

Studies on dilute solution of rodlike macroions: Part 4 — Aggregation with enhanced interchain orientational correlation

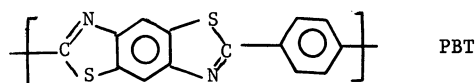
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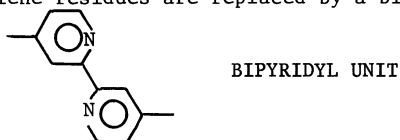
Abstract - Polarized and depolarized absolute intensity light scattering, photon correlation light scattering and viscometry studies are reported on solutions in methane sulfonic acid, MSA, poly(1,4-phenylene-2,6-benzobisthiazole), PBT, and copolymers of PBT containing a bipyridyl moiety in place of some of the phenylene residues. It is found that addition of the potassium salt of MSA to the solutions reduces the second virial coefficient and causes pronounced increase in the depolarized scattering, with accompanying changes in other properties studied. The photon correlation light scattering is analyzed in terms of pseudo-components comprising aggregates with substantial orientational correlation among the rodlike chain elements. This behavior may be in accord with predicted behavior for the phase equilibria for rodlike chains.

INTRODUCTION

Light scattering studies (ref. 1-3) on dilute solution of the polymer poly(1,4-phenylene-2,6-benzobisthiazole), PBT, have shown it to have a rodlike conformation, with a persistence length ρ comparable with or greater than the chain contour length L , and the polymer is known to be heavily protonated in the protic acids used to prepare its solutions. Despite the macroion character of the chain in solution, it has been found that (probably metastable) aggregates can exist in which the rodlike molecules are associated in parallel arrays (ref. 1,3). In this study, copolymers of PBT,



in which a small fraction of the phenylene residues are replaced by a bipyridyl unit are examined.



This unit introduces the possibility for rotational isomerizations that will reduce ρ , and make the root mean square radius of gyration R_G much smaller than its value $L/\sqrt{12}$ for a rodlike chain. The copolymers will be designated by the notation PBT-co-m, where $m/100$ is the mole fraction of the phenylene residues replaced in the copolymer. As illustrated by the rotational conformer shown for the bipyridyl unit, a staggered rodlike conformer is available to this PBT-co-m, which may explain the appearance of nematic solutions with the copolymer at high enough concentration. In this study, polarized and depolarized light scattering was used to determine the Rayleigh ratios $R_{VV}(q)$ and $R_{HV}(q)$, respectively, and photon correlation light scattering was used to determine the intensity autocorrelation function $g^{(2)}(\tau, q)$, all as a function of the polymer concentration c and the scattering angle θ , with $q = (4\pi/\lambda) \sin(\theta/2)$. With polydispersed samples, these are given in terms of summations over the scattering entities (ref. 1,3-5).

$$\frac{R_{VV}(0)}{K} = \sum_i M_i \left(1 + \frac{4}{5} \delta_i^2\right) c_i - 2 \sum_i \sum_j M_i M_j (A_2)_{ij} c_i c_j + \dots \quad (1)$$

$$\left(\frac{R_{VV}(q)}{c}\right)^0 = \left(\frac{1}{c} \sum_i R_{VV,i}(q)\right)^0 \quad (2a)$$

$$\left(\frac{R_{Vv,i}(q)}{Kc}\right)^0 = c^{-1} M_i c_i \left(1 + \frac{4}{5} \delta_i^2\right) \left\{1 - \frac{1}{3} J_i R_{G,i}^2 q^2 + \dots\right\} \quad (2b)$$

$$J_i^{-1} = \left[1 - \frac{4}{5} (f_1 \delta)_i + \frac{4}{7} (f_2 \delta)_i^2\right] / \left(1 + \frac{4}{5} \delta_i^2\right) \quad (2c)$$

$$\frac{R_{Hv}(q)}{K} = \frac{3}{5} \sum_i M_i c_i \delta_i^2 \left[1 - \frac{3}{7} f_{3,i} R_{G,i}^2 q^2 + \dots\right] \quad (3)$$

$$\left(\frac{g^{(2)}(\tau, q) - 1}{g^{(2)}(0, q) - 1}\right)^0 = \left\{\sum_i r_i(q) \exp(-\gamma_i q^2 \tau)\right\}^2 \quad (4a)$$

$$r_i(q) = \left(\frac{R_{Vv,i}(q)}{R_{Vv}(q)}\right)^0 \quad (4b)$$

Here, K is an optical constant, superscript (0) indicates a quantity extrapolated to infinite dilution, $R_{G,i}$ is the root-mean square radius of gyration for component i , having molecular weight M_i and concentration c_i , δ_i and the $(f_1 \delta)_i$ depend on the orientational correlation among the scattering elements in component i , $(A_2)_{ij}$ is an interaction coefficient, equal to the second virial coefficient for $i=j$, and γ_i is a constant for each i (for $R_{G,i} q$ less than about 3), conveniently expressed as a hydrodynamic radius $R_{H,i}$, with

$$R_{H,i} = kT/6\pi\eta_s \gamma_i \quad (5)$$

Equations 1-5 are most frequently applied to describe the effects of the molecular weight distribution of fully dissolved solute. Here, these expressions will be used to characterize the properties of pseudo-components representing the fully dissolved species as one pseudo-component (with neglect of its molecular weight distribution), and the aggregates as additional pseudo-components. This procedure is a useful approximation provided the pseudo-components (hereafter referred to simply as components) differ sufficiently in their properties (ref. 3). Data on any nonexponential nature of $(g^{(2)}(\tau, q))^{1/2}$ will be utilized to determine $r_i(q)$ and $R_{H,i}$ for the components. If the treatment is reasonable, it is expected that $R_{H,i}$ will be independent of q , but that $r_i(q)$ will vary significantly with q as dictated by Eqn. 2. The estimates for $r_i(q)$ can subsequently be used in analysis of $R_{Vv}(q)$ to determine approximations to $R_{G,i}$.

The solutions to be considered will be solutions of PBT or PBT-co-m in methane sulfonic acid, MSA, or in MSA in which the potassium salt of the acid is dissolved. With the latter solvent, A_2 appears to decrease toward zero, and a substantial increase in $R_{Hv}(q)$ is observed.

EXPERIMENTAL

The PBT-co-m copolymers were provided by Dr. R.C. Evers, Wright-Patterson Air Force Base, Ohio. They were received as dry powders prepared by precipitation from the polyphosphoric acid, PPA, polymerization solvent in water, followed by extensive washing in water to remove residual P_2O_5 . The PBT polymers used here are described in detail in (ref. 1). The MSA was distilled under vacuum and stored as described in (ref. 1-3). The potassium salt of MSA was prepared by titration of MSA with potassium hydroxide. The salt crystals were recrystallized from water and dried for use. Polymers were dried under vacuum prior to use. Solutions in MSA containing the salt were prepared in two ways with PBT-co-5: the polymer was dissolved in MSA containing the salt or the salt was dissolved in a solution of the polymer in MSA. Solutions of PBT were prepared by the latter method.

The light scattering methods used here are those described in (refs. 1 and 3). Solutions were prepared for light scattering by dilution of a stock solution with the appropriate solvent. Before dilution, the stock solution was subjected to sonication for 1 hour, followed by centrifugation (ca 5000 G) for 24 hrs to reduce aggregation (ref. 3). The stock solution was then diluted and filtered through a 2-5 μ m teflon membrane filter into light scattering cells (5 ml volume). The cell was sealed under vacuum to prevent contamination by moisture, which is known to promote aggregation. Light scattering data were obtained directly on these solutions, as well as these solutions after an additional period of centrifugation (24 hr) using a swing-bucket rotor. In no case did this result in detectable removal of the solute.

Photon correlation data were obtained with 514.5 nm wavelength light. Fluorescence and absorption corrections to the observed intensities were made as in (ref. 1). In part, fluorescent contribution to the measured intensity was minimized by placing a narrow band-pass interference filter centered at the wavelength λ_0 of the incident beam in front of the photomultiplier. Fluorescence at this wavelength could affect estimates of the observed scattering (especially $R_{Hv}(q)$). The (relative) scattering I_+ between crossed polars was routinely measured at 20 nm increments over the range from 50 nm below λ_0 to 700 nm using

an interference filter with variable transmission along its length (Oriel, model 57480). In this way, true $R_{Hv}(q)$ scattering was readily apparent in comparison with fluorescence at λ_0 . In addition, the interpolated fluorescence at λ_0 and a convenient wavelength λ_1 about 30 nm larger than λ_0 could be determined. These data were subsequently used to deduce fluorescence corrections needed to compute $R_{Vv}(q)$ and $R_{Hv}(q)$ from experimental data on the observed intensities at λ_0 and λ_1 .

Solution viscosities were measured with a suspended level, Cannon-Obbelohde viscometers, making sequential dilutions in the viscometer. The solution was maintained under dry N_2 at all times. Data on the relative viscosity $\eta_{rel} = \eta/\eta_s$, with η_s the solvent viscosity, were analyzed with the expressions ($\eta_{sp} = \eta_{rel} - 1$):

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c + \dots \tag{6}$$

$$\frac{\ln \eta_{rel}}{c} = [\eta] - (\frac{1}{2} - k')[\eta]^2 c + \dots \tag{7}$$

$$[\eta]_c \equiv c^{-1} [2(\eta_{sp} - \ln \eta_{rel})]^{1/2} \tag{8a}$$

$$[\eta]_c = [\eta] - (\frac{1}{3} - k') [\eta]^2 c + \dots \tag{8b}$$

Of these, $[\eta]_c$ is often found to be nearly independent of c over the range of c of interest inasmuch as $k' \approx 1/3$.

RESULTS

Solutions in methane sulfonic acid

The viscometric results are conveniently given in terms of $[\eta]_c$. For most polymer solutions, $[\eta]_c$ is a close approximation to $[\eta]$. For some of the solutions studied here, $[\eta]_c$ exhibited dependence on c that could be empirically represented by the empirical expression

$$[\eta]_c^{-1} = [\eta]_{APP}^{-1} + mc^{1/2} \tag{9}$$

Values of $[\eta]_{APP}$ may most reliably be considered to represent $[\eta]$ when m is zero. Examples are known (ref. 2) for which $[\eta]_c$ could be fitted by Eqn. 9 for $[\eta]_c > 0.05$, but for which deviation occurred for smaller c such that $[\eta]_{APP} > [\eta]$. Nevertheless, with the solutions studied here, Eqn. 9 appears to apply to c as low as could be studied, so we will consider that $[\eta]_{APP}$ is a reasonable approximation to $[\eta]$. Values of $[\eta] \approx [\eta]_{APP}$ and $\partial[\eta]^{-1}/\partial c^{1/2}$ are listed in Table 1.

TABLE 1. Light scattering and viscometric data on solutions in methane sulfonic acid

Polymer	PBT-co-5 No salt	PBT-co-5 with salt ^a	PBT-72 ^b No salt	PBT-72 with salt ^c
X	0.05	0.05	0	0
ρ/nm	19	19	--	--
$[\eta]/m1g^{-1}$	1,250	610	1,620	970
$[\eta]^{1/2} \partial[\eta]^{-1} / \partial c^{1/2}$	0.92	0	0	-0.47
$(R_{Vv}(0)/Kc)^0$	100,000	250,000	34,000	1,500,000
$\{\partial \ln(c/R_{Vv}(0))^{1/2} / \partial c\}^0 / m1g^{-1}$	1,500	0	1,030	2,100
$\{3[\partial \ln(c/R_{Vv}(0)) / \partial q^2]^0\} / nm$	40	50-100	43	315
$(5/3)(R_{Hv}(0)/Kc)^0$	< 100	6,500	3,300	33,000
$\{\partial \ln(c/R_{Hv}(0))^{1/2} / \partial c\}^0 / m1g^{-1}$	--	-400	0	0
$[(7/3)(\partial \ln(c/R_{Hv}(0)) / \partial q^2)^0] / nm$	--	30-50	24	60
$R_{H,1} / nm$	3-5	4	13	5.3
$R_{H,2} / nm$	17-30	9-14	--	40
$R_{H,3} / nm$	--	110-180	--	180

a) 0.45N for $[\eta]$; 0.56N for the light scattering data b) Data from reference 1
 c) 1.0N for $[\eta]$; 0.3 N for the light scattering data

For the solutions of PBT-co-5, $R_{HV}(q)$ is negligibly small. Thus, for the data shown in Fig. 1, the relative intensity I_+ observed between crossed polars over the wavelength 480 to 700 nm with 514 nm wavelength incident light is smaller, and not larger than the fluorescence excitation at 514 nm. Centrifugation of these solutions produced only modest effect on $R_{VV}(0)$ as shown in Fig. 2. Data on $g^{(2)}(\tau, q)$ were found to be nonexponential for solutions of PBT-co-5, and could be analyzed with Eqn. 4. This effect is pronounced for the solutions prior to centrifugation, giving rise to components with $R_{H,i}$ equal to 3-5 and 17-30 nm, see Table 1; in calculation of R_H with Eqn. 5, $\eta_s/\text{Pa}\cdot\text{s}$ for MSA is equal to $8.64 \times 10^{-7} \exp(2800/T)$. Data on $r_i(q)$ and $R_{H,i}$ for solutions of PBT-co-5 in MSA are given in Fig. 3. The component with $R_{H,i} = 17-30$ nm dominates the data on $R_{VV}(q)$. Parameters deduced from $c/R_{VV}(q)$ are listed in Table 1.

Fig. 1 The relative depolarized intensity I_+ as a function of the wavelength λ for 514.5 nm wavelength excitation: --- 0.51 g/l in MSA, and — 0.51 g/l in MSA with 0.56N of the potassium salt of MSA.

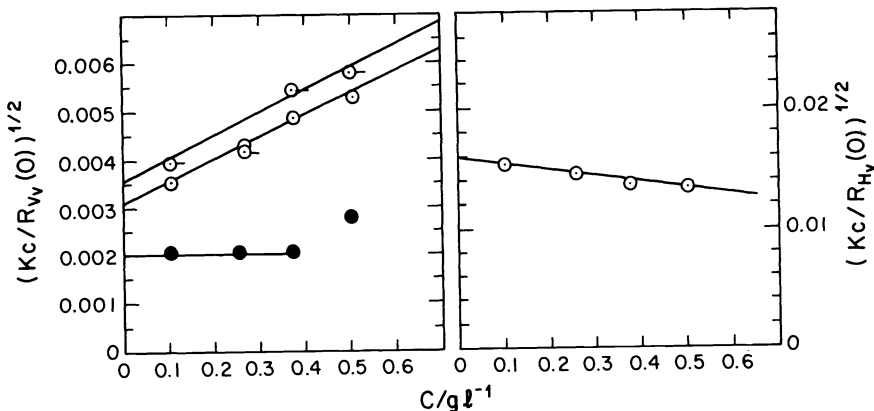
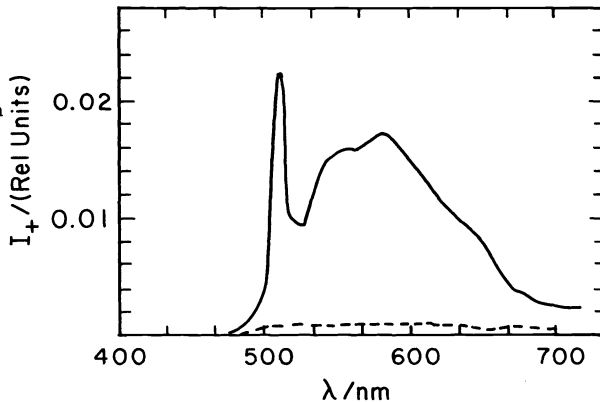


Fig. 2. Light scattering data on solutions of PBT-co-5. Right: $(Kc/R_{VV}(0))^{1/2}$ vs c for solutions in MSA, \square , filtered solution, \diamond , centrifuged sample, and in MSA containing 0.56N of the potassium salt of MSA, \bullet ; Left: $(Kc/R_{HV}(0))^{1/2}$ vs c for solutions in MSA containing 0.56N salt as above.

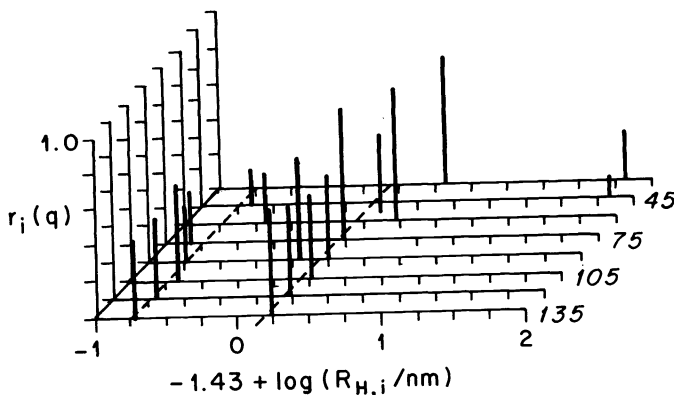


Fig. 3. Representative data for $R_{H,i}$ and $r_i(q)$ for the scattering angles $30 \leq \theta \leq 135$ as labeled. The data are for PBT-co-5 in MSA with $c = 0.25$ g/l.

Solutions in methane sulfonic acid containing salt

As above, the viscometric data are presented in terms of $[\eta]_c$. Estimates of $[\eta] \approx [\eta]_{APP}$ and $\partial[\eta]_c^{-1}/\partial c^{1/2}$ obtained with Eqn. 9 are entered in Table 1 for solutions containing the potassium salt of MSA.

As shown in Fig. 1, addition of salt to solution of PBT-co-5 in MSA results in a marked increase in the fluorescence I_{\perp} over a wide range in wavelength, along with a clear marked increase in $R_{HV}(q)$. The results for $Kc/R_{HV}(0)$ and $Kc/R_{VV}(0)$ are given in Fig. 2, and parameters extracted from the data on $Kc/R_{VV}(q)$ and $Kc/R_{HV}(q)$ are listed in Table 1. Since the effects observed are about the same for solutions prepared by dissolving the polymer in MSA containing salt, or by dissolving the salt in MSA containing the polymer, these are not distinguished here. Analysis of $g^{(2)}(\tau, q)$ for solutions of PBT-co-5 with Eqns. 4-5 results in three components. Values of $R_{H,i}$ are given in Table 1; in calculating $R_{H,i}$ from γ_i , η_s is computed from $\partial(\eta_s/mPa \cdot s)/\partial(m/mol \ l^{-1}) = 0.142$, with m the concentration of the salt. Use of the corresponding data on $r_i(q)$ and Eqn. 2 provide estimates for $(R_G^2/M)_i$. For PBT-co-5, over most of the scattering angles, the scattering is dominated by the component with $R_{H,i} = 9-14$ nm. Consequently, the estimate of $[3(R_{VV}(0)/c)^0(\partial(c/R_{VV}(q))/\partial q^2)^0]^{1/2}$ for this component is similar to that obtained for the total scattering if the analysis is restricted to scattering angles above 60 deg., namely about 100 nm. Qualitatively, similar results were obtained for solutions containing 1 and 1.5N salt.

With PBT, the solution in MSA exhibits $R_{HV}(q)$ scattering appropriate to the molecular anisotropy δ of the rodlike chain (ref. 1). Addition of the potassium salt results in 5 to 10-fold increase in $R_{HV}(0)$, as shown in Fig. 4. Similarly, $R_{VV}(0)$ is increased appreciably, see Fig. 4, and $g^{(2)}(\tau, q)$, which is essentially an exponential function for the solution in MSA, is markedly nonexponential with the addition of salt. Values of $R_{H,i}$ are entered in Table 1. The component with largest $R_{H,i}$ dominates $R_{VV}(0)$, although this component is not necessarily present in large concentration.

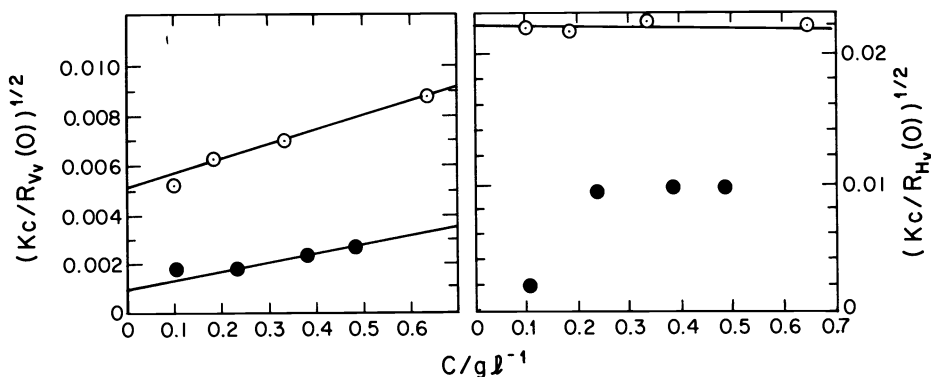


Fig. 4. Light scattering data for PBT-72. Right: $(Kc/R_{VV}(0))^{1/2}$ vs c for solutions in MSA, \circ , and in MSA containing 0.3N of the potassium salt of MSA, \bullet ; Left: $(Kc/R_{HV}(0))^{1/2}$ vs c with the symbols identified as above.

DISCUSSION

Solutions in MSA

The depolarized scattering is given in terms of the optical anisotropy δ by the expression

$$R_{HV}(0) = \frac{3}{5} Kc M_w \delta^2 \tag{10}$$

$$\delta^2 = \delta_0^2 \left(\frac{1}{n} \right)^2 \sum_i \sum_j \frac{3 \langle \cos^2 \gamma_{ij} \rangle - 1}{2} \tag{11}$$

with the sums over all of the rodlike chain segments, where γ_{ij} is the angle between the optical axes of segments i and j , each of which has an intrinsic optical anisotropy δ_0 ($\delta_0 = 0.5$ for PBT). For the copolymers studied here, in the extreme case with no rotational restriction at the bipyridyl unit Eqn. 10 becomes

$$R_{Hv}(0) = \frac{3}{5} Kc(M_R)_w \delta_0^2 \quad (12)$$

where M_R is the molecular weight of the rodlike PBT chain sequence in the copolymer. If the fraction $(1-x) > 0$ of the phenylene moieties replaced by bipyridyl units are randomly distributed, then $(M_R)_w \approx m_0(2-x)/x$, where m_0 is the PBT repeat unit molecular weight ($m_0 = 266$). With $\delta_0 = 0.5$, it is seen that $R_{Hv}(0)$ is small for the value of x of interest here. An improved estimate for $R_{Hv}(0)$ can be made using Eqn. 11 for δ provided the orientational distribution among the segments is known. For the wormlike chain model, which should be reasonable for the fully dissolved copolymers, Eqn. 11 gives (ref. 4,6-8)

$$\delta^2 = \delta_0^2 (2\rho/3L) \{1 - (\rho/3L)[1 - \exp(-3L/\rho)]\} \quad (13)$$

where ρ is the persistence length, L the chain contour length, δ_0 the intrinsic anisotropy, and ℓ the length of a chain element with molecular weight m_0 . For the wormlike chain (ref. 4)

$$R_G^2 = \frac{L\rho}{3} S(\rho/L) \quad (14a)$$

$$S(y) = 1 - 3y + 6y^2 - 6y^3[1 - \exp(-y^{-1})] \quad (14b)$$

$$S(y) \approx (1 + 4y)^{-1} \quad (14c)$$

For a polydispersed polymer with a Schulz-Zimm distribution of M , the light scattering averaged mean square radius of gyration is given by

$$R_{G,LS}^2 = \frac{L_z \rho}{3} \bar{S}(\rho/L_z) \quad (15a)$$

$$\bar{S}(y) = 1 - 3y + 6y^2 \frac{h+2}{h+1} - 6y^3 \frac{(h+2)^2}{h(h+1)} \left\{ 1 - \left[1 + \frac{1}{y(h+2)} \right]^{-h} \right\} \quad (15b)$$

$$\bar{S}(y) \approx [1 + 4y(h+2)/(h+3)]^{-1} \quad (15c)$$

where $1+h^{-1} = M_w/M_n$ and $L_z = M_z/M_L = (h+2)M_w/(h+1)M_L$; with M_L the mass per unit length. Using Eqn. 15 data on $\partial[Kc/R_{Vv}(q)]/\partial q^2$ provide an estimate for $\rho[(h+2)/(h+1)]\bar{S}(\rho/L_z)$. With the copolymers of interest here, $R_{G,LS}^2$ must also be averaged to account for the distribution of the chain lengths ℓ_1 between the bipyridyl moieties. If the latter is independent of L , then for small ρ/L , $\bar{S}(\rho/L_z) \approx 1$ and a simple arithmetic average over the distribution of ρ is appropriate. Thus, with Eqn. 15,

$$\bar{S}(\rho/L_z) = 9M_L \frac{(h+1)}{(h+2)} \lim_{q \rightarrow 0} \frac{\partial[Kc/R_{Vv}(q)]}{\partial q^2} \quad (16)$$

Calculations of R_H for the wormlike chain models (ref. 9) can be represented by the relation

$$R_H = L/2 [(27L/16\rho)^{\epsilon/2} + \ln^\epsilon (3L/2a)]^{-1/\epsilon} \quad (17)$$

where a is the chain diameter and $\epsilon=2$, so that for small ρ/L , $R_H \approx 2R_G/3$, as expected for a flexible chain polymer.

An estimate for ρ for the copolymers of interest here may be obtained by representing the chain as a sequence of rodlike elements of length $\ell_1 = M_p/M_L$ alternating with elements of length ℓ_2 equal to the distance between the centers of adjacent pyridyl rings, with a fixed angle α between successive elements. Then, (ref. 10)

$$2\rho = \frac{\ell_1^2 + \ell_2^2}{\ell_1 + \ell_2} \left\{ \frac{1+q}{1-q} - \frac{2(\ell_1 - \ell_2)^2}{\ell_1^2 + \ell_2^2} (q + q^3) \right\} \quad (18)$$

where $q = \cos \alpha$. Since $\ell_1 \gg \ell_2 \approx 0.44$ nm, $\ell_1 \approx (M_R)_n/M_L \approx \ell/x$ if random placement of the bipyridyl units is assumed, where $\ell = m_0/M_L$, and the factor in brackets is about equal to 1.54.

The M_w obtained for PBT-co-5 is unexpectedly large for a step-growth polymer. Moreover, analysis of $g^{(2)}(\tau, q)$ with Eqn. 4 reveals two (pseudo) components, with the major

contribution to $g^{(2)}(\tau, q)$ having $R_H \approx 17-30$ nm over the range of c studied, with a minor contribution having $R_H \approx 3-5$ nm. The latter is attributed to low molecular weight rodlike chains with contour length $L_z \approx 15$ nm that is smaller than the length $(M_R)_z/M_L \approx 70$ nm expected between bipyrindyl units with PBT-co-5. The component with $R_H \approx 17-30$ nm is essentially the only contribution to $R_V(q)$. The estimate $\rho \bar{S}(\rho/L_z)$ estimated with the latter using Eqn. 16 is smaller than expected (e.g. 11 nm even if the factor $(h+1)/(h+2) \approx 1$). Moreover, using Eqn. 17, the observed R_H correspond to calculated M_z smaller than the observed M_w . These disparities are attributed to aggregation, which results in a supramolecular structure containing several chains. The viscometric data are in accord with this conjecture. Thus, in general,

$$[\eta] = K\pi N_A R_G^2 R_H M^{-1} \quad (19)$$

with $K=1$ for rodlike chains and $K=3$ for flexible chain polymers with large M . With the estimate $R_H \approx 20$ nm and $R_G^2/M_w = 3 \partial[Kc/R_{VV}(q)]/\partial q^2 \approx 0.016$ nm² d⁻¹, use of Eqn. 19 gives $[\eta] \approx 1800$ ml g⁻¹, in comparison with the observed value of 1250 ml g⁻¹ with Eqns. 8 and 9 in the limit of infinite distribution, whereas $[\eta]_c$ decreases with increasing c (e.g., $\partial[\eta]^{-1}/\partial c^{1/2} \approx 0.026$ ml^{1/2} g^{-1/2}). The supramolecular structure is considered to have a configuration similar to that for a randomly branched polymer. Hence, Eqn. 19 provides a reasonable estimate for $[\eta]$, and $R_H \approx 2R_G/3$. With such a structure, for a strong excluded volume effect, it is reasonable to use the approximation $A_z M_w \approx [\eta]_c$ at each c , so that $R_{VV}(0)$ can be expressed in the form

$$\frac{Kc}{R_{VV}(0)} = (M_{w,0} v_w)^{-1} (1 + [\eta]_c c)^2 \quad (20)$$

where $M_{w,0}$ is the true molecular weight, and v_w is the degree of association, dependence on c . With Eqn. 20, $M_{w,0} v_w$ increases two-fold over the range of c studied, with $M_{w,0} v_w \approx 10(M_R)_w$ at infinite dilution, where $(M_R)_w$ is the calculated molecular weight of the rodlike chain sequences.

Solutions in MSA containing salt

The substantial changes in $R_{VV}(q)$ and $R_{HV}(q)$ caused by the addition of the potassium salt of MSA are attributed to enhanced intermolecular orientational and spatial order. With PBT, this effect results in a large increase in v_w , with considerable orientational orientation among the rodlike chains in the aggregates. Thus, data on $R_{VV}(0)$ and $R_{HV}(0)$ gives v_w from (see Eqns. 1-3)

$$(M_D)_w v_w = \left(\frac{R_{VV}(0)}{Kc} - (4/3) \frac{R_{HV}(0)}{Kc} \right)^0 \quad (21)$$

where M_D the molecular weight of the rodlike chain. Comparison of the data on solutions without salt ($v_w \approx 1$) with data for the solution containing salt gives $v_w \approx 50$ for the latter. With the expression

$$R_{HV}(0) = \frac{3}{5} Kc (M_D)_w v_w \delta_0^2 g_2 \quad (22)$$

the data on $(R_{HV}(0)/c)^0$ give $g_2 = 0.2$ for the orientational correlation among the rodlike chains in the aggregates. Lacking a model for the supramolecular structure, g_2 cannot be directly interpreted, but it is assumed that $\langle \cos^2 \theta \rangle$ is common for all chains, where θ the angle between the axes of two chains, with the average carried out over all such pairs, then

$$g_2 = \frac{3 \langle \cos^2 \theta \rangle - 1}{2} \quad (23)$$

and the results indicate a tendency for the chains to tend towards a parallel array in the aggregate.

The data on $R_{VV}(0)/c$ for the three larger concentrations give $\partial \ln(c/R_{VV}(0))/\partial c \approx 2100$ ml, which is larger than the corresponding value obtained (ref. 1) in MSA (e.g., Table 1). In addition, the data give very large $R_{VV}(0)/c$ for the smallest c and $[\eta]_c$ decreases with increasing c . The latter suggest that the state of aggregation, or the structure of the aggregates change with c , making detailed interpretation of the dependence on c hazardous.

The data on $g^{(2)}(\tau, q)$ for the PBT solution containing salt exhibits a component with $R_H \approx 40$ nm that dominates the scattering at most angles. Additional components with $R_H \approx 5-7$ nm and very large R_H (variable with c , in the range 400 to 4000 nm) are also observed. Application of Eqns. 1-4 to the data on $R_{VV}(q)$ results in an estimate of 40 nm for $J^{-1} R_G$ for the component with $R_H \approx 40$ nm. The latter is similar to the data reported (ref. 1) for the polymer in the solution in MSA, but R_H is larger than the value of 13 nm reported for the MSA solution, suggesting that this component may be sheath like in its overall shape, with a large number of the rodlike molecules packed in a more-or-less parallel array. Since the

data do not provide a relative concentration of the components, an estimate for the molecular weight of the component, and hence its degree of association is not directly available. The components with large R_H also exhibit values for $b_{V_V}^2 = -3 \ln[R_{V_V}(q)r_i(q)]/q^2$ for small q that are large and variable with c (e.g., b_{V_V} 200-250 nm). The data on $b_{H_V}^2 = -(7/3) \ln[R_{H_V}(q)]/q^2$ give a large correlation length, e.g., b_{H_V} 30 nm. As shown in Fig. , the data at the lowest c studied show more intense $R_{V_V}(0)$ scattering than that for the larger c , with even larger b_{H_V} . Since arrangement of the rodlike chains in the supramolecular structure is unknown, f_3 (e.g. Eqn. 3) is not known and R_G cannot be computed from b_{H_V} . Nevertheless, it is evident that the solution contains large aggregates with the chain with their axes nearly parallel.

Similar effects are observed with PBT-co-5 in that $R_{H_V}(q)$ is increased substantially on the addition of salt, with an accompanying increase in $(R_{V_V}(0)/c)^0$. In addition, $\partial[Kc/R_{V_V}(q)]/\partial q^2$ is not independent of c and a component with $R_H \approx 110-180$ nm appears in the contribution to $g^{(2)}(\tau, q)$. The modest increase in $(R_{V_V}(0)/c)^0$ obtained on the addition of salt shows that relatively little additional association in comparison with the MSA solution. Rather, it appears that the principal effect is to increase the orientational correlation among the chains in the aggregates, e.g., the increased $R_{H_V}(q)$. The negligible variation of $[\eta]_c$ with c indicates that these aggregates are (meta) stable toward dilution. In that case, the negligible dependence of $c/R_{V_V}(0)$ on c indicates that $A_2 \approx 0$. The similar value of $R_{H,i}$ and for the major component in MSA and one of the major components in the salt solution shows that the overall shape of some of the aggregates is not much altered by the addition of salt --the components with larger $R_{H,i}$ observed with the salt solution may be caused by aggregation of the smaller aggregate structure.

Theoretical studies on the phase equilibria (ref. 10,11) of mesogenic polymer solutions suggest that if A_2 is small enough and c large enough, the mesogenic solutions will separate into two phases, a disordered solution with very small c , and an ordered solution with large c . Such effects have been reported with solutions of poly(benyl-L-glutamate) for concentrated solutions (ref. 13). This phase separation could be promoted by the creation of supramolecular aggregates, which effectively increases the local concentration c_{loc} for the polymer in the aggregates. It is possible that the effect on $R_{H_V}(q)$, etc. observed on the addition of salt to MSA solutions is caused by the predicted phase separation for small A_2 , with the effect being enhanced here, because $c_{loc} > c$. Similar considerations may be responsible for the marked tendency of rodlike chains to exhibit aggregation since the dissolution process requires passage through a concentrated solution, which may be unfavorable unless the effective polymer interactions are strongly repulsive (i.e. unless A_2 is large and positive).

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