Acknowledgment. We acknowledge very fruitful discussions with J. F. Joanny, R. Klein, H. Frisch, and M. Milas.

References and Notes

(1) Schaefer, D. W.; Han, C. C. In *Dynamic Light Scattering and Velocimetry. Applications of Photon Correlation Spectroscopy*: Pecora, R, Ed.; Plenum Press: New York, 1984.
(2) Tirrell, M. *Rubber Chem. Technol.* **1984**, *57*, 523.
(3) Graesley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1.
(4) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(5) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(6) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: London, 1979.
(7) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Int. Ser. Monographs. Phys. 73; Clarendon Press: Oxford, 1982.
(8) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 560.
(9) Edwards, S. F.; Evans, K. F. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 113.
(10) Frenkel, D.; Maguire, J. F. *Phys. Rev. Lett.* **1981**, *47*, 1025.
(11) Doi, M.; Yamamoto, I.; Kano, F. *J. Phys. Soc. Jpn.* **1985**, *53*, 3000.
(12) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(13) Odijk, T. *Macromolecules* **1980**, *16*, 1340.
(14) Doi, M. *J. Polym. Sci., Polym. Symp.* **1985**, *73*, 93.
(15) Semenov, A. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 317.
(16) Zero, K. M.; Pecora, R. *Macromolecules* **1982**, *15*, 87.
(17) Russo, P. S. *Macromolecules* **1985**, *18*, 2733.
(18) Pecora, R. *J. Polym. Sci., Polym. Symp.* **1985**, *73*, 83.
(19) Fujime, S.; Takasaki-Oshita, M.; Maeda, T. *Macromolecules* **1987**, *20*, 1292.
(20) Coriello, T.; Burchard, W.; Dentini, M.; Crescenzi, V. *Macromolecules* **1987**, *20*, 1102.
(21) Léger, L., private communication.
(22) Davoust, J.; Devaux, P. F.; Léger, L. *EMBO J.* **1982**, *1*, 1233.
(23) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953**, *57*, 958.
(24) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(25) Odijk, T.; Houwaart, A. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 627.
(26) The diameter d_e for the determination of the excluded volume was calculated for an ionic strength of 0.1 M NaCl by using the theory of: Skolnick, J.; Fixman, M. *Macromolecules* **1977**, *10*, 944.
(27) Flory, P. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1971.
(28) Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *B26*, 1137.
(29) Riseman, J.; Kirkwood, J. G. *J. Chem. Phys.* **1950**, *18*, 512. Kirkwood, J. K.; Auer, P. L. *J. Chem. Phys.* **1951**, *19*, 281.
(30) Holzwarth, G. *Carbohydr. Res.* **1978**, *66*, 173.
(31) Milas, M.; Rinaudo, M.; Tinland, B. *Carbohydr. Polym.* **1986**, *6*, 95.
(32) Labeled polymers with L = 990 nm at c_1 = 0.1 g/L were mixed into unlabeled polymers with L = 770, 1700, and 2600 nm at two different concentrations (c_u : 4.5 g/L and c_u = 27 g/L). We obtain $D_s \simeq 1 \times 10^{-8}$ cm^2/s for all samples at c_u = 4.5 g/L and $D_s \simeq 0.7 \times 10^{-8}$ cm^2/s for all samples at c_u = 27 g/L.
(33) Estimation of the hydrodynamic diameter of xanthan (c.f., Figure 1) appears difficult to us. In a first approximation we use the geometric diameter $d \simeq 1.1$ nm as calculated from $m = 1.67 \times 10^{-14}$ g/cm and a density of 1.62 g/cm^3.

Registry No. Xanthan, 11138-66-2.

Chain Stiffness and Excluded-Volume Effects in Dilute Polymer Solutions. Poly(isophthaloyl-*trans*-2,5-dimethylpiperazine)

Tooru Kitagawa, Jiro Sadanobu,[†] and Takashi Norisuye*

Department of Macromolecular Science, Osaka University, Toyonaka, Osaka 560, Japan.
Received May 1, 1989; Revised Manuscript Received July 3, 1989

ABSTRACT: Small-angle X-ray scattering, light scattering, and viscosity measurements were made on 18 sharp fractions of poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) (PIDP), a flexible polyamide, ranging in weight-average molecular weight M_w from 2.6×10^3 to 2.4×10^6, with *N*-methyl-2-pyrrolidone (NMP) at 25 °C as the solvent. Both gyration radius and intrinsic viscosity data showed PIDP in NMP to be essentially unperturbed below $M_w \sim 10^4$ and perturbed above it by volume effect. When modeled by Kratky and Porod's wormlike chain, the unperturbed PIDP chain was characterized by a persistence length of 1.2 nm and a molar mass per unit contour length of 310 nm^{-1}. It was found that the combination of the Yamakawa–Stockmayer perturbation theory for the radius expansion factor of a wormlike chain and the Domb–Barrett equation for a flexible chain accurately describes the dimensional behavior of PIDP in NMP over the entire range of M_w studied.

Excluded-volume effects in dilute polymer solutions have been discussed mostly with theories[1,2] formulated for perfectly flexible chains in which the probability of segment collision vanishes only in the limit of zero chain length. In an actual polymer molecule, flexible or stiff, the probability must become zero at a certain nonzero chain length.[3,4] Thus we should treat even a flexible polymer as semiflexible to explain dilute-solution properties of linear polymers over a broad range of chain stiffness or chain length. In experimental studies on flexible polymers, measured properties, especially radii of gyration $\langle S^2\rangle^{1/2}$, without excluded volume at low molecular weights may be analyzed with a relevant model for semiflexible polymers, and thereby volume effects can be estimated separately from stiffness effects. Such attempts were made by Tsuji et al.[5] for Bisphenol A polycarbonate and by Huber et al.[6] for polystyrene with Kratky and Porod's wormlike chain[7] as the model, but the $\langle S^2\rangle$ data obtained were not extensive enough to allow quantitative discussions on volume effects.

The present work is concerned with a similar attempt made for poly(isophthaloyl-*trans*-2,5-dimethylpiperazine) (PIDP), a polyamide consisting of repeating units shown in Figure 1. We made small-angle X-ray scatter-

---

[†] Present address: Products Development Research Laboratories, Teijin Co., Iwakuni 740, Japan.

0024-9297/90/2223-0602$02.50/0

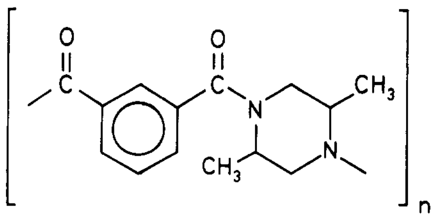

Figure 1. Repeating unit of PIDP.

ing (SAXS), light scattering, and viscosity measurements on 18 PIDP fractions in *N*-methyl-2-pyrrolidone (NMP) at 25 °C. The results for $\langle S^2 \rangle^{1/2}$ were compared with the combination[8] of the Yamakawa–Stockmayer perturbation theory[9] for the radius expansion factor of a wormlike chain and the Domb–Barrett equation[10] for that of a flexible chain.

Yamakawa and Shimada[8] recently showed that this combined theory explains quantitatively the chain length dependence of $\langle S^2 \rangle$ computed for a simulated polymethylene-like chain but does not explain that determined by Murakami et al.[11] for poly(hexyl isocyanate), a typical stiff polymer, in hexane. The $\langle S^2 \rangle$ data for these polymer chains without excluded volume are described by Benoit and Doty's expression[12] for unperturbed wormlike chains. Thus, Yamakawa and Shimada's finding appears to indicate that flexible and stiff polymers, when perturbed by volume effect, differ in dimensional behavior. However, since the simulation data refer to a particular polymethylene-like chain, we considered that the combined theory seemingly valid for flexible polymers ought to be checked directly by experiment. In this connection, we note that, although, according to our previous study,[13] PIDP exhibits an unmistakable semiflexibility in trifluoroethanol or in *m*-cresol, it is flexible in NMP as shown below.

Experimental Section

Samples. Five PIDP fractions were added to the previously investigated 13 fractions,[13] F-1, F-2, ..., F-13, for the present work. The new fractions were prepared by solution polycondensation of isophthaloyl chloride and *trans*-2,5-dimethylpiperazine, followed by purification and repeated fractional precipitation, in the manner described previously.[13] They were designated below as f-1, f-2, ..., f-5 in order of higher molecular weight.

Small-Angle X-ray Scattering. Intensities of X-ray scattered from 10 lower molecular weight fractions of PIDP in NMP at 25 °C were measured in an angular range from 0.24 to 4.9° on a SAXS apparatus at the Institute for Protein Research, Osaka University; the apparatus consists of an X-ray generator (Rigaku D9C, 40 kV × 36 mA), a modified Rigaku SAXS camera,[14] and a one-dimensional position-sensitive proportional counter (PSPC) with a spatial resolution of 0.1265 or 0.06325 mm per channel.

A cylindrical quartz capillary (1-mm diameter) with Teflon tubes at both ends was used for the scattering cell. A given test solution was sucked into the capillary cell fixed in a cell jacket, after being filtered through a Millipore filter (Type FG, 0.2 μm). The cell had been rinsed with aliquots of the solution five times. Intensity data for the solution were accumulated for 6×10^3 or 1×10^4 s. Before and after the measurement, solvent intensities were measured, and their mean was used in calculating the slit-uncorrected excess scattering intensity for the solution at each scattering angle θ. Glatter's iterative method[15] was used for slit correction to obtain the desired excess intensity I_θ at θ. The I_θ data obtained as a function of θ and polymer mass concentration c were analyzed in the following way.

Generally, I_θ is written as

$$(c/I_\theta)^{1/2} = G[1 + (1/6)k^2\langle S^2 \rangle_z + ... + A_2 M_w Q(k)c + ...] \quad (1)$$

with

$$G = \lim_{c,\theta \to 0} (c/I_\theta)^{1/2} \quad (2)$$

and

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

where $\langle S^2 \rangle_z$ is the *z*-average mean-square radius of gyration of the polymer, M_w its weight-average molecular weight, A_2 the second virial coefficient, $Q(k)$ $[=1 + O(k^2)]$ the contribution from intermolecular interference of scattered beams, and λ the wavelength of X-ray (0.1542 nm). We first determined the intercepts A and initial slopes B of $(c/I_\theta)^{1/2}$ vs k^2 plots at finite c for a given PIDP fraction and then extrapolated A to $c = 0$ to obtain G. From the G and B we evaluated $\langle S^2 \rangle_{z,\mathrm{app}}$ at c defined by

$$\langle S^2 \rangle_{z,\mathrm{app}} \equiv 6B/G = \langle S^2 \rangle_z + 6A_2M_w\{[Q(k) - 1]/k^2\}_{k=0}c + ... \quad (4)$$

Finally, $\langle S^2 \rangle_z$ was obtained by extrapolating $\langle S^2 \rangle_{z,\mathrm{app}}$ to infinite dilution. If as is usually the case for low molecular weight polymer samples, $A_2M_w[Q(k) - 1]/k^2$ at $k = 0$ is small, $\langle S^2 \rangle_{z,\mathrm{app}}$ should be insensitive to c.

Light Scattering. Intensity measurements on eight higher molecular weight fractions, F-1 through F-8, in NMP at 25 °C were made on a Fica 50 light scattering photometer at θ between 15° and 150° with vertically polarized incident light of 436- or 546-nm wavelength. Except for fractions F-7 and F-8, the same experimental procedures as in our previous work[13] on PIDP were employed, and the data for Kc/R_θ were analyzed by Berry's square root plot[16] to evaluate M_w, $\langle S^2 \rangle_z$, and A_2. Here, K is the optical constant, and R_θ, the reduced scattering intensity at θ; in light scattering, λ in eq 3 is replaced by the wavelength λ' of incident light in solution. For the two fractions F-7 and F-8, optical clarification of solutions was effected by filtration through two Millipore filters (Type FG, 0.2 μm) connected in series, and the scattering data obtained were treated in a manner similar to that employed for SAXS data to evaluate $\langle S^2 \rangle_z$; in this case, $(Kc/R_\theta)^{1/2}$ [instead of $(c/I_\theta)^{1/2}$ in eq 1] gives M_w and A_2 too. For the specific refractive index increment of PIDP in NMP at 25 °C, use was made of our previous values,[13] 0.131 cm^3 g^{-1} at 436 nm and 0.123 cm^3 g^{-1} at 546 nm.

Sedimentation Equilibrium. Weight-average molecular weights of five fractions, f-1, f-2, ..., f-5, were determined by sedimentation equilibrium in a Spinco Model E ultracentrifuge, with NMP at 25 °C as the solvent (see ref 13 for the experimental details). Ratios of M_z (the *z*-average molecular weight) to M_w were also estimated by the method[17] described elsewhere. They were about 1.2 for fraction f-1 and less than or nearly equal to 1.1 for the other fractions, indicating that the fractins newly prepared in this work are narrow in molecular weight distribution. Sadanobu et al.[13] previously found from gel permeation chromatography that fractions F-1, F-3, F-5, and F-6 were as homogeneous in molecular weight as Pressure Chemicals' standard polystyrenes.

Viscometry. Zero-shear rate intrinsic viscosities, $[\eta]$, and Huggins' constants, k', for all PIDP fractions in NMP at 25 °C were determined using a low-shear four-bulb capillary viscometer (for fractions F-1, F-2, and F-3) or conventional capillary viscometers of the Ubbelohde type (for the rest).

Results

Figures 2 and 3 illustrate, respectively, the angular dependence of $(c/I_\theta)^{1/2}$ for PIDP fraction F-12 from SAXS and the concentration dependence of SAXS and light-scattering $\langle S^2 \rangle_{z,\mathrm{app}}$ for the indicated fractions. The latter shows that as expected, $\langle S^2 \rangle_{z,\mathrm{app}}$ is insensitive to c. The angular dependence of light-scattering intensity at infinite dilution for higher molecular weight fractions is depicted in Figure 4.

The values of $\langle S^2 \rangle_z^{1/2}$ obtained are summarized in Table I, along with those of M_w and A_2. The parenthesized M_w values for fractions F-1 through F-8 are the averages of the previous[13] and present evaluations in trifluoroethanol and NMP, respectively. They are used in the sub-

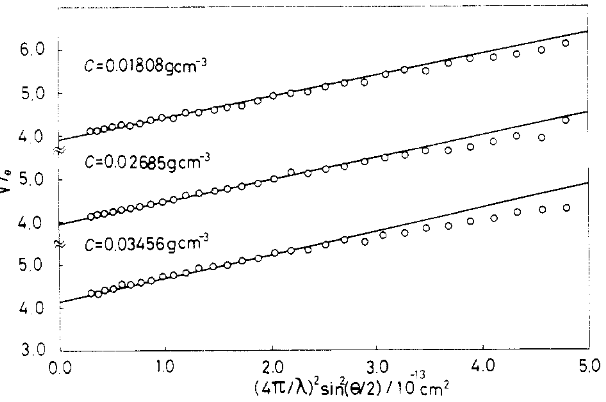

Figure 2. Angular dependence of SAXS intensity for PIDP fraction F-12 in NMP at 25 °C. The excess intensity I_θ is expressed in terms of counts of PSPC.

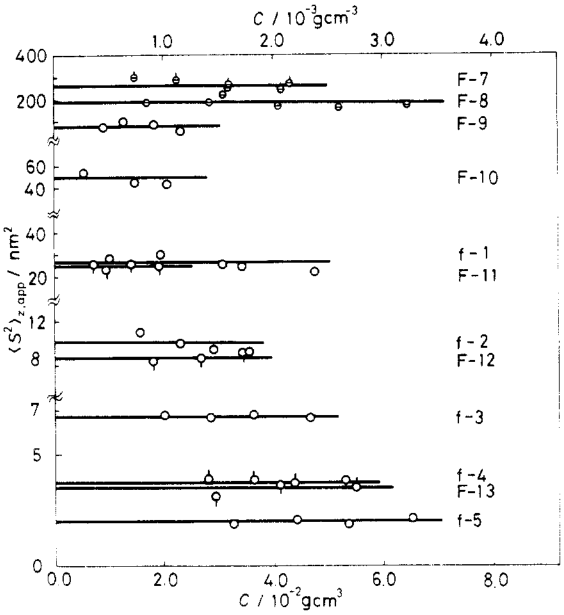

Figure 3. Concentration dependence of $\langle S^2\rangle_{z,\mathrm{app}}$ for indicated PIDP fractions in NMP at 25 °C. ⊖, from light scattering (upper c scale); ○, from SAXS (lower c scale).

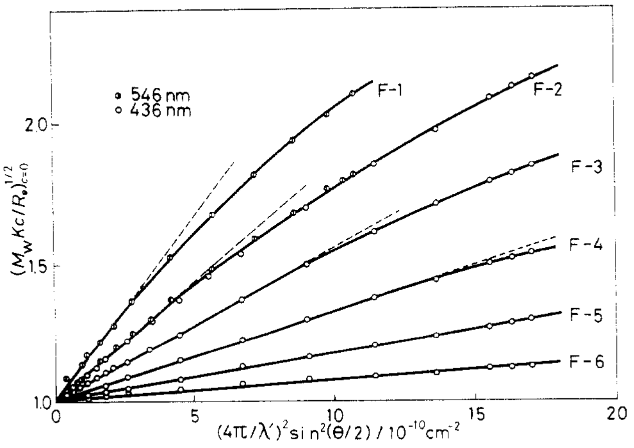

Figure 4. Angular dependence of light-scattering intensity at infinite dilution for indicated PIDP fractions in NMP at 25 °C.

Table I
Results from Small-Angle X-ray and Light Scattering Measurements on PIDP Fractions in NMP at 25 °C

fraction	$M_w \times 10^4$	$\langle S^2\rangle_z^{1/2}$, nm	A_2, $\times 10^{-4}$ mol cm^3 g^{-2}
F-1	237 (237)[a]	87.2	3.22
F-2	173 (171)[a]	71.0	3.53
F-3	128 (126)[a]	57.8	3.72
F-4	81.2 (80.8)[a]	44.6	3.95
F-5	51.6 (51.1)[a]	32.7	4.22
F-6	24.6 (24.4)[a]	21.6	5.49
F-7	16.0 (15.6)[a]	16.2 (±0.7)	4.9
F-8	10.3 (10.1)[a]	13.3 (±0.7)	5.1
F-9	5.52[b]	9.0 (±1.0)	
F-10	3.33[b]	7.1 (±0.5)	
f-1	1.92[c]	5.2 (±0.3)	12[c]
F-11	1.58[b]	5.0 (±0.2)	
f-2	0.990[c]	3.2 (±0.2)	17[c]
F-12	0.783[b]	2.9 (±0.1)	
f-3	0.650[c]	2.6	20[c]
f-4	0.405[c]	1.9	21[c]
F-13	0.367[b]	1.9	
f-5	0.260[c]	1.4[d]	22[c]

[a] Average of the previous[13] and present M_w values. [b] Previous data[13] from light scattering in trifluoroethanol. [c] From sedimentation equilibrium. [d] The effect of the finite chain thickness on $\langle S^2\rangle_z^{1/2}$ is negligible unless the diameter of the PIDP chain is larger than 1.0 nm (see the caption to Figure 6 for the estimated diameter).

Table II
Results from Viscosity Measurements on PIDP Fractions in NMP at 25 °C

fraction	$[\eta]$, $\times 10^2$ cm^3 g^{-1}	k'
F-1	6.44	0.33
F-2	5.02	0.33
F-3	3.97	0.34
F-4	2.87	0.37
F-5	2.06	0.39
F-6	1.23	0.39
F-7	0.926	0.39
F-8	0.680	0.37
F-9	0.490	0.41
F-10	0.335	0.42
f-1	0.239	0.45
F-11	0.204	0.46
f-2	0.157	0.50
F-12	0.126	0.52
f-3	0.114	0.63
f-4	0.0859	0.70
F-13	0.0800	0.64
f-5	0.0621	0.81

sequent data presentation and analysis.

Figure 5 shows the molecular weight dependence of $\langle S^2\rangle_z^{1/2}$ for PIDP in NMP. The data points for M_w above 5×10^4 obey the asymptotic relation $\langle S^2\rangle^{1/2} \propto M_w^{0.6}$ established for flexible polymers in good solvents, indicating that, at least in this molecular weight region, the PIDP molecule behaves as a random coil expanded by excluded-volume effect.

Table II presents the values of $[\eta]$ and k' for all the PIDP fractions in NMP at 25 °C. These $[\eta]$ values are plotted double-logarithmically against M_w in Figure 6. The solid curve fitting the plotted points slightly bends upward with slopes 0.64–0.73, but for M_w above 5×10^4 it is approximated by a straight line with a slope 0.70 (see the next section for the interpretation of the dashed line). The viscosity exponent 0.70–0.73 seems to be consistent with the above finding from $\langle S^2\rangle_z$ that high molecular weight PIDP in NMP is randomly coiled.

Discussion

Estimation of Unperturbed Dimensions. To estimate the unperturbed dimensions of PIDP in the given solvent NMP, we first apply Stockmayer and Fixman's plot[19] to the $[\eta]$ data in Table II. Figure 7 shows that the plot constructed is linear in a region of $M_w^{1/2}$ from 230 to 1100. Assuming $\Phi_{0\infty}$ (Flory's viscosity factor in the unperturbed state) to be 2.5×10^{23} mol^{-1}, we get a

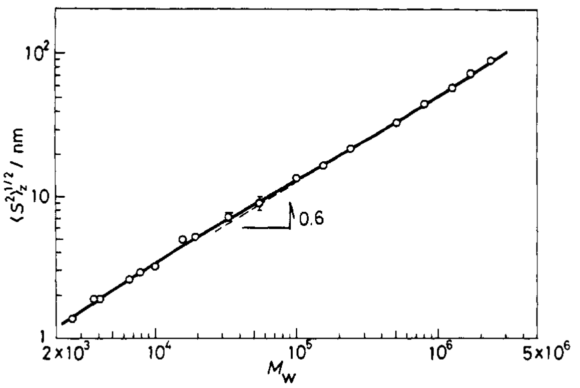

Figure 5. Molecular weight dependence of $\langle S^2\rangle_z^{1/2}$ for PIDP in NMP at 25 °C. Dashed line, asymptotic slope of 0.6; error bars, uncertainties of $\langle S^2\rangle_z^{1/2}$ indicated in Table I.

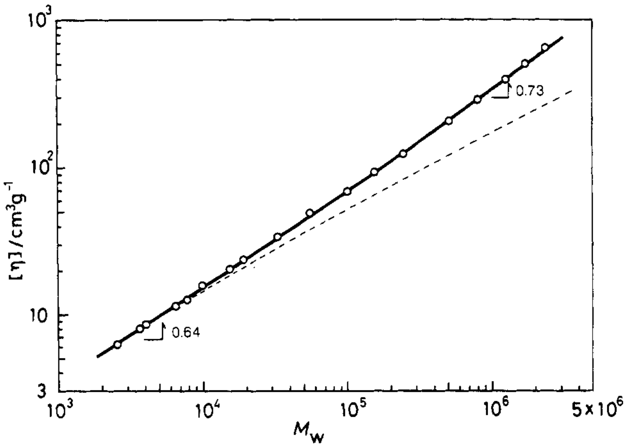

Figure 6. Double-logarithmic plot of $[\eta]$ vs M_w for PIDP in NMP at 25 °C. Dashed line, calculated from the theory of Yoshizaki et al.[18] for an unperturbed wormlike touched-bead chain with $q = 1.2$ nm, $M_L = 310$ nm^{-1}, $\Phi_{0\infty} = 2.5 \times 10^{23}$ mol^{-1}, and d (the diameter of a bead) = 0.86 nm.

value of 1.26×10^{-17} cm^2 for $(\langle S^2\rangle_0/M)_\infty$ from the ordinate intercept of the indicated straight line. Here, $\langle S^2\rangle_0$ denotes the value of $\langle S^2\rangle$ in the unperturbed state, and the subscript ∞ signifies the limit of infinite chain length (or the coil limit). The plotted points for $M_w^{1/2}$ below 230 progressively deviate downward from the straight line with decreasing $M_w^{1/2}$. This pronounced short-chain effect may be taken as a reflection of a finite stiffness of the PIDP chain.

We model low molecular weight PIDP in NMP by the Kratky-Porod wormlike chain[7] (without excluded volume). The well-known expression[12] for $\langle S^2\rangle_0$ of this model chain is

$$\langle S^2\rangle_0 = \frac{qL}{3} - q^2 + \frac{2q^3}{L}\left[1 - \frac{q}{L}(1 - e^{-L/q})\right] \qquad (5)$$

Here, q and L are the persistance length and the contour length of the chain, respectively. The latter is related to the molecular weight M by $L = M/M_L$ with M_L being the molar mass per unit contour length. When q is much smaller than M/M_L, eq 5 with $L = M/M_L$ is approximated by

$$\langle S^2\rangle_0 = (q/3M_L)M - q^2 \qquad (6)$$

the maximum deviation from the exact $\langle S^2\rangle_0$ value being 5% for $M/2qM_L > 6$. Equation 6 indicates that if this condition for $M/2qM_L$ is satisfied, q and M_L are separately estimated from a linear plot of $\langle S^2\rangle_z$ vs M_w.

Figure 8 shows that a linear relation as predicted by eq 6 approximately holds for our $\langle S^2\rangle_z$ data at low M_w.

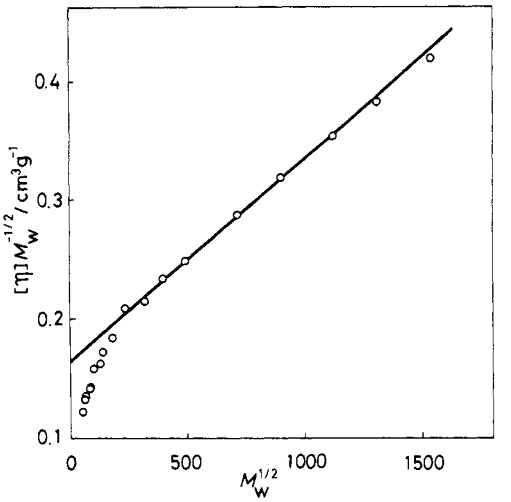

Figure 7. Stockmayer–Fixman plot for PIDP in NMP at 25 °C.

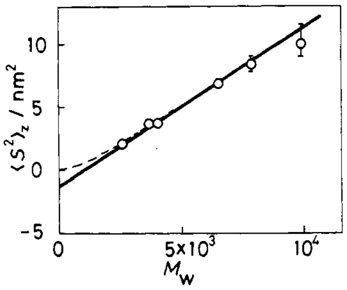

Figure 8. Plot of $\langle S^2\rangle_z$ vs M_w for low molecular weight fractions of PIDP in NMP. Dashed line, calculated from eq 5 with $q = 1.2$ nm and $M_L = 310$ nm^{-1}.

In drawing the straight line, we have ignored the data point with the large error bar at $M_w = 9.9 \times 10^3$. This line gives $q^2 = 1.4 \times 10^{-14}$ cm^2 and $q/3M_L = 1.28 \times 10^{-17}$ cm^2, which in turn yield 1.2 nm for q and 310 nm^{-1} for M_L. The value of 1.28×10^{-17} cm^2 for $q/3M_L$, i.e., for $(\langle S^2\rangle_0/M)_\infty$, is quite close to that (1.26×10^{-17} cm^2) estimated above from the Stockmayer–Fixman plot. The agreement convinces us that the unperturbed wormlike model for PIDP at low M_w ($<10^4$) is consistent with its perturbed random coil at high M_w ($>5 \times 10^4$). The dashed curve in the figure represents $\langle S^2\rangle_0$ calculated from eq 5 with $q = 1.2$ nm and $M_L = 310$ nm^{-1}.

The small intercept of the straight line in Figure 8 implies that, in the range of M_w studied, $\langle S^2\rangle_0$ of the PIDP chain is determined, to a great extent, by the ratio of q to M_L. Because of this feature, the separately estimated q and M_L values are not very accurate. Nevertheless, the M_L value of 310 nm^{-1} is compatible with the chemical structure of PIDP[20] and close to those (300–360 nm^{-1}) determined by Motowoka et al.[21,22] for poly(phthaloyl-*trans*-2,5-dimethylpiperazine) and poly(terephthaloyl-*trans*-2,5-dimethylpiperazine), the two polyamide isomers of PIDP, in various solvents. Our q of 1.2 nm in NMP is much smaller than the previously estimated values[13] for PIDP in other solvents (4.9 nm in *m*-cresol and 3.1 nm in trifluoroethanol). This finding exemplifies a strong solvent effect on chain stiffness, but at present no reasonable explanation for it can be made. Itou et al.[23] found that q of poly(hexyl isocyanate) also varies from 21 to 42 nm depending on the kind of solvent.

The dashed line in Figure 6 represents the values of $[\eta]$ calculated from the theory of Yoshizaki et al.[18] for an unperturbed wormlike touched-bead chain with $q = 1.2$

nm, M_L = 310 nm^{-1}, $\Phi_{0\infty}$ = 2.5 × 10^{23} mol^{-1}, and d (the diameter of a bead) = 0.86 nm. The last parameter value was chosen so that, for these q, M_L, and $\Phi_{0\infty}$, theoretical [η] values agree most closely with our data at low M_w. The theoretical curve is seen to start deviating from the data points at $M_w \sim 10^4$. Its slope for M_w above 5 × 10^4 is almost 0.5, the exponent expected for unperturbed long flexible chains, being consistent with the use of the Stockmayer–Fixman plot in this molecular weight region (see Figure 7).

In short, the PIDP molecule in NMP behaves like an unperturbed wormlike chain with q = 1.2 nm and M_L = 310 nm^{-1} below $M_w \sim 10^4$ and like a flexible chain perturbed by excluded-volume effect above $M_w \sim 5 \times 10^4$.

Excluded-Volume Effects on Dimensions. The Yamakawa–Stockmayer (YS) perturbation theory[9] for the radius expansion factor α_s of a wormlike bead chain is written in the form

$$\alpha_s^2 \equiv \langle S^2\rangle/\langle S^2\rangle_0 = 1 + (67/70)K(n_K)z + \ldots \quad (7)$$

with

$$z = (3/2\pi)^{3/2}Bn_K^{1/2} \quad (8)$$

and

$$B = \beta/2qb^2 \quad (9)$$

In these equations, $K(n_K)$ is a known function[9] of Kuhn's statistical segment number n_K ($\equiv M/2qM_L$) only, β the binary cluster integral for a pair of beads, and b the spacing of two adjacent beads along the chain contour. The first-order coefficient $67K(n_K)/70$ of the excluded-volume parameter z is essentially zero for $n_K \lesssim 1$ and approaches 134/105 for the coil limiting value as n_K increases.[9]

Yamakawa and Shimada[8] combined eq 7 with the Domb–Barrett (DB) equation[10] for α_s of a flexible chain to obtain[24]

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

with

$$z^* = (3/4)K(n_K)z \quad (11)$$

In the limit of $n_K = \infty$, z^* becomes equal to z and eq 10 reduces to the original DB equation. If z is increased indefinitely, the original DB equation gives $\alpha_s^2 = 1.55z^{2/5}$, which is substantially the same as the relation[26] derived on the basis of computer data:

$$\alpha_s^2 = 1.53z^{2/5} \quad (12)$$

Equations 7–11 along with eq 5 indicate that in Yamakawa and Shimada's scheme, the molecular weight dependence of $\langle S^2\rangle$ of a perturbed wormlike bead chain is determined by q, M_L, and B. For PIDP in NMP, only the last parameter remains to be determined. It was estimated as follows.

From eq 12 with $\langle S^2\rangle_{0\infty} = qM/3M_L$, we have

$$\langle S^2\rangle/M = 1.53(q/3M_L)(3/2\pi)^{3/5}B^{2/5}(M/2qM_L)^{1/5} \qquad n_K, z \rightarrow \infty \quad (13)$$

which predicts that, in the asymptotic limit (n_K, $z \rightarrow \infty$), $\langle S^2\rangle/M$ varies in proportion to $M^{1/5}$. Figure 9 shows our $\langle S^2\rangle_z$ data for M_w above 5 × 10^4 to bear out the predicted linearity. The indicated straight line with q = 1.2 nm and M_L = 310 nm^{-1} gives 0.16 for B.

In Figure 10, our radius of gyration data are compared with the theoretical curve (the solid line) computed from eq 10 and 5 with q = 1.2 nm, M_L = 310 nm^{-1}, and B = 0.16. The agreement is satisfactory throughout the entire range of molecular weight studied. The dashed line in the figure represents the theoretical $\langle S^2\rangle_0^{1/2}$ calculated for unperturbed PIDP (B = 0). It begins to deviate from data points at $M_w \sim 10^4$ as is the case for [η] in Figure 6. The Kuhn segment number at the M_w of 10^4 is about 10. Thus, the excluded-volume effects on $\langle S^2\rangle_z$ and [η] of PIDP in NMP become experimentally visible or practically significant when n_K exceeds 10. This n_K value, denoted below by n_{Kc}, is not very different from 3–5 predicted by Yamakawa and Shimada[8] from computer simulation for polymethylene-like chains, but it is appreciably smaller than the experimental value[3] of 50 for poly(hexyl isocyanate) (PHIC) with q = 42 nm in hexane. We note that neither Yamakawa and Shimada's computer simulation nor the YS + DB theory can explain the behavior of the PHIC chain essentially unperturbed up to this large n_K.

Since the relation $\langle S^2\rangle^{1/2} \propto M^{0.6}$ for fully perturbed coils holds for our data above $M_w \sim 5 \times 10^4$, the crossover of the PIDP chain from the substantially unperturbed to the fully perturbed state is found to range in M_w roughly from 10^4 to 5 × 10^4, i.e., in n_K from 10 to 70. In this region, the deviations of our $\langle S^2\rangle_z^{1/2}$ data from the unperturbed curve stay small, as can be seen in Figure 10. In contrast to the gradual change in $\langle S^2\rangle_z^{1/2}$ of PIDP, the crossover of the PHIC chain in hexane appears

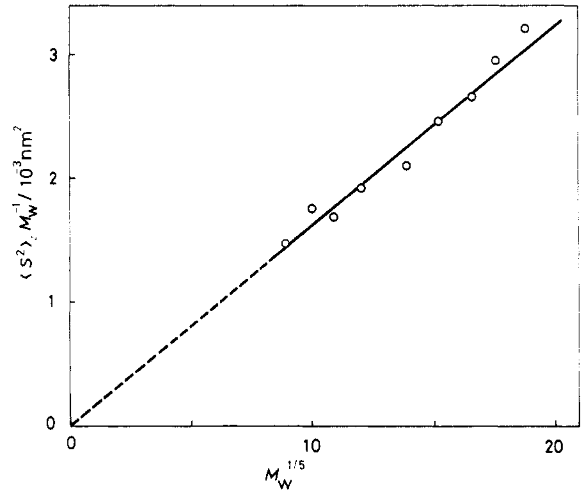

Figure 9. Plot of $\langle S^2\rangle_z/M_w$ vs $M_w^{1/5}$ for high molecular weight fractions of PIDP in NMP.

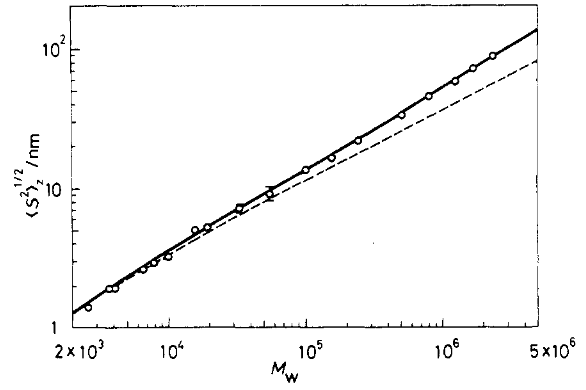

Figure 10. Comparison between theoretical and experimental radii of gyration. Circles, data for PIDP in NMP at 25 °C; solid line, calculated from eq 10, 11, and 5 with q = 1.2 nm, M_L = 310 nm^{-1}, and B = 0.16; dashed line, calculated from eq 5 with the same q and M_L values.

to occur suddenly at an n_K of about 50.[3,11] Thus, we find that the subtle difference in crossover behavior has led to the above-mentioned considerable difference in n_{Kc} between the two polymers.

In conclusion, the combination of the YS theory and the DB equation accurately describes the dimensional behavior of flexible PIDP in NMP over a wide range of molecular weight. This combined theory seems to lack something important only for stiff chains, since it fails to explain the crossover behavior of PHIC, a typical stiff polymer, in hexane.

Acknowledgment. We thank Professor A. Teramoto for valuable comments on this manuscript. The present SAXS experiment was made possible by the courtesy and guidance of Professor Y. Katsube and Dr. M. Sato of the Institute for Protein Research, Osaka University, to whom many thanks are due. Thanks are extended to a Grant-in-Aid for Scientific Research, the Ministry of Education, Science and Culture, Japan.

References and Notes

(1) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(2) Freed, K. F. *Renormalization Group Theory of Macromolecules*; John Wiley & Sons: New York, 1987.
(3) Norisuye, T.; Fujita, H. *Polym. J.* **1982,** *14,* 143.
(4) Fujita, H. *Macromolecules* **1988,** *21,* 179.
(5) Tsuji, T.; Norisuye, T.; Fujita, H. *Polym. J.* **1975,** *7,* 558.
(6) Huber, K.; Bantle, S.; Lutz, P.; Burchard, W. *Macromolecules* **1985,** *18,* 1461.
(7) Kratky, O.; Porod, G. *Recl. Trav. Chim. Pays-Bas* **1949,** *68,* 1106.
(8) Yamakawa, H.; Shimada, J. *J. Chem. Phys.* **1985,** *83,* 2607.
(9) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972,** *57,* 2843.
(10) Domb, C.; Barrett, A. J. *Polymer* **1976,** *17,* 179.
(11) Murakami, H.; Norisuye, T.; Fujita, H. *Macromolecules* **1980,** *13,* 345.
(12) Benoit, H.; Doty, P. *J. Phys. Chem.* **1953,** *57,* 958.
(13) Sadanobu, J.; Norisuye, T.; Fujita, H. *Polym. J.* **1981,** *13,* 75.
(14) Morimoto, Y. Ph.D. Thesis, Osaka University, 1987.
(15) Glatter, O. *J. Appl. Crystallogr.* **1974,** *7,* 147.
(16) Berry, G. *J. Chem. Phys.* **1966,** *44,* 4550.
(17) Norisuye, T.; Yanaki, T.; Fujita, H. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 547.
(18) Yoshizaki, T.; Nitta, I.; Yamakawa, H. *Macromolecules* **1988,** *21,* 165.
(19) Stockmayer, W. H.; Fixman, M. *J. Polym. Sci.* **1963,** *C1,* 13.
(20) The chemical structure of PIDP suggests that M_L be about 300 nm^{-1}.
(21) Motowoka, M.; Norisuye, T.; Fujita, H. *Polym. J.* **1977,** *9,* 613.
(22) Motowoka, M.; Fujita, H.; Norisuye, T. *Polym. J.* **1978,** *10,* 331.
(23) Itou, T.; Chikiri, H.; Teramoto, A.; Aharoni, S. M. *Polym. J.* **1988,** *20,* 143.
(24) The coefficient -1.39 of z^{*2} in the term $\exp(-0.85z^* - 1.39z^{*2})$ of eq 10 should be -0.67,[25] but the error has no significant effect.
(25) Suzuki, H. *Kaigai Kobunshi Kenkyu* **1985,** *31,* 205.
(26) (a) Lax, M.; Barrett, A. J.; Domb, C. *J. Phys. A.: Math. Gen.* **1978,** *11,* 361. (b) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978,** *11,* 1180.

Registry No. PIDP (copolymer), 52283-11-1; PIDP (sru), 32031-91-7.

Dynamics of Copolymer and Homopolymer Mixtures in Bulk and in Solution via the Random Phase Approximation[†]

A. Ziya Akcasu[*] and M. Tombakoglu

Department of Nuclear Engineering, The University of Michigan, Ann Arbor, Michigan 48109. *Received April 25, 1989*

ABSTRACT: The dynamics of copolymer and homopolymer mixtures with an arbitrary number of components both in bulk and in solution is studied within the framework of the mean field theory, and an expression of the first cumulant of the dynamic scattering function of a labeled component is obtained in terms of the static and dynamic single-chain properties and the Flory interaction parameters. In particular, a new result is obtained to relate the mobility of the labeled chain to the mobilities of the other components, treating one of the homopolymer species as the "matrix" and using incompressibility. The case of polymers in solution is studied as a special case by treating the solvent as the matrix. The new results differ from the reported theoretical results for binary homopolymer and copolymer solutions, as well as copolymers in a homopolymer matrix. The origin of this discrepancy is explained.

Introduction

In this paper we formulate the dynamic random-phase approximation[1] (or the mean field theory) in matrix form so that it can readily be applied to mixtures of homopolymers and copolymers with an arbitrary number of components both in bulk and in solution and comment on its relation to the formulation based on the Zwanzig–Mori[2] projection operator technique. The work presented in this paper is an extension of our earlier work on the same topic in which we considered only binary polymer blends and copolymer melts.[3] Specifically, we calculate the dynamic scattering function of a labeled polymer species in the presence of others, treating one of the homopolymer component as the "matrix". We obtain the expression for the first cumulant and the relaxation frequencies of various modes in terms of the dynamic and static properties of a single chain and the Flory κ parameters. The results are extended to polymers in solution by treating the solvent as the matrix in the general formulation. When specialized to the case of binary homopolymer and copolymer solutions, our results differ from those reported earlier by Benmouna et al.[4,5] in the calculation of the mobilities and relaxation frequencies.

[†] Dedicated to Professor Walther Burchard on the occasion of his sixtieth birthday.

0024-9297/90/2223-0607$02.50/0 © 1990 American Chemical Society