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

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ABSTRACT: A number of narrow-distribution fractions of poly(terephthaloyl-*trans*-2,5-dimethylpiperazine) (PTDP) ranging in $\bar{M}_w$ (weight-average molecular weight) from 5,000 to 300,000 were prepared, and their molecular weights, z -average mean-square radii of gyration $\langle S^2 \rangle_z$, second virial coefficients A_2 , and intrinsic viscosities $[\eta]$ in appropriate solvents were measured. Trifluoroethanol (TFE) was used for the light-scattering study and *m*-cresol and TFE for the viscosity study. It was found that the observed data were quantitatively interpretable in terms of the Benoit–Doty theory for $\langle S^2 \rangle$ and the Yamakawa–Fujii theory for $[\eta]$ of unperturbed wormlike chains. The persistence lengths q obtained in TFE and *m*-cresol were about 70 Å, which suggests that the PTDP chain is fairly stiff. This q value is about 1.5 times larger than that of poly(phthaloyl-*trans*-2,5-dimethylpiperazine) (PPDP) in *m*-cresol. PPDP and PTDP differ only in the position at which the phenyl ring is linked to the piperazine ring.

KEY WORDS Poly(terephthaloyl-*trans*-2,5-dimethylpiperazine)/Poly-(phthaloyl-*trans*-2,5-dimethylpiperazine) / Wormlike Chain / Persistence Length / Dilute Solution / Light Scattering / Intrinsic Viscosity / Optical Anisotropy / Yamakawa–Fujii Theory / Benoit–Doty Theory /

In a previous paper¹ we reported that the dimensional and hydrodynamic behavior of poly(phthaloyl-*trans*-2,5-dimethylpiperazine) (PPDP) in dilute solution can be described quantitatively by the theory for unperturbed wormlike chains.^{2,3} This finding was consistent with the prediction that the internal rotation about C— ϕ bonds in PPDP should be considerably hindered, so that the PPDP chain ought to be fairly stiff (see Figure 1). However, the values of the persistence length q estimated in various solvents (30–50 Å) suggested that the internal rotation concerned would not be as sterically hindered as had been anticipated.

Poly(terephthaloyl-*trans*-2,5-dimethylpiperazine) (PTDP) has the same chemical constituent as PPDP, but the two polymers differ in the position at which the phenyl and piperazine rings are linked together, as shown in Figure 1. This difference in structure suggests that the

Figure 1. Repeat units of the PPDP and PTDP chains.

PTDP chain should have a more extended configuration than does the PPDP chain. In fact, the intrinsic viscosities for PTDP in *m*-cresol quoted in Morgan's book⁴ are consistently higher than those¹ for PPDP in the same solvent. Thus, the PTDP molecule in solution is expected to show dimensional and hydrodynamic behavior more characteristic of stiff chains. The present paper reports an experimental study carried out to confirm this prediction. For this purpose, we prepared a number of narrow-distribution fractions of the polymer, measured their $\bar{M}_w$ (weight-average molecular weight), $\bar{M}_n$ (number-average molecular weight), $\langle S^2 \rangle_z$ (z-average mean-square radius of gyration), A_2 (second virial coefficient), and $[\eta]$ (intrinsic viscosity) in appropriate solvents, and analyzed the observed data in terms of the established theory for unperturbed wormlike chains.

EXPERIMENTAL

Polymer Samples

High molecular weight samples of PTDP were prepared by low-temperature solution polycondensation of terephthaloyl chloride and *trans*-2,5-dimethylpiperazine, according to the method of Morgan and Kwolek.⁵ The terephthaloyl chloride used was recrystallized twice from *n*-hexane, and the *trans*-2,5-dimethylpiperazine was recrystallized in the manner described previously.¹ Low-molecular weight samples of PTDP were obtained by interfacial polycondensation, according to the method of Katz.⁶

Table I shows the intrinsic viscosities in *m*-cresol at 25°C and the yields of the six un-

fractionated samples thus prepared.

Fractionation

These samples were separated into a number of fractions by fractional precipitation with chloroform containing 5 vol% of phenol as a solvent and hexane as a precipitant. PTDP was scarcely soluble in pure chloroform but readily dissolved in phenol. The procedure taken in the fractional precipitation was as follows.

A given PTDP sample was dissolved in chloroform containing 5 vol% of phenol at a concentration ranging from 0.5 to 1.0%. The solution was placed in a fractionation vessel thermostated at 20°C and an appropriate quantity of either *n*-hexane or a 1:1 mixture of hexane and chloroform was added with vigorous stirring until the solution became turbid. The turbidity disappeared completely when the solution was cooled to 10°C. Then it was warmed back to 20°C and allowed to stand. The resulting turbid solution rapidly separated into two phases. After a few hours of standing the lower phase was removed from the fractionation vessel by decantation, and the polymer was reprecipitated with the addition of a 3:1 mixture of hexane and methanol, washed successively with ethanol and acetone, and then dried in a vacuum oven. The upper phase was subjected to a series of further fractionations by the same procedure as described above. By repeating these procedures, 5 fractions were separated from Sample 1, 6 fractions from Sample 2, 8 fractions from Sample 3, 6 fractions from Sample 4, 9 fractions from Sample 5, and 16 fractions (designated the f-series in the subsequent presentation) from Sample 6.

Except for these from Sample 6, the fractions having nearly identical intrinsic viscosities (in *m*-cresol at 25°C) were combined and refractionated, again using the same procedure as above. Appropriate fractions were chosen from the final products and designated as the F-series.

Osmometry

Osmotic pressures of the fractions F-4, F-6, and F-8 in a 5:95 (by volume) mixture of *m*-cresol and tetrachloromethane at 30°C were measured by use of a modified Zimm—Myerson osmometer⁷ and Sartorius membrane filters

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

Sample code	$[\eta]$, dl/g ^c	Yield, %	Method
1	3.61	87.6	a
2	2.22	84.0	a
3	3.27	88.2	a
4	2.10	98.0	a
5	3.21	93.4	a
6	1.00	95.8	b

^a Morgan and Kwolek.⁵

^b Katz.⁶

^c Measured in *m*-cresol at 25°C.

SM-11536. The conditioning of the membranes was made by the usual method. The time to reach osmotic equilibrium ranged from one to three days. No leakage of the polymer solute through the membrane was observed.

$\bar{M}_n$ (number-average molecular weight) and A_2 (second virial coefficient) were evaluated, respectively, from the intercept and slope of the plot of $(\pi/RTc)^{1/2}$ vs. c . Here π is the osmotic pressure, c is the polymer mass concentration, and R and T have the usual meaning.

Light-Scattering Photometry

Light scattering from trifluoroethanol (TFE) solutions of PTDP at 25°C was measured for all 15 fractions by use of a Fica 50 automatic photogoniometer in an angular range from 30 to 142.5°, with vertically polarized or unpolarized light of 436 nm in wavelength. The procedures used were the same as described elsewhere.⁸ The absolute Rayleigh ratio for benzene at 25°C and 436 nm was taken to be $46.5 \times 10^{-6} \text{ cm}^{-1}$ for the calibration of the apparatus.⁹ The depolarization of benzene was found to be 0.432 at 436 nm, in close agreement with the reported values.¹⁰

Polymer solutions and the solvent were freed from dust and microgels by centrifuging them at 4.5×10^4 gravities for 4 hr in a Sorvall Type RC2-B centrifuge. They were then directly placed in the light-scattering cell by using carefully cleaned pipettes.

The observed intensities of scattering light as a function of polymer mass concentration c and scattering angle θ were analyzed by means of Berry's square-root plot¹¹ to evaluate $\bar{M}_w$ (weight-average molecular weight), $\langle S^2 \rangle_z$ (z-average mean-square radius of gyration), and A_2 .

The specific refractive index increment $(\partial n/\partial c)_0$ of PTDP in trifluoroethanol at 25°C was determined by a differential refractometer of the Schultz—Cantow type. The values of $(\partial n/\partial c)_0$ for light of 436 and 546 nm were found to be 0.278 and 0.266 cm³/g, respectively. These values obeyed the Gradstone—Dale relationship, which had been established for PPDP in our previous paper.¹

Viscometry

Viscosities of all 15 fractions of PTDP in trifluoroethanol and *m*-cresol at 25°C were

measured by use of capillary viscometers of the Ubbelohde suspended-level type. The data were not corrected for kinetic energy and shear-rate dependence, since the fraction F-1 (the highest molecular weight fraction) in *m*-cresol did not show non-Newtonian behavior when examined in a low-shear rotational viscometer of the Zimm—Crothers type.¹² The intrinsic viscosity $[\eta]$ and the Huggins coefficient k' for each fraction was determined from both the Huggins plot¹³ and the Mead—Fuoss plot.¹⁴

Partial Specific Volume

The densities of polymer solutions and solvents at 25°C were measured by use of a Lipkin—Davison pycnometer of about 5-ml capacity. The partial specific volume $\bar{v}$ was determined from the slope of a plot of solution density vs. polymer mass concentration, which was strictly linear in the range of low concentrations studied. The values of $\bar{v}$ in trifluoroethanol and *m*-cresol were 0.777 and 0.772 cm³/g, respectively.

RESULTS

Optical Anisotropy Correction

Figure 2 shows plots of $(Kc/R_{90})^{1/2}$ vs. c for the fractions f-13, f-14, and f-15 in trifluoroethanol at 25°C, where K is the conventional

Figure 2. Concentration dependence of $(Kc/R_{90})^{1/2}$ for PTDP fractions f-13, f-14, and f-15 in trifluoroethanol at 25°C: ○, U_u ; ○●, U_v ; ●, values corrected for optical anisotropy.

Table II. Numerical results from light-scattering and osmotic pressure measurements on PTDP fractions

Fraction	Light scattering, in TFE at 25°C			Osmotic pressure, in mixed solvent at 30°C		$\bar{M}_w/\bar{M}_n$
	$\bar{M}_w \times 10^{-4}$	$A_2 \times 10^4$, cm ³ mol/g ²	$\langle S^2 \rangle_z^{1/2}$, Å	$\bar{M}_n \times 10^{-4}$	$A_2 \times 10^4$, cm ³ mol/g ²	
F-1	31.9	21.7	439	—	—	—
F-2	24.3	22.7	380	—	—	—
F-3	19.8	22.9	341	—	—	—
F-4	15.0	23.8	295	14.4	15.6	1.04
F-5	10.9	27.6	250	—	—	—
F-6	6.85	29.6	193	6.82	19.1	1.00
F-7	5.86	29.2	174	—	—	—
F-8	3.88	34.9	136	3.80	18.6	1.02
f-3	3.05	35.5	116	—	—	—
f-7	2.65	37.9	106	—	—	—
f-9	1.82	41.5	—	—	—	—
f-11	1.32	47.0	—	—	—	—
f-13	0.900	54.2	(2.5) ^a	—	—	—
f-14	0.660	58.6	(3.1) ^a	—	—	—
f-15	0.521	65.7	(3.8) ^a	—	—	—

^a The values parenthesized are the "optical anisotropy," δ , $\times 10^3$.

light-scattering factor and R_{90} denotes the reduced intensity of scattered light at 90° scattering angle for either vertically polarized incident light (U_v) or unpolarized light (U_u). It is recognized from Figure 2 that the intensities of scattered light for U_v and U_u , denoted here by R_{U_v} and R_{U_u} , do not agree with each other. This is attributed to an optical anisotropy of the scattered units of PTDP. No difference between R_{U_v} and R_{U_u} was observed within experimental errors for all fractions other than f-13, f-14, and f-15.

We find from the theory of elastic light scattering for wormlike chains consisting of optically anisotropic units¹⁵ that

$$R_{U_u}(90^\circ, c) - \frac{1}{2}R_{U_v}(90^\circ, c) = 3Kc\bar{M}_w\delta \quad (1)$$

where δ is the "optical anisotropy" defined by eq 9 (see below). With this relation the values of $Kc\bar{M}_w\delta$ for the fractions f-13, f-14, and f-15 were calculated from the data in Figure 2, and the results were used to obtain the "corrected" values of $(Kc/R_{90})^{1/2}$, which are indicated by the closed circles in this figure. The "corrected" values were then analyzed by the conventional method to determine $\bar{M}_w$ and A_2 . This procedure is adaptable because these three fractions are so low in molecular weight that the angular

dependence of their scattered light may be ignored. With $\bar{M}_w$ known, δ was computed from $K\bar{M}_w\delta$ determined above. The values of $\bar{M}_w$, A_2 , and δ obtained in this way for the fractions f-13, f-14, and f-15 are given in Table II. The indicated values of δ suggest that the optical anisotropies of higher molecular weight fractions than these three have little effect on the light-scattering data. Therefore the observed data on these other fractions were not corrected for optical anisotropy.

Molecular Weight and Second Virial Coefficient

Figure 3 shows the plots of $(Kc/R_0)^{1/2}$ vs. c for PTDP fractions in trifluoroethanol at 25°C, where R_0 is the reduced intensity of scattered light extrapolated to zero scattering angle. The values of $\bar{M}_w$ and A_2 evaluated from the straight lines in Figure 3 are summarized in Table II.

Figure 4 illustrates osmotic pressure data on PTDP fractions in a mixture of *m*-cresol and tetrachloromethane at 30°C. The values of $\bar{M}_n$ and A_2 estimated from the indicated lines are also given in Table II. The ratios of $\bar{M}_w$ to $\bar{M}_n$ shown in the seventh column of Table II are very close to unity, suggesting that each of the fractions studied in this work was quite narrow in molecular weight distribution.

Figure 3. Concentration dependence of $(Kc/R_0)^{1/2}$ for PTDP fractions in trifluoroethanol at 25°C: $\odot$, upper c -scale; $\circ$, lower c -scale.

Figure 4. Concentration dependence of $(\pi/RTc)^{1/2}$ for PTDP fractions F-4, F-6, and F-8 in a 5:95 (by volume) mixture of *m*-cresol and tetrachloromethane at 30°C.

Figure 5. Angular dependence of $(\bar{M}_w Kc/R_\theta)^{1/2}$ for PTDP fractions in trifluoroethanol at 25°C.

Mean-Square Radius of Gyration

Figure 5 illustrates the plots of $(\bar{M}_w Kc/R_\theta)^{1/2}_{c=0}$ vs. $\sin^2(\theta/2)$ for PTDP fractions in trifluoroethanol at 25°C, where R_θ denotes the reduced intensity of scattered light at a scattering angle θ . The fourth column of Table II gives the values of $\langle S^2 \rangle_z^{1/2}$ estimated from the slopes of the indicated straight lines.

When these values of $\langle S^2 \rangle_z^{1/2}$ are double-logarithmically plotted against $\bar{M}_w$, they follow a curve which is slightly convex upward and becomes linear, with a slope of 0.50, as $\bar{M}_w$ increases. This characteristic dependence of $\langle S^2 \rangle_z^{1/2}$ on molecular weight is consistent with the expected semiflexible nature of the PTDP molecule. No great reliance can be put on the values of $\langle S^2 \rangle_z^{1/2}$ for the fractions F-8, f-3, and f-7, because the slopes of the plots of $(\bar{M}_w Kc/R_\theta)^{1/2}_{c=0}$ vs. $\sin^2(\theta/2)$ for these fractions are very small, as can be seen in Figure 5.

Intrinsic Viscosity

Table III summarizes the values of $[\eta]$ and k' for all the fractions in trifluoroethanol and *m*-cresol at 25°C. An interesting feature is that for each fraction the value of $[\eta]$ in *m*-cresol is larger by a constant factor of 1.42 ± 0.08 than that in trifluoroethanol. The $\log [\eta]$ vs. $\log \bar{M}_w$ plots of PTDP in either of these two solvents are not simply fitted by a straight line (see Figure 9) in contrast to those usually obtained with flexible linear polymers. It is to be added here that the $[\eta] - \bar{M}_w$ relationship for PTDP in *m*-cresol cited

Table III. Numerical results from viscosity measurements on PTDP fractions in TFE and *m*-cresol at 25°C

Fraction	TFE		<i>m</i> -Cresol	
	$[\eta]$, dl/g	k'	$[\eta]$, dl/g	k'
F-1	5.54	0.33	7.70	0.36
F-2	4.43	0.33	6.36	0.35
F-3	4.02	0.31	5.53	0.39
F-4	3.25	0.34	4.43	0.38
F-5	2.60	0.37	3.62	0.38
F-6	1.82	0.30	2.44	0.33
F-7	1.49	0.32	2.24	0.38
F-8	1.10	0.44	1.59	0.36
f-3	0.930	0.34	1.36	0.35
f-7	0.806	0.36	1.19	0.40
f-9	0.595	0.40	0.886	0.35
f-11	0.452	0.37	0.656	0.33
f-13	0.325	0.42	0.478	0.40
f-14	0.260	0.42	0.368	0.43
f-15	0.217	0.43	0.296	0.48

in Morgan's book⁴ runs fairly close to our data points in the same solvent.

DISCUSSION

Previous Method of Data Analysis

We assume the wormlike chain model for PTDP and neglect excluded-volume effects. First we outline the method of data analysis presented and used in the previous paper¹ under these approximations.

For unperturbed wormlike chains the intrinsic viscosity $[\eta]$ and the mean-square radius of gyration $\langle S^2 \rangle$ are expressed by^{16,17}

$$[\eta] = \frac{[\Phi_\infty / (M_L/2q)^{3/2}] M^{1/2}}{[1 - (2qM_L)^{1/2} g(d/2q) M^{-1/2} + O(qM_L M^{-1})]} \quad (2)$$

$$\langle S^2 \rangle = (q/3M_L)M - q^2 \{1 - 2qM_L/M + 2(qM_L/M)^2 [1 - \exp(-M/qM_L)]\} \quad (3)$$

Here M is the molecular weight, q is the persistence length, M_L is the molecular weight per unit length, d is the diameter of the wormlike cylinder, $g(d/2q)$ is a known function of $d/2q$, and Φ_∞ is the limiting value of the Flory viscosity factor Φ for indefinitely large molecular weight M , where Φ is defined by²

$$[\eta] = \Phi(6\langle S^2 \rangle)^{3/2}/M \quad (4)$$

From eq 2 it follows that

$$M^{1/2}/[\eta] = [(M_L/2q)^{3/2}/\Phi_\infty][1 - (2qM_L)^{1/2} g(d/2q) M^{-1/2} + O(qM_L M^{-1})] \quad (5)$$

which indicates that the two quantities $(M_L/2q)^{3/2}/\Phi_\infty$ and $-(2qM_L)^{1/2} g(d/2q)$ can be determined from the intercept and initial slope of a plot of $M^{1/2}/[\eta]$ vs. $M^{1/2}$. Equations 2 through 4 may be combined to give

$$1/\Phi = (1/\Phi_\infty)[1 - (2qM_L)^{1/2} g(d/2q) M^{-1/2} + O(qM_L M^{-1})] \quad (6)$$

Hence Φ_∞ can be evaluated from the intercept of a plot of $1/\Phi$ vs. $M^{-1/2}$. We wish to remark that it is appropriate to treat Φ_∞ as a parameter to be determined experimentally, since any actually accessible polymer sample is always polydisperse in molecular weight, whereas the theoretical value of Φ_∞ is as yet known only for perfectly monodisperse samples. For an unequivocal determination of wormlike chain parameters q , M_L , and d we need one more relation, together with eq 5 and 6. As such a relation our previous treatment assumed the approximation

$$\bar{v} = \pi N_A d^2 / 4M_L \quad (7)$$

for the partial specific volume of the polymer, where N_A denotes Avogadro's number.

When this method of analysis was applied to the present data on PTDP, it became evident that no unambiguous determination of Φ_∞ could be made by the method based on eq 6. In Figure 6 the observed values of $1/\Phi$ for PTDP fractions in trifluoroethanol are plotted against $\bar{M}_w^{-1/2}$. We see that it is impossible to extrapolate the data points to $\bar{M}_w^{-1/2} = 0$ with any degree of certainty. For this reason we abandoned

Figure 6. Plots of $1/\Phi$ vs. $\bar{M}_w^{-1/2}$ for PTDP fractions in trifluoroethanol at 25°C.

the previous method of data analysis and looked for a workable alternative.

Alternative Method of Data Analysis

It follows from eq 3 that $\langle S^2 \rangle$ is asymptotically represented by

$$\langle S^2 \rangle = (q/3M_L)M - q^2 \quad (8)$$

This indicates that the relation between $\langle S^2 \rangle$ and M approaches a straight line with a slope $q/3M_L$ and an intercept $-q^2$ as M increases. Hence, in principle, q and M_L may be evaluated if we can find such an asymptote experimentally. In Figure 7, the observed values of $\langle S^2 \rangle_z$ for PTDP in trifluoroethanol are plotted against $\bar{M}_w$. The data points are fitted by a straight line with a small negative intercept. If this line is taken as the asymptote for this system, we find $q = 67 \pm 4 \text{ \AA}$ and $M_L = 36 \pm 2 \text{ daltons/\AA}$ from its slope and intercept. Although these values must be accepted with reservation, because the intercept of the asymptote is too small to estimate q accurately, the inclination of the asymptote can be determined with a high degree of accuracy, and yields $1.84 \times 10^{-16} \text{ cm}^2$ for the quantity q/M_L . With the value of q/M_L known in this way, we can evaluate Φ_∞ from the intercept of $M^{1/2}/[\eta]$

Figure 7. Plots of $\langle S^2 \rangle_z$ vs. $\bar{M}_w$ for PTDP fractions in trifluoroethanol at 25°C; dashed line, theoretical values calculated from eq 3, using the values of the parameters listed in Table IV.

Figure 8. Plots of $\bar{M}_w^{1/2}/[\eta]$ vs. $\bar{M}_w^{-1/2}$ for PTDP fractions in trifluoroethanol and *m*-cresol at 25°C.

plotted vs. $M^{-1/2}$. We can then evaluate q , M_L , and d from the initial slope of this plot and the experimental value of $\bar{v}$ substituted into eq 7.

Figure 8 shows the plots of $\bar{M}_w^{1/2}/[\eta]$ vs. $\bar{M}_w^{-1/2}$ for PTDP fractions in trifluoroethanol and *m*-cresol at 25°C. It is seen that the intercept and initial slope of each plot can be determined with no great uncertainty. For the trifluoroethanol solution the intercept of the plot and the q/M_L value given above yield $(2.19 \pm 0.05) \times 10^{23}$ for Φ_∞ . Note that this value is still about 20% lower than the well-known theoretical value predicted for monodisperse linear polymers, despite the fact that our PTDP fractions have the $\bar{M}_w/\bar{M}_n$ ratios unusually close to unity. For the *m*-cresol solution we did not make light-scattering measurements and hence computed q/M_L from the intercept of the plot in Figure 8, assuming that the Φ_∞ value obtained for the trifluoroethanol solution is valid for this system as well. The resulting q/M_L was $2.39 \times 10^{-16} \text{ cm}^2$.

Table IV summarizes the values of q , M_L , and d determined for PTDP in trifluoroethanol and *m*-cresol at 25°C. The observed values of $\bar{v}$ used in the computations were 0.777 and 0.772 cm^3/g for trifluoroethanol and *m*-cresol, respectively. For comparison, this table also shows the values of q , M_L , and d for PPDP in *m*-cresol at 25°C. These values have been obtained by using the previously reported intrinsic viscosity data¹ and the newly measured $\bar{v}$ value (0.778 cm^3/g), together with $\Phi_\infty = 2.05 \times 10^{23}$ assumed on the basis of our previous finding.¹

In Table IV, the M_L values (31 and 35 daltons/ $\text{\AA}$)

Table IV. Wormlike chain parameters of PTDP and PPDP

Polymer	Solvent	q , Å	M_L , daltons/Å	d , Å	$\phi_\infty \times 10^{-23}$
PTDP	<i>m</i> -Cresol	74 ± 2	31 ± 1	7.1 ± 0.1	a
	TFE	64 ± 2	35 ± 1	7.6 ± 0.1	2.19 ± 0.05
PPDP	<i>m</i> -Cresol	46 ± 1	35 ± 1	7.5 ± 0.1	b

^a Assumed $\phi_\infty = 2.19 \times 10^{23}$.

^b Assumed $\phi_\infty = 2.05 \times 10^{23}$.

for PTDP in two different solvents may be compared to 30.3 daltons/Å, the molecular weight per unit length in the N-N direction of the piperazine ring of the PTDP molecule (see Figure 1). The d values obtained also seem reasonable, but much cannot be said of them because the quantity d in the Yamakawa—Fujii theory of intrinsic viscosity is simply a parameter which has little to do with the detailed molecular structure of a polymer chain. More significant is the result that the q values for PTDP are about 1.5 times larger than that for PPDP. The implication is that the PTDP molecule in dilute solution behaves as a stiffer (wormlike) chain than the PPDP molecule, and thus confirms the prediction in the Introduction.

Comparison of Experiment and Theory

With the numerical values of the parameters given in Table IV, $\langle S^2 \rangle$ and $[\eta]$ may be computed as functions of molecular weight for any of the three polymer—solvent systems indicated in the table. The dashed line in Figure 7 shows the result so calculated. Actually, it coincides with the solid line drawn in the figure at molecular weights above 10^4 .

The calculated values of $[\eta]$ are compared with the corresponding experimental values in Figure 9. For the computation the numerical tables kindly provided by Professor Yamakawa was used. The theoretical curves have been truncated at molecular weights corresponding to $450(M_L/q)d^2$, because he remarked that the Yamakawa—Fujii numerical results might be less accurate for molecular weights lower than this limit. The calculated curves fit the data points quite satisfactorily in the region of $\bar{M}_w$ above 3×10^4 . However, we can see a clear trend that for $\bar{M}_w$ below about 2×10^4 the measured intrinsic viscosities decrease more slowly with decreasing $\bar{M}_w$ than predicted by the

Yamakawa—Fujii theory. This discrepancy is in the plausible direction if we consider that the Yamakawa—Fujii theory ignores the contributions from the end surfaces of a wormlike cylinder.

Finally, we compute the “optical anisotropy” δ of the PTDP chain in trifluoroethanol at 25°C. The quantity δ for wormlike chains is expressed by¹⁵

$$\delta = (2\varepsilon^2/45)[x^{-1} - x^{-2}[1 - \exp(-x)]] \quad (9)$$

where $x = 3M/(qM_L)$ and $\varepsilon = 3(\alpha_1 - \alpha_2)/(\alpha_1 + 2\alpha_2)$, with α_1 and α_2 being the longitudinal and

Figure 9. Comparison of the observed $[\eta]$ in trifluoroethanol and *m*-cresol with the theoretical values calculated from the Yamakawa—Fujii theory,¹⁶ using the values of the parameters listed in Table IV: ○, PTDP; ⊙, PPDP.

Figure 10. Molecular weight dependence of "optical anisotropy" δ for PTDP fractions in trifluoroethanol at 25°C; solid line, theoretical values calculated from eq 9, using $\alpha_2/\alpha_1=0.47$ and the values of the parameters listed in Table IV.

transverse polarizabilities per unit length of the chain, respectively. Figure 10 shows the computed values of δ as a function of molecular weight for the chains in which $q=64 \text{ \AA}$, $M_L=35$ daltons/ $\text{\AA}$, and $\alpha_2/\alpha_1=0.47$. Actually, this value of α_2/α_1 has been chosen so that the calculated curve fits the three data points plotted in the figure. The curve indicates that no optical anisotropy correction is needed for light-scattering data on PTDP other than the fractions f-13, f-14, and f-15 in trifluoroethanol, as was assumed in the present analysis.

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