Stiff-Chain Behavior of Poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) in Dilute Solution

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ABSTRACT: For narrow-distribution fractions of poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) (PIDP) with weight-average molecular weights M_w from 3.7×10^3 to 2.4×10^6 g mol⁻¹, z -average mean-square radii of gyration $\langle S^2 \rangle_z$ and intrinsic viscosities $[\eta]$ in trifluoroethanol (TFE) and *m*-cresol were measured at 25°C. From the $[\eta]$ data for $M_w < 10^5$ g mol⁻¹, which exhibited the expected stiff-chain behavior, the persistence lengths of PIDP in *m*-cresol and TFE were determined to be 4.9 ± 0.3 nm and 3.1 ± 0.2 nm, respectively, using Yamakawa-Fujii's theory for unperturbed wormlike cylinders and assuming the M_L and d values estimated previously by Motowoka *et al.* for poly(phthaloyl-*trans*-2,5-dimethylpiperazine) and poly(terephthaloyl-*trans*-2,5-dimethylpiperazine) in various solvents including *m*-cresol and TFE. Here M_L is the molar mass per unit contour length and d is the diameter of the cylinder. Double-logarithmic plots of $\langle S^2 \rangle_z^{1/2}$ and $[\eta]$ against M_w in the region of higher M_w exhibited features usually observed with flexible polymers in good solvents. This result can be explained by the fact that, though semiflexible, the PIDP chain in solution suffers excluded-volume effects if its length exceeds a certain value. In terms of the number of Kuhn's statistical segments, this critical chain length for PIDP is about 50 in TFE and 150 in *m*-cresol.

KEY WORDS Poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) / Wormlike Chain / Persistence Length / Dilute Solution / Light Scattering / Mean-Square Radius of Gyration / Intrinsic Viscosity / Excluded-Volume Effect / Expansion Factor /

Motowoka *et al.*^{1,2} concluded from measurements of dilute solution properties that poly(phthaloyl-*trans*-2,5-dimethylpiperazine) (PPDP) and poly(terephthaloyl-*trans*-2,5-dimethylpiperazine) (PTDP), two of the three polyamide isomers shown in Figure 1, behave like an unperturbed wormlike chain in solution and that PTDP is 1.5 times as stiff as PPDP if the stiffness is expressed in terms of the persistence length. To estimate the persistence length of the remaining one of the three isomers, *i.e.*, the *meta*-linked poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) (PIDP), we measured z -average mean-square radii of gyration $\langle S^2 \rangle_z$ and intrinsic viscosities $[\eta]$ of narrow-distribution samples of this polymer over a range of weight-average molecular weight M_w from 3.7×10^3 to 2.4×10^6 g mol⁻¹. This maximum M_w was several times as large as any one of those treated in Motowoka's studies on PPDP¹ and PTDP.² Except

at relatively low M_w , the data exhibited features usually observed for long flexible polymers in good solvents. In this paper, we report these experimental results and consider their significance in the study of semiflexible polymers in dilute solution.

EXPERIMENTAL

Samples

High-molecular-weight samples of PIDP were prepared by interfacial polycondensation of isophthaloyl chloride and *trans*-2,5-dimethylpiperazine, according to the method of Katz.³ The isophthaloyl chloride was recrystallized from hexane; and the *trans*-2,5-dimethylpiperazine was purified by the procedure described previously.¹ Low-molecular-weight samples were obtained by the low-temperature solution polycondensation method of Morgan and Kwolek.⁴ Ten samples so prepared

Figure 1. Repeat units of three polyamide isomers PIDP, PTDP, and PPDP.

were thoroughly washed with water and acetone. Their intrinsic viscosities in *m*-cresol at 25°C as well as their yields are presented in Table I.

Fractionation

These ten samples were fractionated with dichloromethane containing 10 vol% ethanol as a solvent and hexane as a precipitant. PIDP dissolved in this mixed solvent more readily than in pure dichloromethane. The fractionation was carried out according to the following method.

A given sample was dissolved in the mixed solvent at a concentration between 3×10^{-4} and 5×10^{-3} g cm⁻³. At 25°C, hexane was added until the solution became turbid. When the turbid solution was cooled and kept at about 5°C, the turbidity disappeared. The solution was then warmed to 25°C and allowed to separate into two phases. After the concentrated phase had been removed, the supernatant phase was treated in the same way. By repeating this process, each sample was divided into three to eight parts. Fractions with nearly identical intrinsic viscosities (in *m*-cresol at 25°C) were combined, and each of the combined fractions was divided into several parts by the same method as described above. This refractionation was repeated four to six times. From about 50 products obtained, 13 appropriate fractions were selected, and each of

Table I. Polycondensation of isophthaloyl chloride and *trans*-2,5-dimethylpiperazine

Sample code	Method	$[\eta] \times 10^{-2c}$	Yield
		cm ³ g ⁻¹	%
1	a	2.30	65.7
2	a	2.85	78.3
3	a	1.94	81.5
4	a	1.35	74.8
5	b	6.95	90.8
6	b	7.65	95.3
7	b	7.01	82.6
8	a	1.19	71.6
9	a	0.252	47.4
10	a	1.04	51.8

^a Solution polycondensation.⁴

^b Interfacial polycondensation.³

^c Measured in *m*-cresol at 25°C.

these were further divided into three parts. The middle parts, designated below as F-1, F-2, ..., F-13, were chosen for the present study. These final fractions were purified by reprecipitating from dichloromethane solutions into hexane and dried *in vacuo* at room temperature.

The molecular weight distributions of fractions F-1, F-3, F-5, and F-6 were investigated by gel-permeation chromatography (GPC) (Toyo Soda Model HLC--801) with chloroform as the solvent. The flow rate was 0.83 cm³ min⁻¹. The ultraviolet(UV)-detected GPC diagrams indicated these fractions to be as homogeneous in molecular weight as Pressure Chemical's standard polystyrenes.

Light Scattering

Intensities of light scattered from PIDP in trifluoroethanol (TFE) at 25°C were measured on a Fica 50 automatic light-scattering photometer, at angles from 18° to 135° for higher-molecular-weight fractions (F-1 to F-8) and at a fixed angle of 90° for lower-molecular-weight fractions (F-9 to F-13). Vertically polarized incident light of 546 nm wavelength was used for the three highest-molecular-weight fractions and that of 436 nm for the rest. The experimental procedures were the same as those employed in Motowoka's studies^{1,2} on PPDP and PTDP. The data were analyzed by Berry's square-root plot⁵ to evaluate M_w , $\langle S^2 \rangle_z$, and A_2 (the second

virial coefficient).

The three lowest-molecular-weight fractions F-11, F-12, and F-13 in TFE at 25°C were also examined with unpolarized incident light. The estimated M_w and A_2 were in close agreement with those obtained with vertically polarized incident light. From this agreement, we concluded that the optical anisotropy of the PIDP molecule was negligible in the range of molecular weight studied.

To check M_w from light scattering, sedimentation-equilibrium measurements were made on fractions F-7, F-8, F-11, and F-13 in a Spinco Model E ultracentrifuge, with *N*-methyl-2-pyrrolidone (NMP) at 25°C as the solvent. A Kel-F 12-mm double-sector cell was used; the length of the liquid column was adjusted 1.0 to 2.0 mm. The rotor was operated at 13000 rpm for fraction F-7, 16000 rpm for fraction F-8, 24000 rpm for fraction F-11,

and 30000 rpm for fraction F-13. Rayleigh fringe patterns were photographed on Kodak spectroscopic plates and read with a Nikon Shadowgraph Model 6.

Specific refractive-index increments for PIDP in TFE were $0.279 \text{ cm}^3 \text{ g}^{-1}$ at 436 nm and $0.267 \text{ cm}^3 \text{ g}^{-1}$ at 546 nm and those in NMP were $0.131 \text{ cm}^3 \text{ g}^{-1}$ at 436 nm and $0.123 \text{ cm}^3 \text{ g}^{-1}$ at 546 nm, all at 25°C. These values agreed with those for PPDP¹ and PTDP² in the same solvents. The partial specific volume of PIDP in NMP at 25°C was $0.779 \text{ cm}^3 \text{ g}^{-1}$, and this also agreed with the value¹ for PPDP in the same solvent.

Viscometry

Most of the viscosity measurements were made in conventional capillary viscometers of the Ubbelohde type. For fractions F-1 to F-4 in TFE

Figure 2. Concentration dependence of $(Kc/R_0)^{1/2}$ for PIDP fractions in TFE at 25°C. K is the light-scattering constant, R_0 is the reduced scattered intensity at zero scattering angle, and c is the polymer mass concentration.

and *m*-cresol and fraction F-5 in *m*-cresol, either a low-shear four-bulb capillary viscometer⁶ or a rotational viscometer⁷ of the Zimm-Crothers type was used.

RESULTS

Molecular Weight and Mean-Square Radius of Gyration

Figures 2 and 3 illustrate the concentration dependence of $(Kc/R_0)^{1/2}$ and $(Kc/R_{90})^{1/2}$, respectively, for PIDP fractions in TFE at 25°C, where K is the light-scattering constant, R_0 and R_{90} are the reduced scattered intensities at 0° and 90° scattering angles, respectively, and c is the polymer mass concentration. The values of M_w and A_2 evaluated from the indicated straight lines are summarized in Table II, together with those of M_w and A_2 (in NMP) determined from sedimentation equilibrium. The M_w values determined by the two methods agree within experimental error. We note that the A_2

values in TFE are about ten times as large as the values for flexible polymers in good solvents.⁸

Figure 4 shows the angular dependence of scattered intensity at infinite dilution for PIDP fractions in TFE at 25°C. The values of $\langle S^2 \rangle_z^{1/2}$ evaluated from the slopes of the dashed lines (the initial tangents of the solid curves) are presented in the fourth column of Table II, and plotted double-logarithmically against M_w in Figure 5. The data points can be fitted by a straight line with slope 0.60.

Intrinsic Viscosity

Table III summarizes the values of $[\eta]$ and k' (the Huggins constant) for PIDP fractions in *m*-cresol and TFE at 25°C. For any fraction, the $[\eta]$ value in *m*-cresol is larger than that in TFE by a constant factor of 1.45 ± 0.08 . It is of interest that Motowoka *et al.*² found $[\eta]_{m\text{-cresol}}/[\eta]_{\text{TFE}}$ to be 1.42 ± 0.08 for the PTDP fractions examined. In Figure 6, the molecular weight dependence of $[\eta]$ for PIDP in *m*-cresol is compared with that for PPDP¹ and PTDP² in the

Figure 3. Concentration dependence of scattered intensity at 90° scattering angle for PIDP fractions in TFE at 25°C.

Table II. Results from light-scattering measurements on PIDP fractions in TFE at 25°C

Fraction	$M_w \times 10^{-4}$	$A_2 \times 10^4$	$\langle S^2 \rangle_z^{1/2}$
	g mol ⁻¹	mol cm ³ g ⁻²	nm
F-1	237	9.34	122
F-2	171	10.3	98.6
F-3	125	11.5	81.5
F-4	80.4	12.6	64.0
F-5	50.6	14.1	48.6
F-6	24.1	16.1	30.1
F-7	15.2	18.5	22.8
F-8	14.7 ^a	(8.9) ^a	17.5
	9.85	21.0	
F-9	5.52	24.8	
	9.63 ^a	(9.5) ^a	
F-10	3.33	27.8	
F-11	1.58	33.4	
F-12	1.55 ^a	(16) ^a	
	0.783	38.4	
F-13	0.367	46.4	
	0.368 ^a	(40) ^a	

^a Sedimentation equilibrium in NMP at 25°C. **Figure 4.** Angular dependence of scattered intensity at infinite dilution for PIDP fractions in TFE at 25°C. R_θ is the reduced scattered intensity at scattering angle θ , n_0 is the refractive index of the solvent, and λ_0 is the wavelength of incident light in vacuum. **Figure 5.** Molecular weight dependence of $\langle S^2 \rangle_z^{1/2}$ for PIDP in TFE at 25°C.

same solvent. An interesting feature is that the three curves are nearly parallel. At the same M_w , $[\eta]$ is larger in the order of *ortho*-, *meta*-, and *para*-linked chains, which suggests that the average molecular dimensions of the three isomers increase in this

order. The slope of each curve increases as M_w decreases; that for PIDP is 0.75 above $M_w = 6 \times 10^4$ g mol⁻¹ and approaches 0.94 at low molecular weight. Figure 7 compares $[\eta]$ for PIDP and PTDP² in TFE; the data for PPDP in this solvent were not reported in our previous paper. We see that the two curves are parallel and that the $[\eta]$ for PIDP are consistently smaller than those for PTDP. The slope of the curve for PIDP is 0.77 above $M_w = 3 \times 10^4$ g mol⁻¹ and about 0.85 at the lowest M_w .

Table III. Results from viscosity measurements on PIDP fractions in TFE and *m*-cresol at 25°C

Fraction	In TFE		In <i>m</i> -cresol	
	$[\eta] \times 10^{-2}$	k'	$[\eta] \times 10^{-2}$	k'
	cm ³ g ⁻¹		cm ³ g ⁻¹	
F-1	19.4	0.31	26.8	0.33
F-2	14.8	0.31	20.6	0.32
F-3	11.6	0.32	16.2	0.33
F-4	8.09	0.31	11.5	0.33
F-5	5.70	0.31	8.08	0.37
F-6	3.22	0.31	4.68	0.37
F-7	2.29	0.32	3.39	0.37
F-8	1.61	0.33	2.41	0.36
F-9	1.04	0.35	1.59	0.38
F-10	0.695	0.36	1.06	0.38
F-11	0.386	0.38	0.585	0.42
F-12	0.208	0.45	0.305	0.49
F-13	0.112	0.60	0.155	0.58

DISCUSSION

Stiffness of the PIDP Chain

The downward curvature of the viscosity plots in Figures 6 and 7 is an indication of the semiflexibility of the PIDP chain. One may be prone to estimate the stiffness by using Yamakawa-Fujii's theory⁹ of $[\eta]$ for the unperturbed wormlike chain, as was done for PPDP and PTDP by Motowoka *et al.*^{1,2} However, the matter is not so simple, because the linear behavior of these viscosity plots in the high-molecular-weight region is not compatible with the prediction of Yamakawa-Fujii's theory. Furthermore, the Benoit-Doty expression¹⁰ for $\langle S^2 \rangle$ of the unperturbed wormlike chain fails to

Figure 6. Molecular-weight dependence of $[\eta]$ for three polyamide isomers PPDP, PIDP, and PTDP in *m*-cresol at 25°C.

Figure 7. Molecular-weight dependence of $[\eta]$ for PIDP and PTDP in TFE at 25°C.

Figure 8. Comparison between the measured values of $[\eta]$ for PIDP in *m*-cresol and TFE, and the theoretical values for the unperturbed wormlike cylinders with $q=4.9$ nm, $M_L=330$ nm⁻¹, $d=0.73$ nm for *m*-cresol, and $q=3.1$ nm and the same M_L and d values for TFE.

predict the slope 0.6 of the straight line fitting the $\langle S^2 \rangle_z^{1/2}$ data in Figure 5.

Under these circumstances, we must be content

with estimating the persistence length q by assuming suitable values for the molar mass M_L per unit contour length and the diameter d of the unper-

Table IV. Persistence lengths for PIDP, PPDP, and PTDP in *m*-cresol and TFE at 25°C

Polymer	In <i>m</i> -cresol q/nm	In TFE q/nm
PIDP	4.9 ± 0.3	3.1 ± 0.2
PPDP ^a	4.6 ± 0.1	—
PTDP ^a	7.4 ± 0.2	6.4 ± 0.2

^a Taken from ref 2.

turbed wormlike cylinder chosen as the model for low-molecular-weight PIDP. Motowoka *et al.*^{1,2} found that the M_L and d of PPDP and PTDP in various solvents including TFE and *m*-cresol were $330 \pm 20 \text{ nm}^{-1}$ and $0.73 \pm 0.3 \text{ nm}$, respectively. We assumed these values to be good approximations to the M_L and d of PIDP and sought a q value which would allow Yamakawa–Fujii's theory⁹ to fit our $[\eta]$ data on PIDP in the low-molecular-weight region. The solid lines in Figure 8 show the theoretical values computed by fixing M_L and d to 330 nm^{-1} and 0.73 nm , respectively, and choosing q to be 4.9 nm for *m*-cresol and 3.1 nm for TFE. It is seen that they fit the *m*-cresol data up to $M_w = 5 \times 10^5 \text{ g mol}^{-1}$ and the TFE data up to $M_w = 10^5 \text{ g mol}^{-1}$. The best-fit values of q depend on the choice of M_L and d . The ranges of q shown in Table IV correspond to the ranges of M_L and d estimated by Motowoka *et al.* for PPDP and PTDP. Comparing the q values of the three isomers in *m*-cresol, we find that the stiffness of PIDP is comparable to that of PPDP, but distinctly lower than that of PTDP. However, the viscosity data in Figure 6 suggest that if, as was assumed above, PIDP and PPDP have the same M_L and d , the q for the former should be distinctly larger than that for the latter. This discrepancy is primarily attributed not to the improper values assumed for M_L and d of PIDP but to the difference that Motowoka *et al.* estimated q from the data at high molecular weights using the asymptotic form of Yamakawa–Fujii's theory, while we fitted this theory to the data at low molecular weights.

Excluded-Volume Effects

In Figure 9, the experimental values of the reduced root-mean-square radius of gyration $\langle S^2 \rangle_z^{1/2}/2q$ for PIDP and PTDP in TFE and those

Figure 9. Reduced root-mean-square radii of gyration $\langle S^2 \rangle_z^{1/2}/2q$ plotted against $M_w/2qM_L$ for PIDP and PTDP in TFE and for PPDP in chloroform and *N*-methyl-2-pyrrolidone.

for PPDP in NMP and chloroform are plotted against the number of Kuhn's statistical segments $n_K \equiv M_w/2qM_L$, where we have taken $q = 3.1 \text{ nm}$ and $M_L = 330 \text{ nm}^{-1}$ for PIDP and Motowoka's q and M_L values^{1,2} for the others. The solid curve in this figure represents the Benoit–Doty theory¹⁰ for an unperturbed wormlike chain:

$$\frac{\langle S^2 \rangle}{(2q)^2} = \frac{M}{12qM_L} - \frac{1}{4} + \frac{qM_L}{2M} - \frac{q^2 M_L^2}{2M^2} \left[1 - \exp\left(-\frac{M}{qM_L}\right) \right] \quad (1)$$

where M is the molecular weight of the chain. For n_K below 80 the plotted points for the three isomers fall on the solid curve. For n_K above 80, the points for PPDP keep following the same line, but those for PIDP appear above it and follow a different straight line. This last behavior implies that PIDP in TFE undergoes excluded-volume effect when the chain length measured in terms of n_K exceeds 80. In this connection, it is interesting to note that the values of A_2 for PIDP in TFE are two to three times as large as those for PPDP in NMP and chloroform.¹

In Figure 8, the $[\eta]$ data for TFE in the region of M_w above 10^5 g mol^{-1} show a similar deviation from the theoretical curve for unperturbed wormlike cylinders. This phenomenon is further evi-

dence for the fact that PIDP in TFE starts suffering excluded-volume effect when the molecular weight reaches a certain "critical" value. The value 10^5 g mol^{-1} for this critical molecular weight corresponds to an n_k^c (the critical n_k) of about 50, which is in fair agreement with 80 obtained above from the radius of gyration data. The critical molecular weight found from the *m*-cresol data in Figure 8 is about $5 \times 10^5 \text{ g mol}^{-1}$, which gives an n_k^c value of about 150, with $q = 4.9 \text{ nm}$ and $M_L = 330 \text{ nm}^{-1}$ (see above). Thus, we find that for a given polymer, n_k^c depends on the solvent.

Recently, from measurements of $\langle S^2 \rangle_z$ and $[\eta]$ over a very broad range of molecular weight, Murakami *et al.*¹¹ found that poly(hexyl isocyanate) (PHIC) in hexane suffers excluded-volume effect in a molecular weight region above $3 \times 10^6 \text{ g mol}^{-1}$. This critical molecular weight is 30 times as large as that for PIDP in TFE. However, PHIC in hexane is far stiffer, having a q value (42 nm^{11}) 14 times as large as that for PIDP in TFE. Calculating with these values and $M_L = 715 \text{ nm}^{-1}$ as reported by Murakami *et al.*,¹¹ we find n_k^c for PHIC in hexane to be 50. This is comparable with the n_k^c for PIDP in TFE, suggesting that n_k^c is relatively insensitive to chain stiffness.

According to eq 1, the $\log \langle S^2 \rangle^{1/2}$ vs. $\log M$ plot for an unperturbed wormlike chain accurately follows a straight line with slope 0.5 for $n_k > 80$. Thus, dimensionally, unperturbed wormlike chains with $n_k > 80$ behave like a Gaussian coil. The actual slope of this plot for PIDP in TFE is 0.60, which happens to be equal to the theoretically-predicted asymptotic value^{8,12,13} for flexible polymers in good solvents. Though not shown here, both $A_2 M_w / [\eta]$ and the interpenetration function $\Psi (= A_2 M_w^2 / 4\pi^{3/2} N_A \langle S^2 \rangle_z^{3/2}$ with N_A Avogadro's constant) for PIDP in TFE gradually decrease with increasing M_w and approach 120 and 0.22, respectively, for M_w above $5 \times 10^5 \text{ g mol}^{-1}$, as is usually observed with flexible polymers in good solvents.^{8,14} Further, the viscosity exponent for PIDP in TFE for $M_w > 10^5 \text{ g mol}^{-1}$ is close to the values obtained for such systems.^{6,8,14} However, these facts do not mean that our data on PIDP in TFE for $M_w > 5 \times 10^5 \text{ g mol}^{-1}$ may be analyzed in terms of the theories of excluded-volume effects on flexible polymers. What is needed for correct data analysis is a theory of semiflexible polymers perturbed by excluded-volume effect. Unfortun-

nately, little progress has as yet been made on this theory. At the present, at best, only the following remarks may be made.

For a semiflexible polymer, it is reasonable to define its radius-expansion factor α_s and its viscosity-expansion factor α_η , using $\langle S^2 \rangle^{1/2}$ and $[\eta]^{1/3}$ of the unperturbed wormlike chain with the same q , M_L , and d as the references. Our experimental data on PIDP in TFE indicate that α_s so defined remains less than 1.5 over the entire range of M_w studied, but its dependence on M_w is the same as that expected for flexible polymers greatly perturbed by volume effect. Interestingly, this is in qualitative agreement with the prediction from computer calculations¹⁵⁻¹⁸ that the chain-length dependence of α_s for self-avoiding three-dimensional tetrahedral lattice chains approaches the asymptotic form $N^{0.1}$ (N is the number of repeating units) at an α_s less than 1.5 if the freely-rotating tetrahedral chain is taken as the basis for defining α_s .

If calculated with the q , M_L , and d values for PIDP in TFE (see above), Yamakawa-Fujii's theory⁹ for the unperturbed wormlike cylinder gives a $\log [\eta]$ vs. $\log M$ plot which can be well represented by a straight line with slope 0.60 in the range of M from 5×10^5 to $3 \times 10^6 \text{ g mol}^{-1}$. The actual slope of this plot for PIDP in TFE in the corresponding region of M_w is 0.77. These results give α_η which increases with M_w in proportion to $M_w^{0.057}$. This exponent is about one half the exponent for α_s , indicating that, in the region where α_s is not greatly removed from unity, *i.e.*, the polymer suffers small volume effects, $[\eta]$ is affected less by volume exclusion than is $\langle S^2 \rangle^{3/2}$. A similar difference in the molecular weight dependences of α_s and α_η was observed with a number of flexible polymers^{8,19} and predicted theoretically by several authors.²⁰⁻²³

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