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Orientation fluctuations in concentrated solutions of hairy-rod polymers*)

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*) *Dedicated to Prof. E.W. Fischer on the occasion of his 65th Birthday. His intuitive judgment of results and interpretation based on his "Welt Bild" of Polymer Science is being proven to be correct so far*

Abstract: Photon correlation spectroscopy in the depolarized geometry was employed to measure the orientation relaxation correlation function $C(q,t)$ in poly(p-2,5-dodecyl-1,4-phenylene)/toluene solutions at different scattering wavevectors q. The large optical anisotropy of this hairy rod molecule with an average length $L = 117$ nm allowed a detailed analysis of both amplitude and shape of $C(q,t)$ that revealed two mechanisms for relaxing the orientation fluctuations in the concentrated regime ($10 < cL^3 < 230$). The comparison of the rotational diffusivity and the anisotropic scattering intensity with theoretical, simulation and experimental results of rigid rods indicated quantitatively different behavior for the present stiff-chain bearing two long side groups per repeating unit.

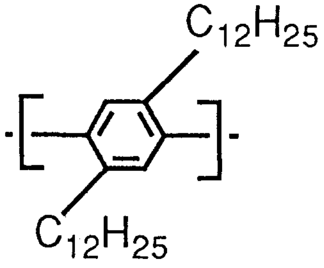
Key words: Photon correlation spectroscopy – orientation relaxation – rotational diffusion – hairy rod polymers

Introduction

Rigid-rod polymers present unique behavior as compared to their flexible counterpart mainly due to the high anisotropic shape of these objects. This shape appears to be the dominant factor that enables rod-like polymers to exhibit characteristic features such as anisotropic diffusion, rotation-translation coupling, enhancement of the topological effects and formation of mesophases [1–5]. On the theoretical side, a cage theory based on reptation arguments [1] and computer simulations [6, 7] have attempted to elucidate the underlying mechanisms for translational and rotational mobilities and predict the dependence of the corresponding transport coefficients on the molecular length (L) and concentration (c).

On the experimental side, investigations of the orientational relaxation and rotational diffusivity, which are of primary interest, are very rare [2, 3]. Rotational motion mainly of poly(γ-benzyl-L-glutamate) in solution and very recently F-actin has been studied by electric birefringence [8, 9] and dynamic light scattering [9–12]. In both experiments, the presence of large inherent anisotropy in the optical polarizability is highly desirable. In this case, employment of the powerful dynamic light-scattering technique, photon correlation spectroscopy (PCS) in the depolarized geometry, will allow a thorough study of the orientational dynamics over a broad time range (10^{-7}–10^3 s).

In this communication, we measure the orientation relaxation function $C(q,t)$ of poly(p-2,5-dodecyl-1,4-phenylene) (PPP)



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in toluene solutions by PCS. Introduction of the flexible side chain is necessary in order to increase the solubility of these anisotropic rods. Based on the high optical anisotropy of this system, $C(q,t)$ has been recorded at different scattering wave vectors q, over the concentration range 1.4 to 33 mg/cm^3 corresponding to 10–230 rods/L^3. The variation of the relaxational characteristics in this hairy rod polymer system with c and q is discussed in the framework of the cage theory [1, 11] and simulations [6, 7]. Two distinct relaxation modes contribute to the orientation function with q and c dependent amplitudes. The rotation diffusion coefficient obtained from the slow relaxation process in the concentrated regime scales with c^{-2}.

Theoretical background

The length L and the diameter b of the molecule define three concentration regimes in which rod-like polymers can, in principle, exhibit different dynamic behavior. The characteristic number concentration $c^* = 1/L^3$ and $c^{**} = 1/(bL^2)$ define the dilute, semidilute and concentrated regions. In the dilute region ($cL^3 < 1$) the orientation correlation function $C(q,t)$ for short ($qL < 1$) rod-like polymers with optical anisotropy β is a single exponential decay function [13]

$$C(q,t) = N\beta^2 \exp\left[-\left(q^2D + 6D_r\right)t\right], \tag{1}$$

where D, D_r, respectively, the translational and the rotational diffusion coefficients in the dilute region, are given by [3]:

$$D_0 = (k_B T/3\pi\eta_s L) \times [\ln(2L/b) - 1/2(\gamma_{||} + \gamma_\perp)] \tag{2a}$$

$$D_{r,0} = (3k_B T/\pi\eta_s L^3)[\ln(2L/b) - \zeta], \tag{2b}$$

with η_s being the solvent viscosity and $\gamma_{||}$, $\gamma_\perp$, and ζ are functions of the aspect ratio (L/b). In practice, this regime can hardly be reached due to the very weak scattering amplitude. When $c/c^* > 1$ the motion of each rod is expected to be hindered by its neighbors. However, as long as $c/c^* < 20$ excluded volume effects on the dynamic properties can be ignored as inferred from translational diffusion data [2]. As the concentration is increased beyond c^{**} the repulsive interactions among rods in the crowded suspension lead to an ordered mesophase, even in the absence of any specific interactions between rods or rods and solvent molecules. This phase transition occurs at about a critical concentration $c_n/c^{**} \approx 5$ or $c_n/c^{**} \approx 10$ according to Onsagar and Flory, respectively [3]. Morever, a suspension of rigid rods is predicted [11] to retain isotropic random orientation as long as $c/c^* < 2.3$; of course, some ordering can occur below this concentration. As the concentration is increased beyond $c/c^* > 20$, the enmeshment of the rodlike polymers should become evident in both the polarized and depolarized dynamic light scattering. For the latter, $C(q,t)$ was calculated numerically by Maeda [14] at the entire q and t region, reformulating the DSO theory [15] for the polarized dynamic light scattering:

$$C(q,t) = \frac{1}{4\pi}\int_t^\infty dt' = \int d\mathbf{u}\, E(\mathbf{q},\mathbf{u}) \times \exp(-t'\Omega_\mathbf{q})\,\Theta_\mathbf{q}\,E^*(\mathbf{q},\mathbf{u}), \tag{3}$$

where $\mathbf{u}$ is the orientation of the rod, $E(\mathbf{q},\mathbf{u}) = \alpha_{VH}$ $S(\mathbf{q},\mathbf{u})$ is the q-component of the electric field of the VH scattered light, $\alpha(\mathbf{u})$ is the polarizability tensor, $S(\mathbf{q},\mathbf{u})$ is the particle structure factor, and $\Theta_\mathbf{q}$, $\Omega_\mathbf{q}$ are the diffusion and interaction operator respectively.

The orientation relaxation $C(q,t)$ is, in principle, a multiexponential function and it becomes identical to Zero-Pecora expression [10] in the limit $qL \to 0$ and $c \to 0$. The latter has an analytical form that consists of four exponentials with concentration-dependent amplitudes. It is worth mentioning, however, that these theoretical approaches neglect the intermolecular interference, i.e., the distinct part of the correlation function.

The initial decay rate $\Gamma = -\lim_{t\to 0}[(d/dt)(C(q,t)/C(q,0))]$ for the VH correlation function assumes the analytical form:

$$\Gamma_{VH} = [D_\perp q^2 + D_r f_1(qL) + (D_{||} - D_\perp)q^2 f_2(qL)]\,A(qL,c) \tag{4}$$

where f_1, f_2 are weight factors and A(qL, c) the excluded volume term, which equals 1 at $c \to 0$. $D_{||}$ and $D_\perp$ denote the coefficients for diffusion parallel and normal to the rod axis respectively.

For infinitely thin rods without hydrodynamic interactions confined in undistorted cages Doi-Edwards (DE) theory [1] assumes that normal diffusivity freezes, i.e., $D_\perp = 0$, whereas parallel diffusivity $D_{||}$ is unhindered and equal to its dilute solution value. The predicted concentration dependence of D_r is strong:

$$D_r = BD_{r,0}\,(c^*/c)^2\ . \tag{5a}$$

$B^{1/2}$ represents the crowding of the rods and it was expected to assume values between 1 and 10. It is observed, however, that B is much larger than 10, showing that enmeshment of rod-like particles is less likely than first suspected. Moreover, D_r does not conform to the c^{-2} dependence over the entire non-dilute region, but rather displays a weaker c-dependence; the relationship of D_r with L and c is not yet fully established. The initial (DE) work [1] with completely closed cages and cage size equal to the average distance of the rods has been refined. Recalculation [11] of the cage size assuming, like in the DE model, equilibrium rod distribution led to the expression:

$$D_r = 21.22\,D_{r,0}/[f^2[(cL^3)^2 - 17.74\,(cL^3)]]\ , \tag{5b}$$

with f being the fraction of L that a rod must translate to escape a cage (in the original version of the DE model $f \approx 1$); for $c/c^* > 500$ Eq. (5b) converges to Eq. (5a).

If the cages can be considered rather dynamically distorted, then two different mechanisms for relaxation of the orientational fluctuation alter the concentration dependence of D_r. In this picture, the expression for the rotational diffusivity is given [6] by:

$$D_r = D_{r,0}/[1 + (1/6\pi)\,cL^3\,Qf\ln((1-f)/f)]\ , \tag{5c}$$

where $Q = 1 + (\pi/2)cL^3\ (b/L)\ (1-2f)^2$. According to Eq. (5c), the importance of the aspect ratio (L/b) increases as the concentration increases. Recent Brownian dynamic simulations [7] have shown that rotation is a diffusive process and supported the concentration dependence of D_r and the two mechanisms for orientational relaxation suggested by this model. Moreover, the translational diffusivity of the rods normal to their axes freezes at much higher concentration than predicted by DE theory.

Experimental

PCS

Photon correlation spectroscopy (PCS) was employed to measure the normalized time correlation functions $G_{VH}(q,t)$ of the depolarized (VH) light scattering intensity at different scattering angles using the ALV-5000 goniometer. The light source was a Nd-Yag laser (Adlas) with wavelength $\lambda = 532$ nm operating at 150 mW single mode. The VH correlation functions were recorded with an ALV-5000 full digital correlator (280 channels) that covers a broad time range (10^{-7}–10^3 s). Under homodyne conditions the normalized field correlation function $g_{VH}(q,t)$ at a given scattering vector q ($|q| = (4\pi\,n/\lambda)\sin(\theta/2)$), n being the refractive index) is related to $G_{VH}(q,t)$ by:

$$G_{VH}(q,t) = A_\infty[1 + f^*\,|\alpha\, g_{VH}(q,t)|^2]\ , \tag{6}$$

where f^* is an instrumental factor, α is the fraction of the total depolarized intensity I_{VH} arising from fluctuations in the optical anisotropy with correlation times slower than about 10^{-7} s and A_∞ is the base line at long delay times. If more than one process contributes to $g_{VH}(q,t)$ an estimation of α_i is necessary in order to assess the intensity $I_i = \alpha_i I_{VH}$ associated with the relaxation [16].

The characteristic relaxational parameters are extracted by carrying out the inverse "Laplace" transform (ILT) of the measured $G_{VH}(q,t)$ assuming a superposition of exponentials:

$$\alpha\, g_{VH}(q,t) = \int_{-\infty}^{\infty} L(\ln\tau)\exp(-t/\tau)\,d\ln\tau\ , \tag{7}$$

where $L(\ln\tau)$ is the spectrum of relaxation times. The ILT analysis was carried out using the "CONTIN" algorithm [17]. For the present solutions both polarized and depolarized time correlation functions (see Fig. 1) display a weak slow process whose origin is unclear. This process leads to a narrow peak in the $L(\ln\tau)$ spectrum that will not be considered here.

Material

The synthesis of a series of poly(p-2,5-di-n-dodecyl-1,4-phenylene) (PPP) has been recently performed and discussed elsewhere [18]. In the present study, we have utilized PPP with weight average molecular weight $M_n = 60\,450\ g$/mol, weight average contour length $L_w = 725$ Å, and a unimodal distribution of molecular weight with a polydispersity $M_w/M_n \cong 2.4$ as determined by GPC. The latter was calibrated with polystyrene standards in toluene. The synthesis of PPP used in the present study occurred at 65 °C by polymerization of bis (1,3-propanediol)ester of 2,5-di-*n*-dodecyl-benzene-1,4-bisboronic acid with 1,4-dibromo-2,5-di-*n*-dodecylbenzene in the presence of 6 meq catalyst [Pd(PPh$_3$)$_4$] in a reaction vessel for 8 days. The polymer was precipitated into acetone, filtered, washed in boiling water, and dried. The polymer was additionally dissolved in toluene, precipitated into acetone collected and vacuum-dried.

Solutions of PPP in toluene suitable for homodyne photon correlation spectroscopic measurements in the range of 1.4–33 mg/cm^3 were prepared by slow evaporation of the solvent from the dilute solution. A dust-free solution of the latter was obtained by slow filtration through a 0.45 μm Teflon Millipore filter into the light-scattering round cell (12.5 mm od). The examined concentration range is well within the semidilute and the concentrated regime; the concentration varies from about 10 to 230 rods/L^3. The solutions were maintained at 80 °C between measurements and equilibrated at the temperature of the experiment (20 °C or 40 °C) for about 1 h before measurements.

Since both VV and VH light-scattering show slower (Eqs. 2) dynamics than anticipated from the GPC L_w value, we utilized polarized light-scattering measurements [19] for further characterization of the sample. The angular dependence of the intensity $I(q) = \alpha I_{VV}(q)$ over the concentration range (1.4–12) mg/cm^3 led to the estimation [20] of the correlation length ξ according to:

$$I(0)/I(q) = 1 + q^2\xi^2 + \cdots \qquad (8)$$

Extrapolation to $c \rightarrow 0$ results to the radius of gyration $R_g(= \xi\sqrt{3}) = 620 \pm 40$ Å. For a polydisperse sample, this R_g is the *z*-average, and related to the weight average contour length L_w by [21]:

$$\overline{R_{gz}^2} = \frac{(m+2)(m+3)}{(m+1)^2}\frac{L_w^2}{12}\,. \qquad (9)$$

This expression assumes rigid rod particles with a Schulz–Zimm molecular weight distribution function, characterized by $m = (M_w/M_n - 1)^{-1}$. The computed L_w thus amounts to 1170 ± 80 Å. Alternatively, the intensity $I(0)$ at $c = 1.4$ mg/cm^3 leads to $M_w = 1.05 \cdot 10^5$ g/mol using R_{VV} (toluene) $= 2.82 \cdot 10^{-5}$ cm^{-1} and $\partial n/\partial c = 0.08$ cm$^3/g$ for the absolute Rayleigh ratio of toluene at $\lambda = 532$ nm and refractive index increment, respectively. Hence, the corresponding L_w is 1260 Å. We use the value of L_w calculated from $\overline{R_{gz}^2}$ for the characterization of the sample because the latter is independent of absolute intensity values. Moreover, the two L_w values are very close, exceeding, however, the value of $L_w = 725$ Å obtained from the M_w of the GPC experiment. Nevertheless, this discrepancy does not necessarily mean molecular association, since GPC probably does not yield absolute M_w values due to calibration reasons, and the measured quantities by light scattering, i.e., intensity and relaxation times are reproducible.

Results

For concentrations less than 4 mg/cm^3, the depolarized intensity was very weak to allow the measurement of $G_{VH}(q,t)$ within reasonable accumulation time (few hours). However, the correlation times for the orientation fluctuations should be longer than the shortest time of PCS as anticipated by the average size of the rods estimated by the translational diffusion coefficient. The latter measured in the isotropic light-scattering experiment for $c = 1.4$ mg/cm^3 amounts to the translational diffusion $D = 7.6 \times 10^{-8}$ cm^2/s at 20 °C [19]. Application of Eq. (2a) for bare rigid rods in the dilute regime with rod diameter $b = 1.7$ nm would lead to a very high value for the contour length ($\simeq$ 500 nm). A use, however, of the DE value $D = D_0/2$ in the semidilute region [1] would yield about half of the preceding value, i.e., 235 nm. It was however been argued [14] that for large rods, D could fall even below this DE value. These estimates for translational diffusivity are rather model dependent and hence can lead to ambiguous values for L. Instead, the comparison between theoretical and experimental translation diffusion D rather implies a slowing down of the center of mass motion of the present hairy rod.

The concentrations examined in the present investigation are well within the semidilute region. Using $L_w = 1170$ Å, the characteristic concentrations c^* and c^{**} amount to 0.017% and 1.17%, respectively. Whereas the Onsagar prediction for the nematic transition is $c_n = 5.96\%$. Hence, the experiment covers the reduced concentration $c/c^* = cL^3$ range from about 10 to 230 or c/c^{**}

$= cbL^2$ varies from 0.14 to 3.3. Furthermore, the present sample can be considered rigid on the account of recent molecular dynamic calculations [22] that estimated the persistence length of poly(p-phenylene) to be about 130 nm. The rotational diffusion constant $D_{r,0}$ in the dilute region can then be computed (Eq. (2b)) to be 16990 s^{-1} at 20 °C.

Figure 1 shows experimental net correlation functions $[G_{VH}(q,t) - 1]/f^*$ for the 1.4 mg/cm^3 ($cL^3 = 82$) solution at three different angles at 20 °C. The intensity I_{VH} is q-dependent as indicated by the increase of the amplitude α of the $G_{VH}(q,t)$ at short times and it suggests long rods, i.e., $qL > 1$. In contrast to the polarized intensity correlation functions (Fig. 1) arising from concentration fluctuations, the somewhat faster $G_{VH}(q,t)$ display a bimodal distribution relaxation fluctuation $L(\ln\tau)$. The high depolarization ratio (~ 0.2) of this solution justifies the choice of the poly(p-phenylene) for depolarized light scattering studies. Hence, the quality of the experimental $G_{VH}(q,t)$ allows a detailed analysis of shape of the orientation relaxation function (Eq. (2)).

For long rods ($qL \geq 1$), $G_{VH}(q,t)$ depends on the probing wavelength (q^{-1}), albeit this variation is less strong than for $G_{VV}(q,t)$ (Fig. 1). Moreover, at constant q, the increase of rod concentration is expected, on the ground of topological and thermodynamic reasons, to affect the orientational dynamics. An example of these dependences is presented in Fig. 2, where for $cL^3 = 167$ and $q = 0.034$ nm^{-1} $G_{VH}(q,t)$ is found to vary with q and c respectively. Besides the increase in the amplitude α with increasing $1/q$ and c, there is a concurrent narrowing of the shape of $G_{VH}(q,t)$.

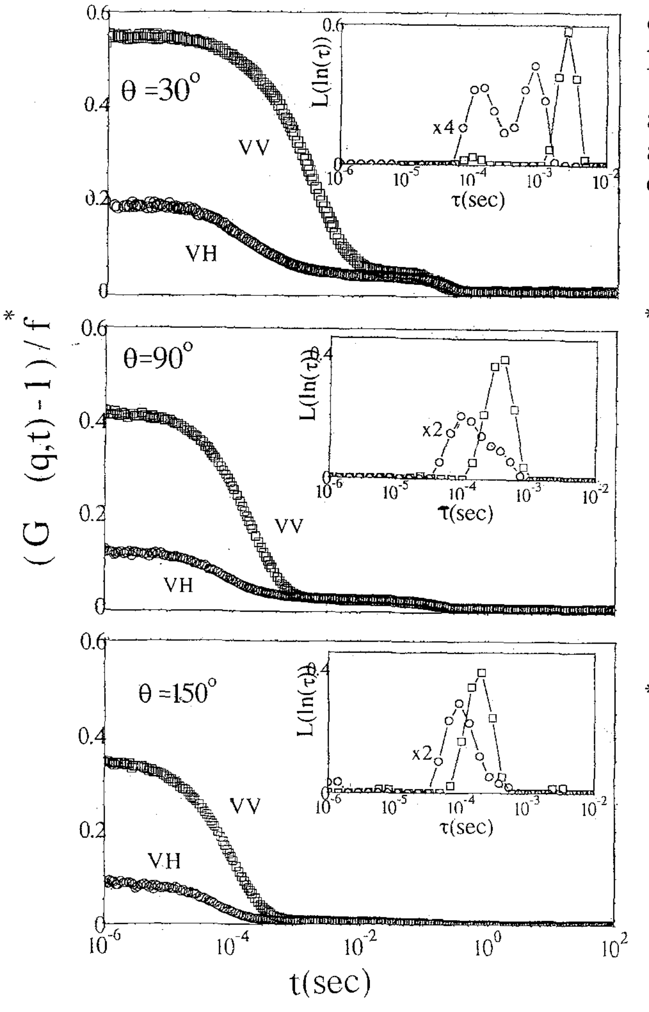

Fig. 1. Experimental net polarized and depolarized correlation functions of 1.4 mg/cm^3 solution of PPP in toluene at three different scattering angles (θ) at 20 °C. The inverse Laplace transform of these functions as shown in the inset

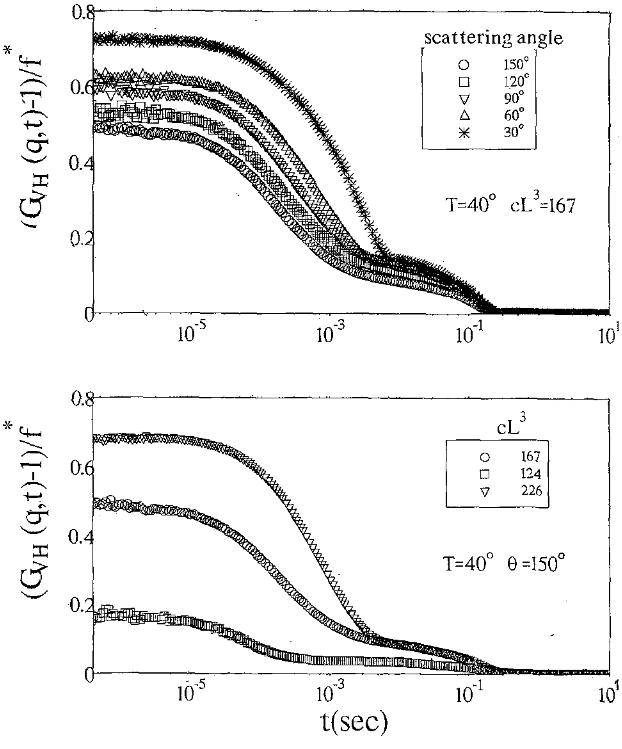

Fig. 2 Depolarized time correlation functions for PPP/toluene solution at 40 °C and a) at $c = 1.8$ mg/cm^3 and at different scattering angles and b) at $q = 0.034$ nm^{-1} for three different PPP concentrations

This modification becomes evident in the form of $L(\ln\tau)$ that displays a bimodal shape with increasing domination of the slow mode as the rod concentration increases and q decreases. The enhancement of the slow mode relates to the concurrent increase of the I_{VH} intensity with solute concentration beyond the expected linear c-dependence at low concentration (see Fig. 6 below). The rate of increase of the most probable relaxation rate Γ of the distribution with q decreases at high q's. This behavior should be compared with the q^2-dependence of the single relaxation rate of the concentration fluctuations [19] (see also Fig. 1).

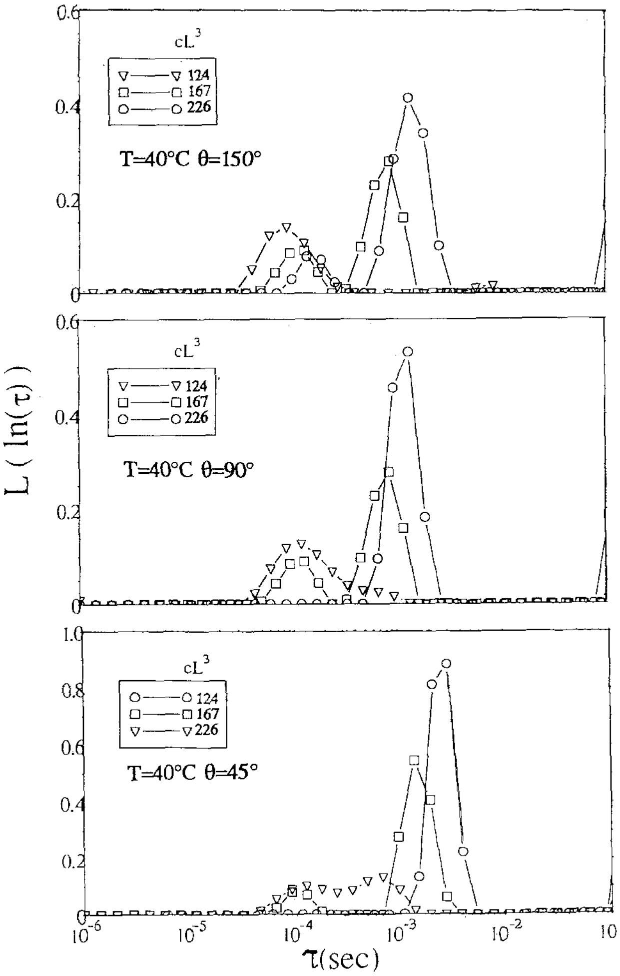

Fig. 3. Distribution $L(\ln\tau)$, of orientation relaxation times obtained from the experimental $G(q,t)$ of Fig. 2 at three scattering angles for three concentrations

Prior to the discussion of these pertinent features of the anisotropic light scattering from rigid rod solutions, it is crucial to assess undesirable polydispersity effects. The unimodal molecular weight distribution function is consistent with the single $L(\ln\tau)$ of the polarized correlation functions. The breadth of this $L(\ln\tau)$ is comparable with other reported systems [11, 23]. Alternatively, the bimodal distribution for the anisotropic scattering (Fig. 1) that depends stronger on L (Eq. 2b) cannot be attributed to length polydispersity based on the variation of $L(\ln\tau)$ with q and c (Fig. 3).

Discussion

The shape of the experimental orientation relaxation function $G(q,t)$ (Figs. 1 and 2) is represented by a bimodal relaxation distribution function (Fig. 3). Based on the concentration dependence of the two relaxation rates (see below), the slow mode is assigned to the actual collective reorientational motion of the polymer. In all treatments of the topological confinements, short time rotations in limited regions are conceivable [6, 7]. In Fixman's model [6], these angular rotations are considered to be unhindered and essentially occur with the dilute solution value of the rotational diffusivity (D_{ro}). Alternatively, the simulation results show that during this time interval the value of the rotation diffusion is intermediate between D_{ro} and the actual long time rotational diffusivity D_{r}.

The ratio $D_{\mathrm{r,f}}/D_{\mathrm{r}}$ for the fast and slow rotational diffusivities that equals to the corresponding ratio of the relaxation rates $(\Gamma_{\mathrm{f}}/\Gamma_{\mathrm{s}})_{q\to 0}$ (see Fig. 4 below) amounts to 5 ± 1 over the examined concentration range. In the multiexponential Eq. (4) and Pecora's [10] expression valid for the semidilute region, this ratio is predicted to assume the somewhat lower value of 20/6. For the present polydisperse system, however, the fast process might also be due to the rotational motion of shorter chains confined in cages formed by longer chains. Both assignments can rationalize the insensitivity of the rate Γ_{f} to q and c variations expected and found for fast rotational motion (in Eq. (4), for $\Gamma_{\mathrm{f}} \gg D_{\perp}q^2$). To elucidate the fast relaxation mechanism of the orientation fluctuations it will be crucial to study PPP samples with narro-

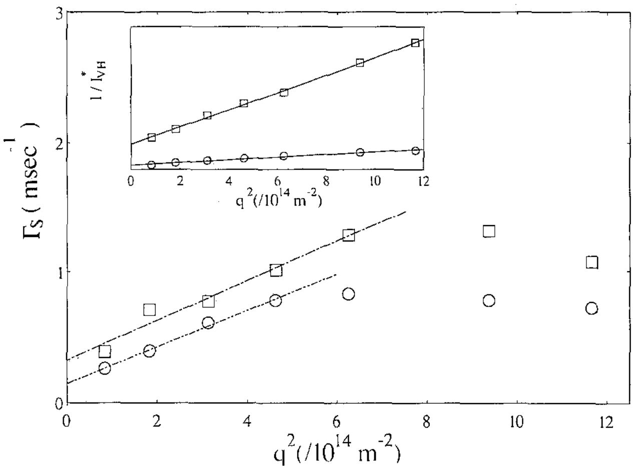

Fig. 4. Variation of the orientation relaxation rate Γ_s, obtained from the slow peak of $L(\ln\tau)$, with the scattering wavevector for two solutions with 0.025 and 0.033 g/cm^3 at 40 °C. For these solutions the variation of the inverse of the depolarized intensity with q^2 is given in the inset

wer molecular weight distribution and different chain lengths.

The slow rate Γ_s at $cL^3 < 100$ displays a q^2 dependence with a non-zero intercept in accordance with Eq. (4). The value Γ_s ($q = 0$) defines D_r, that slows significantly down with increasing c as discussed below. In contrast Γ_s at $cL^3 > 100$ is found to exhibit a peculiar 9-dependence depicted in Fig. 4. For the two highest concentrations, Γ_s becomes virtually q-indenpendent at high q's as can also be seen in Fig. 3. A downward curvature has been reported for the q^2-dependence of the relaxation rate for the concentration fluctuations (polarized light scattering) in PBLG non-dilute solutions [20]; low optical anisotropy has precluded dynamic depolarized experiments. In the framework of the random phase theory of rod like polymers in isotropic solutions, this behavior can be accounted for by introducing a qL dependent osmotic virial coefficient affecting also the isotropic light scattering intensity [14]. In the present case, the depolarized light scattering intensity $I^*_{VH} = \alpha_s I_{VH}$, associated with the slow process, is shown as a function of q in the inset of Fig. 4. This plot displays angular asymmetry over the accessible range of q's that can be described by a correlation length $\xi = 57$ nm for the orientation fluctuations. The change in the q-dependence of the dynamics (Γ_s) at high concentration ($cL^3 > 100$) but not of the anisotropic intensity might reflect a different mechanism for orientation relaxation at high qL. In this q and c range, Γ_s has a local relaxation (q-independent) character. Qualitatively, Eq. (4) for rigid rods would capture this feature provided the excluded volume factor $A(qL,c)$ and/or the weight factors f_1 and f_2 are decreasing functions of qL at high c. In this context, it is worth mentioning the neglect of interparticle correlations in Eq. (3) as mentioned in the theoretical background. Alternatively, it is conceivable that the presence of the long (hexyl) substituents in this hairy rod system might modify the hydrodynamic conditions. Whether the behavior depicted in Fig. 4 is a characteristic feature of hairy rod polymers remains to be checked.

The rotational diffusivity D_r given by the limiting low q value of Γ_s (Eq. (4)) is the quantity of primary interest in all theoretical approaches of the rod-like polymer solutions and decreases as the concentration increases. The experimental data of Fig. 5, while in qualitative agreement with predictions (Eqs. 5a–c) reveal a prolonged concentrated regime. According to Eq. (5c), simulation [7] and dynamic electric birefringence [8, 9] results of PBLG, the crossover to the c^{-2} dependence occurs at $cL^3 > 100$ (inset of Fig. 5). In contrast, the present hairy rod system appears to approach this limit at $cL^3 > 60$. Equation 5b

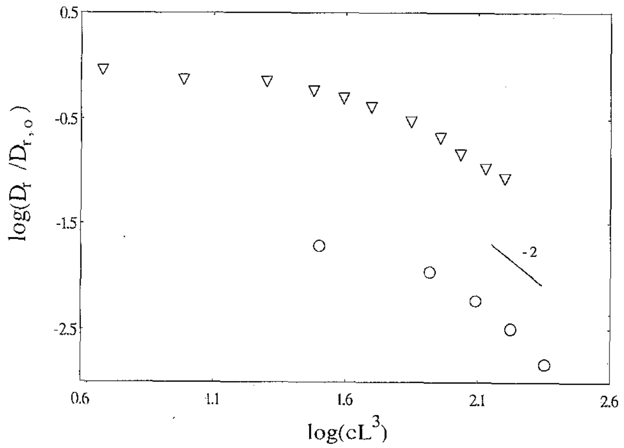

Fig. 5. Concentration dependence of the experimental rotational diffusivity D_r (circles) in PPP/toluene solutions at 40 °C and the simulation results (Ref. 6) (triangles). The scaling prediction of Eq. (5a) is indicated by the slope of the solid line

can account for the c-dependence of the experimental D_r with the fraction $f \cong 0.55$ in the examined cL^3 range. This value that corresponds to translation over about 640 Å for a rod in order to escape a cage reflects some dynamic flexibility of the hairy rods in the context of the DE model ($f = 1$). Alternatively, the crowding parameter B (Eq. (5a)) obtained from the experimental D_r above c^{**} and using $D_{ro} = 16\,990\ \mathrm{s}^{-1}$ amounts to 90. For comparison, computer simulations [7] and experiments [7, 9] in PBLG (for $cL^3 > 300$) are described by B in the range 1000–2000. This rather low value presenting the numbers of rods/L^3 necessary to freeze the rotational motion [3] might reflect the slowing-down effect of the long side chains. This notion is also corroborated by the reduced rotational mobility of the present system as compared to the computer simulations for bare rods (Fig. 5).

The depolarized light-scattering intensity $I^*_{\mathrm{VH}} = (a_s I_{\mathrm{VH}}/I_{\mathrm{T}})$ normalized to the anisotropic intensity I_{T} of the toluene increases linearly with concentration at low c. Strong positive deviations from the linear dependence are observed as the concentration increases towards the critical concentration c_n for the isotropic to nematic transition. For the present system, the intensity at two scattering angles is shown as a function of c/c^{**} at 40 °C. For $c/c^{**} < 2$ that corresponds to $cL^3 < 150$, I^*_{VH} is still proportional to the rod number concentration (inset in Fig. 6). In the upper inset of Fig. 6, the inverse depolarized intensity is plotted versus c/c^{**} at two q's. The clear kink in the concentration dependence of I^*_{VH} indicates the crossover from the linear to the strong nonlinear rise in the depolarized intensity and occurs at $c/c^{**} \simeq 2$ for both q's. The strong rise in the intensity at high c especially at low q's, indicates pronounced orientational correlations when c exceeds $2c$.** The I^*_{VH} diverges at $c/c^{**} \simeq 3.5$ lying between $c/c^{**} \simeq 2.3$ and Onsager's ($c/c^{**} \simeq 5$) predictions (for $c/c^* < 2.3$ an isotropic random orientation is retained [11]). In Maeda's calculation of the depolarized light scattering (Eq. (3)), the intensity at the low angles is predicted to diverge at $c = c_n$. Qualitatively similar increase in the total depolarized intensity with increasing concentration was reported for PBLG solutions [20]. Deviations from the linear dependences were observed for $c/c^{**} > 0.5$ i.e., again at significantly lower concentrations than for the present system.

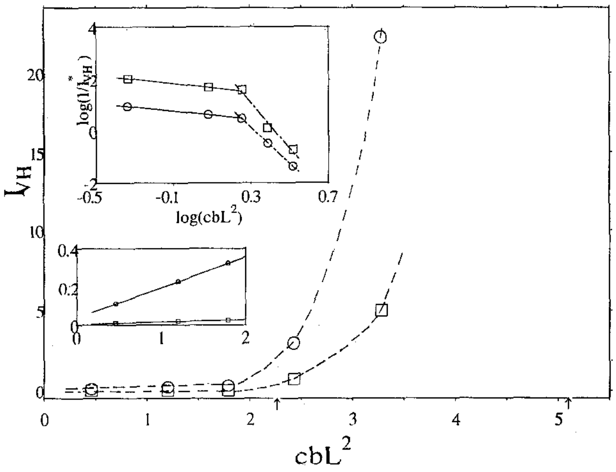

Fig. 6. Depolarized light scattering intensity I^*_{VH} normalized to the anisotropic intensity of the solvent for the slow process (Fig. 3) in PPP/toluene solutions versus concentration at two scattering wavevectors and 40 °C. The insets show the inverse of the intensity versus cbL^2 (upper) and I_{VH} versus cbL^2 in the linear regime (lower). The two arrows denote two characteristic concentrations described in the text

Summing up, the orientation relaxation function $C(q,t)$ of poly(paraphenylene) (PPP) hairy rods in solution can be recorded by PCS due to the significant molecular optical anisotropy and long length. For rod concentrations cL^3 in the range 10 to 230, $C(q,t)$ displays a bimodal relaxation distribution function with increasing contribution of the slow mode as the concentration increases. The mechanisms for relaxing the orientation fluctuations relate to diffusive translation along the rod axis and local rotation both manifested in the q-dependence of the orientational relaxation rate. Based on the variation of the rotational diffusivity D_r and depolarized intensity I_{VH} with cL^3, the PPP hairy rods display quantitatively different orientational relaxation as compared to the rodlike polymers.

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