.711(\lambda L)^{-1/2} + \frac{7}{6}(\lambda L)^{-1} && \text{for } \lambda L > 6 \\ &= (\lambda L)^{-1/2} \exp[-6.611(\lambda L)^{-1} + 0.9198 + 0.03516\lambda L] && \text{for } \lambda L \leq 6 \end{aligned} \quad (4.8)$$

The quantity $K(\lambda L)$ represents the effects of chain stiffness on the intramolecular excluded-volume effect or on the intramolecular contact probability and increases monotonically

from 0 to $4/3$ as λL is increased from 0 to ∞ . Then, in the limit of $\lambda L \rightarrow \infty$ (random-coil limit) the QTP scheme reduces to the TP one, *i.e.*, $\tilde{z} = z$, while in the limit of $\lambda L \rightarrow 0$ (rod limit) $\tilde{z}$ vanishes irrespective of the value of z .

The QTP scheme is formulated on the basis of a model composed of $n+1$ beads of the binary-cluster integral β arrayed with spacing a between them along the KP or helical wormlike (HW) chain⁸ of total contour length L , so that $L = na$. The parameter z may then be written in terms of β , a , and λL as

$$z = (3/2\pi)^{3/2}(\lambda B)(\lambda L)^{1/2} \quad (4.9)$$

where B is the excluded-volume strength defined by

$$B = \beta/a^2 c_\infty^{3/2} \quad (4.10)$$

with

$$c_\infty = \lim_{\lambda L \rightarrow \infty} (6\lambda \langle S^2 \rangle_0 / L) \quad (4.11)$$

As seen from eq 4.11 with eq 4.5, c_∞ is equal to unity for the KP chain.

In the Yamakawa theory^{8,16} of A_2 , effects of chain stiffness and chain ends are taken into account, and A_2 may then be written in the form,

$$A_2 = A_2^{(\text{HW})} + A_2^{(\text{E})} \quad (4.12)$$

where $A_2^{(\text{HW})}$ is a part of A_2 without the effects of chain ends and $A_2^{(\text{E})}$ represents contribution of the effects of chain ends to A_2 . The superscript (HW) attached to the first term indicates that the theory is formulated on the basis of the HW chain, and the following theoretical expression for $A_2^{(\text{HW})}$ reduces to that for the KP chain if c_∞ is set equal to unity.

For the KP (or HW) chain of total contour length L with the excluded-volume strength B , $A_2^{(\text{HW})}$ may be given by

$$A_2^{(\text{HW})} = (N_A c_\infty^{3/2} L^2 B / 2M^2) h(\hat{z}) \quad (4.13)$$

where N_A is the Avogadro constant, M is the polymer molecular weight, and h is given by

$$h(\hat{z}) = (1 + 7.74\hat{z} + 52.3\hat{z}^{27/10})^{-10/27} \quad (4.14)$$

with

$$\hat{z} = \tilde{z} / \alpha_S^3 \quad (4.15)$$

In eq 4.15, $\tilde{z}$ is the intermolecular scaled excluded-volume parameter defined by

$$\tilde{z} = \left[\frac{Q(\lambda L)}{2.865} \right] z \quad (4.16)$$

The coefficient $Q(\lambda L)$ in eq 4.16 as a function of λL represents the effects of chain stiffness on the intermolecular excluded-volume effect and is given in a very good approximation for $\lambda L \gtrsim 1$ by^{8,16}

$$\begin{aligned} Q(\lambda L) = & -\frac{128\sqrt{2}}{15} - 2.531(\lambda L)^{-1/2} - 2.586(\lambda L)^{-1} + 1.985(\lambda L)^{-3/2} \\ & - 1.984(\lambda L)^{-2} - 0.9292(\lambda L)^{-5/2} + 0.1223(\lambda L)^{-3} + \frac{8}{5}x^{5/2} \\ & + \frac{2}{3}x^{3/2}[8 + \frac{1}{6}(\lambda L)^{-1}] + x^{1/2}[8 - 13.53(\lambda L)^{-1} + 0.2804(\lambda L)^{-2}] \\ & - x^{-1/2}(\lambda L)^{-1}[0.3333 - 5.724(\lambda L)^{-1} + 0.7974(\lambda L)^{-2}] \\ & - x^{-3/2}(\lambda L)^{-2}[0.3398 - 0.7146(\lambda L)^{-1}] \end{aligned} \quad (4.17)$$

with

$$x = 1 + 0.961(\lambda L)^{-1} \quad (4.18)$$

It is seen from eq 4.16 with eqs 4.17 and 4.18 that $\tilde{z}$ becomes identical with z in the limit of $\lambda L \rightarrow \infty$ as in the case of $\tilde{z}$ and therefore $A_2^{(\text{HW})}$ reduces to A_2 given by the TP theory.

As for the second term $A_2^{(\text{E})}$ in eq 4.12, we omit its detailed expression^{8,16} since it is not necessary for the present analysis of A_2 . We only note that $A_2^{(\text{E})}$ rapidly decreases to 0 with increasing M and may be neglected for $M \gtrsim 10^5$ for all the polymer-solvent systems examined so far.^{8,12,28–31}

In order to compare the above-mentioned KP theoretical values of $\langle S^2 \rangle$ and A_2 as functions of L with the experimental ones as functions of M , L is related to M by

$$L = M/M_L \quad (4.19)$$

where M_L is the shift factor as defined as the molecular weight per unit contour length of the KP (or HW) chain. We may then determine the three parameters λ^{-1} , M_L , and λB by the curve fitting to the experimental data for $\langle S^2 \rangle$ or A_2 . As already mentioned, we cannot determine them only from the data for $\langle S^2 \rangle$, so that we attempt to carry out the curve fitting to both the data for $\langle S^2 \rangle$ and A_2 simultaneously.

In Figures 4.1 and 4.2, the solid curves represent the best-fit KP theory values of $\langle S^2 \rangle$ and those of A_2 without consideration of the effects of chain ends ($A_2^{(\text{E})} = 0$), respectively, where the former values have been calculated from eq 4.4 with eqs 4.5—4.9 and 4.19 and the latter from eq 4.12 with eqs 4.6—4.9 and 4.13—4.19, with $\lambda^{-1} = 113 \text{ \AA}$, $M_L = 89 \text{ \AA}^{-1}$, and $\lambda B = 0.097$. We note that relative errors in those parameter values are 8, 5, and 10%, respectively, at most. It is seen from the figures that the theoretical values of $\langle S^2 \rangle$ quantitatively reproduce the experimental ones over the whole range of M_w examined and the theoretical values of A_2 ($= A_2^{(\text{HW})}$) may rather well reproduce the experimental ones within experimental error in the range of $M_w \gtrsim 10^5$, where the effects of chain ends may be neglected. In Figure 4.2, the present data points deviate upward progressively from

the theoretical curve with decreasing M_w for $M_w \lesssim 10^5$. It may be regarded as arising from the effects of chain ends ($A_2^{(E)} = 0$). From an analysis of the difference between the observed A_2 and the theoretical $A_2^{(HW)}$, we may obtain information about the excess (effective) binary-cluster integrals of terminal beads.^{8,16} Such an analysis is beyond the scope of the present work, and we do not pursue further it.

In Figure 4.1 are also shown the theoretical values of $\langle S^2 \rangle_0$ (dashed curve) calculated from eq 4.5 with the values of λ^{-1} and M_L determined above. It is seen that the present data points deviate upward progressively from the theoretical $\langle S^2 \rangle_0$ with increasing M_w due to the intramolecular excluded-volume effect.

Finally, it is interesting to analyze the present data for $\langle S^2 \rangle$ shown in Figure 4.1 on the basis of the KP chain without excluded volume, as considered by Matsumoto and Nakagawa.⁶ We have obtained $\lambda^{-1} = 154 \text{ \AA}$ and $M_L = 103 \text{ \AA}^{-1}$ from the curve fitting, although the best-fit unperturbed KP values of $\langle S^2 \rangle_0$ have been omitted in Figure 4.1, for simplicity. Note that the KP chain without excluded volume cannot explain the experimental data for A_2 , needless to say. The value $89 \text{ \AA}^{-1}$ of M_L determined from the present analysis with consideration of the intra- and intermolecular excluded-volume effects is remarkably smaller than the above value $103 \text{ \AA}^{-1}$ and also the literature value $134 \text{ \AA}^{-1}$ by Matsumoto and Nakagawa, both without consideration of the intramolecular excluded-volume effects.

For the PDiPF chain (with $f_r = 0$) in the planar *trans* conformation (with a bond angle of 109°), which is schematically depicted in Figure 4.3(a), M_L may be evaluated to be $80.3 \text{ \AA}^{-1}$. A polymer chain in a helical conformation in principle has an M_L value larger than that for the chain in the planar *trans* conformation, and therefore the (true) M_L value for the PDiPF chain seems larger than $80.3 \text{ \AA}^{-1}$. For trial calculations of

M_L for the PDiPF chain (with $f_r = 0$) in helical conformations, we consider two chains having fixed internal rotation angles $\phi = 30^\circ$ and 60° , which are schematically depicted in Figures 4.3(b) and 4.3(c), respectively. Note that the chain with $\phi = 0^\circ$ is in the planar *trans* conformation. The values of M_L are evaluated to be 81.3 and 84.7 $\text{\AA}^{-1}$ for $\phi = 30^\circ$ and 60° , respectively, which are not very larger than 80.3 $\text{\AA}^{-1}$. Considering this fact, the value 89 $\text{\AA}^{-1}$ of M_L seems reasonable, and analyses of data for PDiPF in THF at 30.0 $^\circ\text{C}$ without consideration of the excluded-volume effects lead to overestimation of the value of M_L and also that of λ^{-1} .

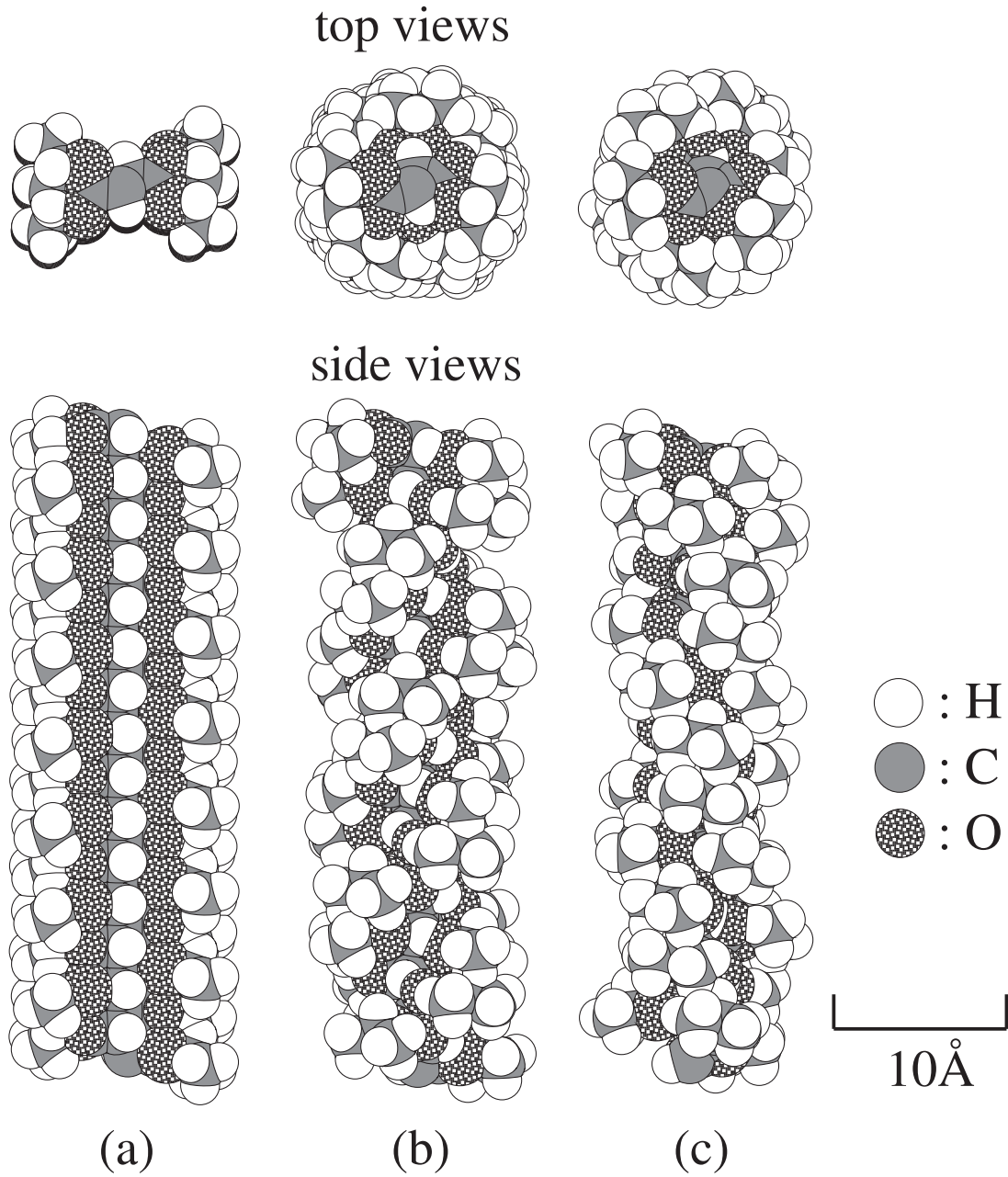


Fig. 4.3. Schematic drawing of chain conformations of PDiPF with $f_r = 0$, where all atoms are depicted by the spheres having the van der Walls radii: (a) planar *trans* conformation with $\phi = 0$; (b) helical conformation with $\phi = 30^\circ$; (c) helical conformation with $\phi = 60^\circ$.

4.5 Concluding Remarks

We have carried out LS measurements to determine $\langle S^2 \rangle$ and A_2 for PDiPF in THF at 30.0 °C and then determined its KP model parameters λ^{-1} and M_L by analyzing the data so obtained on the basis of the corresponding KP (or HW) theories with consideration of the intra- and intermolecular excluded-volume effects. The value 113 Å of λ^{-1} determined in the present analysis is smaller than 220 Å obtained by Matsumoto and Nakagawa⁶ from an analysis of $[\eta]$ without consideration of the intramolecular excluded-volume effect. However, the qualitative characteristic of PDiPF proposed by them is still valid, *i.e.*, its chain stiffness is larger than that of typical flexible polymers such as a-PS and a-PMMA but not so large as that of typical semiflexible polymers such as PHIC. The value 89 Å⁻¹ of M_L is also smaller than their value 134 Å⁻¹, the former value being consistent with that estimated on the basis of the chain conformations of PDiPF. It may then be said that analyses of data for PDiPF in THF at 30.0 °C without consideration of the excluded-volume effects lead to overestimation of both the values of λ^{-1} and M_L .

In order to confirm the result of the present analysis of $\langle S^2 \rangle$ and A_2 , it is desirable to make a study of steady-state transport coefficients such as $[\eta]$ and the translational diffusion coefficient of PDiPF. Thus we proceed to make such a study in a forthcoming paper.

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5 Transport Coefficients of Poly(diisopropyl fumarate)

5.1 Introduction

In Chap. 4, 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).¹ 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 Å, 89 Å^{–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 Å^{–1} so determined is consistent with the value 80.3–84.7 Å^{–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) ($\lambda^{-1} = 840$ Å),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 Å).^{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.

5.2 Experimental Section

5.2.1 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 5.1, 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.

5.2.2 Viscosity

Viscosity measurements were carried out for all the samples listed in Table 5.1 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' .

5.2.3 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 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 μm . 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

$$(1/2) \ln[g^{(2)}(t) - 1] = \text{const} - At \quad (5.1)$$

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 $D^{(\text{LS})}(c)$ at finite c from

$$D^{(\text{LS})}(c) = \lim_{k \rightarrow 0} A/k^2 \quad (5.2)$$

where k is the scattering vector and is given by

$$k = (4\pi/\tilde{\lambda}) \sin(\theta/2) \quad (5.3)$$

with $\tilde{\lambda}$ the wavelength of the incident light in the solvent. At very small c , $D^{(\text{LS})}(c)$ may be expanded as

$$D^{(\text{LS})}(c) = D^{(\text{LS})}(0)(1 + k_{\text{D}}^{(\text{LS})}c + \cdots) \quad (5.4)$$

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

$$D = D^{(\text{LS})}(0) \quad (5.5)$$

The values of the refractive index 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).

Table 5.1. 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	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	-	-

5.3 Results

5.3.1 Intrinsic Viscosity $[\eta]$

Intrinsic viscosity data for all the PDiPF samples in THF at 30.0 °C are summarized in Table 5.2 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 5.1 shows double-logarithmic plots of $[\eta]$ against M_w for PDiPF in THF at 30.0 °C. The unfilled circles represent the present experimental data. The present data points are seen to form a curve convex upward, the slope of which is *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 the effect of chain stiffness of PDiPF, as in the cases of $\langle S^2 \rangle$ and A_2 .¹ In the figure, the solid and dashed curves represent the perturbed and unperturbed KP theoretical values, which are discussed in the next (DISCUSSION) section.

The figure also includes literature data for the same system reported by Matsumoto and Nakagawa¹³ (filled circles). Their data agree with ours within experimental error in the range of $M_w \gtrsim 2 \times 10^5$. On the other hand, however, the former deviate downward from the latter for $M_w \lesssim 2 \times 10^5$. The reason for this deviation is not clear.

Table 5.2. 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

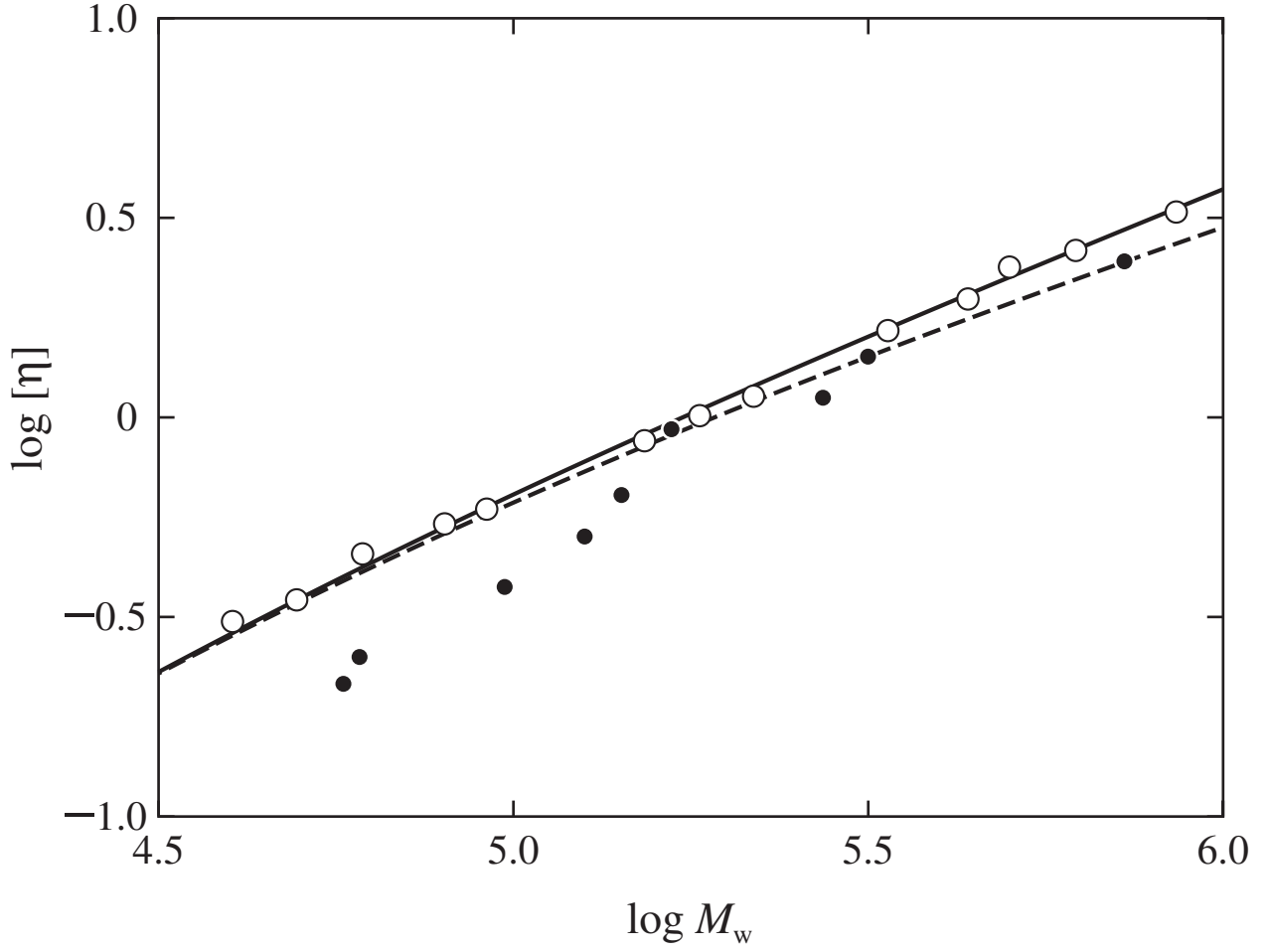


Fig. 5.1. Double-logarithmic plots of $[\eta]$ (in dL/g) against M_w for PDiPF in THF at 30.0 °C: ($\circ$) present data; ($\bullet$) data by Matsumoto and Nakagawa.¹³ The solid and dashed curves represent the best-fit KP theoretical values for the perturbed and unperturbed chains, respectively.

5.3.2 Translational Diffusion Coefficient D and Hydrodynamic Radius R_H

The data points $(1/2) \ln[g^{(2)} - 1]$ 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 in eq 5.1 could be unambiguously determined. Further, in the range of k (or θ) where the DLS measurements were carried out, the ratio 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 5.2 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 5.4 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 5.3. In the last column of the Table are also given the values of the hydrodynamic radius R_H calculated from the defining equation

$$R_H = k_B T / 6\pi\eta_0 D \quad (5.6)$$

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 5.3, R_H (in Å) calculated from eq 5.6 with the present experimental values of D given in the second column of Table 5.3 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.

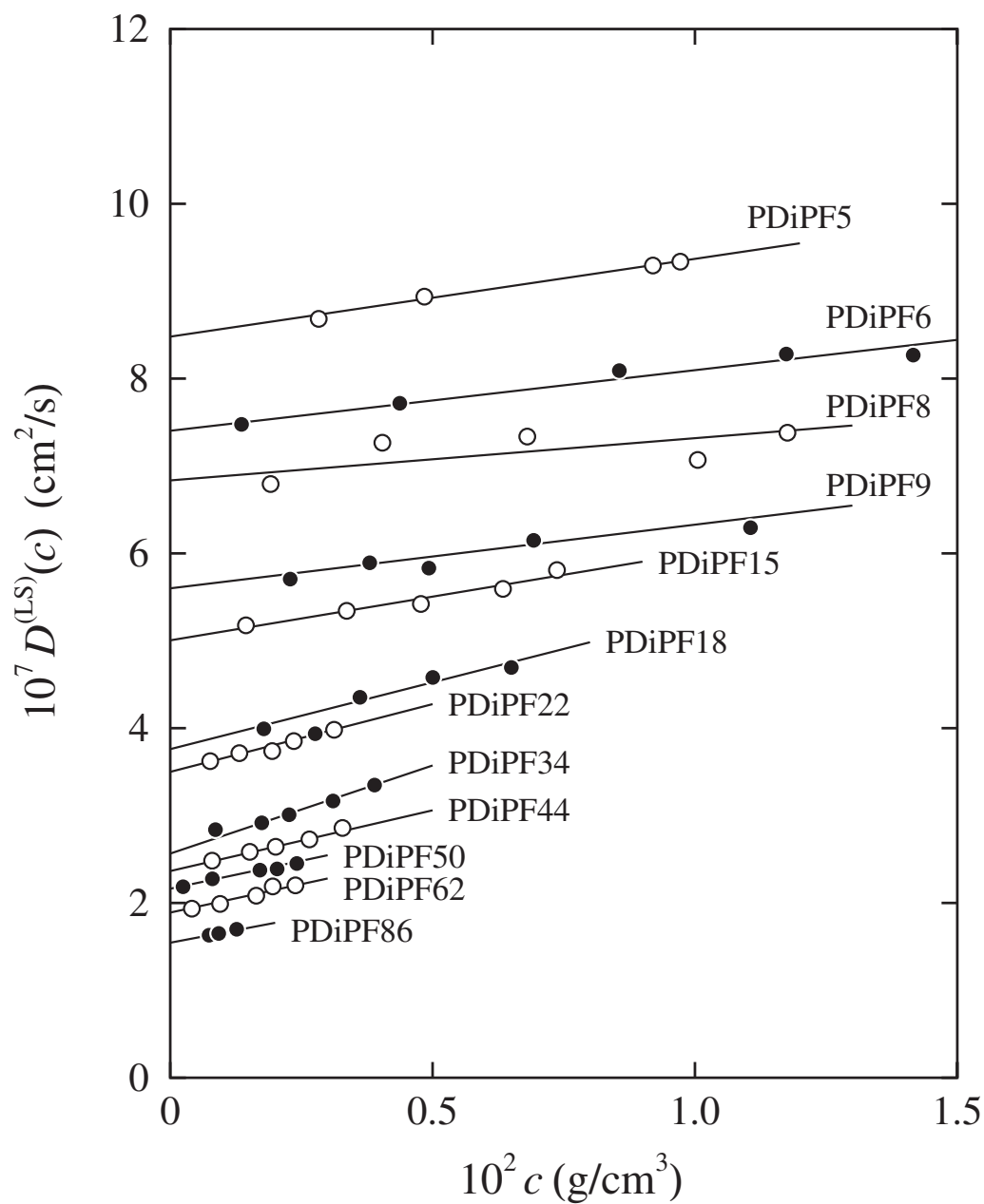


Fig. 5.2. Plots of $D^{(LS)}(c)$ against c for the indicated PDiPF samples in THF at 30.0 °C.

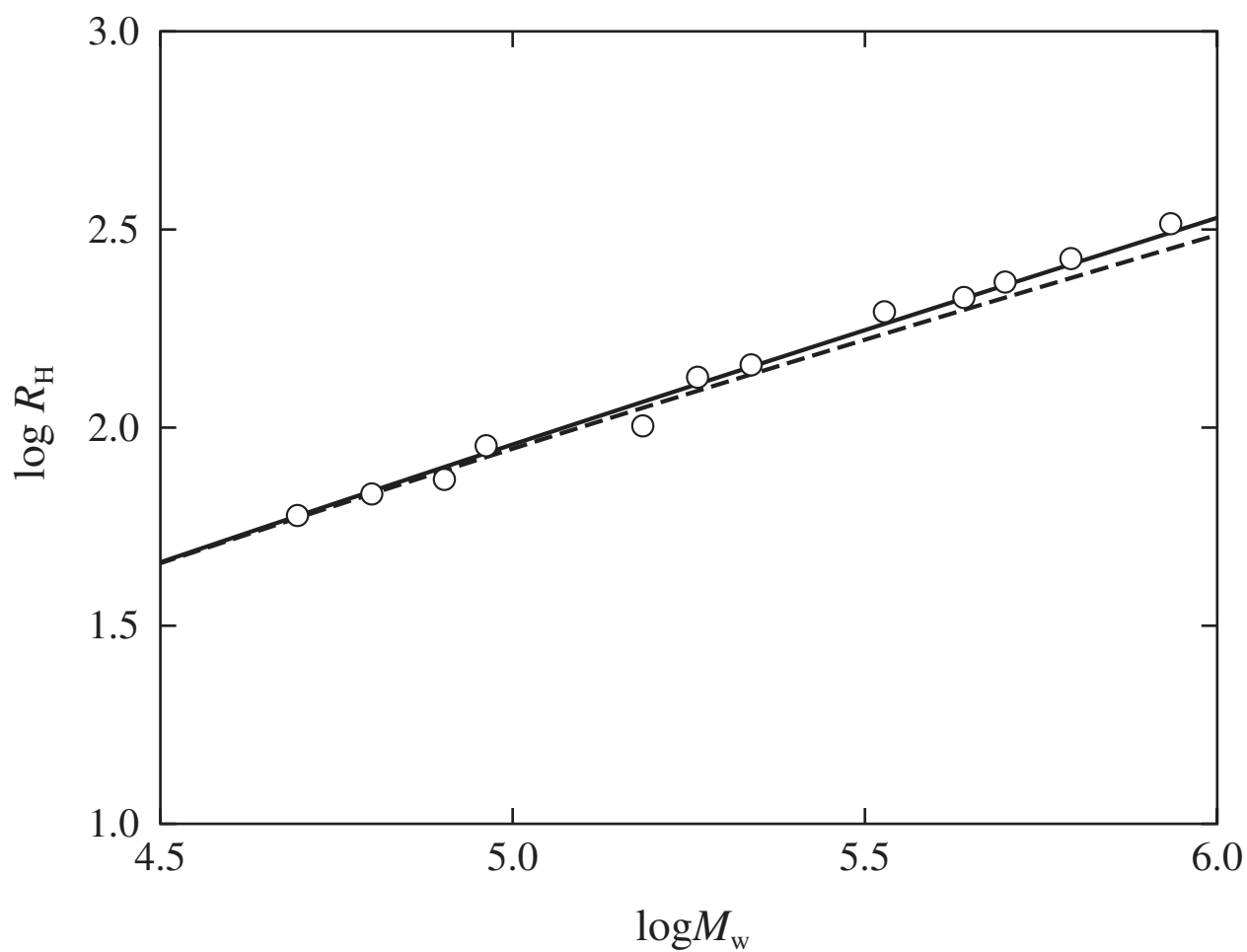


Fig. 5.3. Double-logarithmic plots of R_H (in Å) against M_w for PDiPF in THF at 30.0 °C. The solid and dashed curves represent the best-fit KP theoretical values for the perturbed and unperturbed chains, respectively.

Table 5.3. 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

5.4 Discussion

5.4.1 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,

$$[\eta]_0 = \frac{1}{\lambda^2 M_L} f_{\eta, \text{KP}}(\lambda L; \lambda d) \quad (5.7)$$

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

$$f_{\eta, \text{KP}}(\lambda L) = \lambda^{-1} M_L [\bar{\eta}]_{\text{KP}} \quad (5.8)$$

with $[\eta]_{\text{KP}}$ 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 $[\eta]_{\text{KP}}$ 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 $\lambda L \rightarrow \infty$, $f_{\eta, \text{KP}}$ satisfies the following asymptotic relation,

$$\lim_{\lambda L \rightarrow \infty} \frac{f_{\eta, \text{KP}}(\lambda L)}{(\lambda L)^{1/2}} = \Phi_\infty \quad (5.9)$$

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 $\langle S^2 \rangle^{3/2}$,

$$\Phi = V_H / \langle S^2 \rangle^{3/2} \quad (5.10)$$

with V_H defined from $[\eta]$ as

$$V_H = 6^{-3/2} M [\eta] \quad (5.11)$$

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

$$L = M / M_L \quad (5.12)$$

For the perturbed KP cylinder model, $[\eta]$ may conventionally be expressed as a product of $[\eta]_0$ given by eq 5.7 and the cube of the viscosity-radius expansion factor α_η ,

$$[\eta] = [\eta]_0 \alpha_\eta^3 \quad (5.13)$$

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

$$\tilde{z} = \frac{3}{4} K(\lambda L) z \quad (5.14)$$

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

$$z = (3/2\pi)^{3/2} (\lambda B) (\lambda L)^{1/2} \quad (5.15)$$

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 5.14, the coefficient $K(L)$ as a function of reduced L is given by

$$\begin{aligned} K(L) &= \frac{4}{3} - 2.711L^{-1/2} + \frac{7}{6}L^{-1} && \text{for } L > 6 \\ &= L^{-1/2} \exp(-6.611L^{-1} + 0.9198 + 0.03516L) && \text{for } L \leq 6 \end{aligned} \quad (5.16)$$

It is seen from eq 5.14 with eq 5.16 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 the Barrett equation²⁷ for α_η ,

$$\alpha_\eta = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.1} \quad (5.17)$$

From eq 5.13 with eqs 5.7, 5.12, and eq 5.14—eq 5.17, 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 $113 \text{ \AA}$ 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 5.1, the solid curve associated with the present data points ($\circ$) represents the best-fit perturbed KP theory values calculated from eq 5.13 with eqs 5.7, eq 5.12, and eq 5.14—eq 5.17 with the values $92 \text{ \AA}^{-1}$ and $15 \text{ \AA}$ of M_L and d , respectively. Although the M_L value $92 \text{ \AA}^{-1}$ so determined is slightly (*ca.* 3%) larger than $89 \text{ \AA}^{-1}$ 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 5.1, the dashed curve represents the unperturbed KP theory values calculated from eq 5.7 with eq 5.12 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

5.4.2 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}

$$D_0 = \left(\frac{k_B T}{3\pi\eta_0 L} \right) f_{D,KP}(\lambda L; \lambda d) \quad (5.18)$$

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

$$R_{H,0} = \frac{L}{2f_{D,KP}(\lambda L; \lambda d)} \quad (5.19)$$

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

$$\lim_{\lambda L \rightarrow \infty} \frac{f_{D,KP}(\lambda L; \lambda d)}{(\lambda L)^{1/2}} = \frac{\sqrt{6}}{2} \rho_\infty \quad (5.20)$$

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 $\langle S^2 \rangle^{1/2}$,

$$\rho^{-1} = R_H / \langle S^2 \rangle^{1/2} \quad (5.21)$$

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 ,

$$R_H = R_{H,0} \alpha_H \quad (5.22)$$

In the framework of the 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}

$$\alpha_H = \alpha_H^{(0)} h_H \quad (5.23)$$

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

$$\alpha_H^{(0)} = (1 + 5.93\tilde{z} + 3.59\tilde{z}^2)^{0.1} \quad (5.24)$$

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

$$h_H = \frac{0.88}{1 - 0.12\alpha_S^{-0.43}} \quad (5.25)$$

In eq 5.25, we use the Domb-Barrett equation³² for the gyration-radius expansion factor α_S ,

$$\begin{aligned} \alpha_S^2 = & [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} \\ & \times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \end{aligned} \quad (5.26)$$

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 5.22 with eqs 5.12, eq 5.19, and eq 5.23—eq 5.26, 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 $113 \text{ \AA}$ and 0.097 of λ^{-1} and λB , respectively, and determine M_L and d from a comparison of theory with experiment. In Figure 5.3, the solid curve represents the best-fit perturbed KP theory values calculated from eq 5.22 with eqs 5.12, eq 5.19, and eq 5.23—eq 5.26 with the values $81 \text{ \AA}^{-1}$ and $16 \text{ \AA}$ 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 $81 \text{ \AA}^{-1}$ so determined from D is somewhat smaller than $92 \text{ \AA}^{-1}$ determined above from $[\eta]$ and $89 \text{ \AA}^{-1}$ 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 5.3, the dashed curve represents the unperturbed KP theory values calculated from eq 5.19 with eq 5.12 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 5.1 and also of $\langle S^2 \rangle$.¹

5.4.3 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 5.4 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 5.2) and R_H (Table 5.3) along with the previous results for $\langle S^2 \rangle$ (Table I of ref ¹).

Figure 5.4 shows double-logarithmic plots of Φ (in mol⁻¹) and ρ^{-1} against M_w for PDiPF in THF at 30.0 °C (○) 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 (□).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 ($\lambda^{-1} = 113$ Å) is intermediate between those for a-PS ($\lambda^{-1} = 20.6$ Å) and PHIC ($\lambda^{-1} = 840$ Å).

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 5.1 and 5.3) that Φ and ρ^{-1} become appreciably smaller than respective unperturbed values. Further, the effect is negligibly small, if any, for PHIC in *n*-hexane at 25.0 °C in the range of M_w displayed in Figure 5.4. 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 5.4, the solid curves associated with the data points for PDiPF represent the perturbed KP theoretical values for Φ and ρ^{-1} calculated from eq 5.10 with eq 5.11

and from eq 5.21, 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 Fig. 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.

Table 5.4. Values of Φ and ρ^{-1} (ρ) for Poly(diisopropyl fumarate) in THF at 30.0 °C

sample	$10^{-23}\Phi, \text{mol}^{-1}$	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)

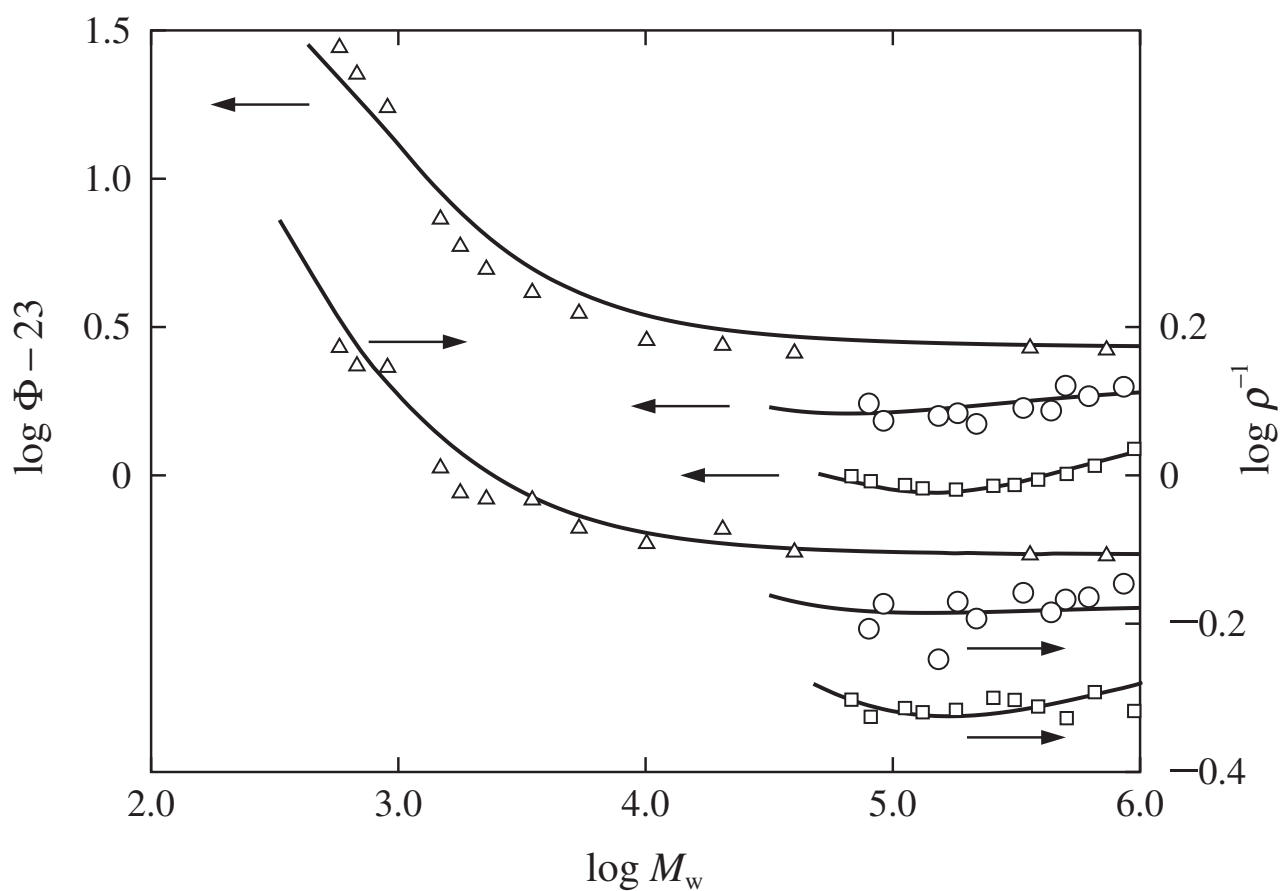


Fig. 5.4. Double-logarithmic plots of Φ (in mol^{-1}) and ρ^{-1} against M_w : ($\circ$) present data for PDiPF in THF at 30.0 °C; ($\triangle$) previous data for a-PS with $f_r = 0.59$ in cyclohexane at 34.5 °C;^{14–16,33–35} ($\square$) literature data for PHIC in *n*-hexane at 25.0 °C.⁹ The solid curve represents the HW or KP theoretical values for each polymer (see the text).

5.4.4 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.

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LIST OF PUBLICATIONS

CHAPTER 2

- 1 Mean-Square Optical Anisotropy of Poly(*n*-hexyl isocyanate) in Dilute Solution, M. Nakatsuji, Y. Ogata, M. Osa, T. Yoshizaki, and H. Yamakawa, *Macromolecules*, **34**, 8512-8517 (2001).

CHAPTER 3

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CHAPTER 4

- 3 Mean-Square Radius of Gyration and Second Virial Coefficient of Poly(diisopropyl fumarate) in Dilute Solution, M. Nakatsuji, M. Hyakutake, M. Osa, and T. Yoshizaki, *Polym. J.*, **40**, 566-571 (2008).

CHAPTER 5

- 4 Transport Coefficients of Poly(diisopropyl fumarate) in Dilute Solution, M. Nakatsuji, K. Soutoku, M. Osa, and T. Yoshizaki, *Polym. J.*, **41**, 83-89 (2009).

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