A Characterization of Orientation in a Highly Oriented Polymeric Fiber by Fluorescence Depolarization: Kevlar 49

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ABSTRACT: The degree of order has been estimated for a commercial aramid fiber, Kevlar 49, poly(*p*-phenyleneterephthalamide), an ultra high modulus, highly oriented fiber material. The uniaxial orientation has been formulated to second order in terms of an orientational distribution function using Legendre polynomials containing both the second and fourth cosine moment averages. These averages have been determined by polarized fluorescence measurements of the intrinsic fluorescence of the sample. Difficulties with depolarization due to intermolecular energy transfer are discussed. The second-order orientational distribution function for the polymer is compared with that for a low molecular weight thermotropic nematic liquid crystal.

New polymers that can exist in liquid crystalline form have brought about the technological possibility of obtaining materials with a very high degree of molecular and physical anisotropy. For the case of aromatic stiff chain polymers, this anisotropy has been exploited to produce a class of fibers (generically referred to as aramid fibers) in which chains to a very large extent lie parallel to the fiber axis, resulting in a fiber with an ultra high modulus and tensile strength.[1-3] Kevlar 49 is a material which is essentially poly(*p*-phenyleneterephthalamide), an aromatic polyamide of chemical structure shown in Figure 1.[4] Since the polymeric chains are in an extended conformation with a well-defined orientation relative to the fiber axis, we may regard the material as a highly anisotropic macroscopic single crystal with defects. (Note that this is distinct from a highly crystalline material containing crystallites, spherulites, folded chains, etc.) Since there are a large number of load bearing chains per unit cross section of the fiber, at least some chemical bonds must be broken if rupture is to occur. These systems realize therefore a substantial fraction of their theoretical maximum strength. The quantitative assessment of the degree of uniaxial orientation of such fibers is now of considerable importance.

Theory

Uniaxially oriented systems can be described by the use of an orientational distribution function, $f(\theta)$, expressed in terms of the complete set of Legendre polynomials $P_l(\cos\theta)$ in a manner similar to that which has been used to express order in nematic liquid crystals.[5] The angle between the fiber axis, Z, and a vector, $\mathbf{M}$, describing a polymer chain segment axis will be denoted by θ (see Figure 2). The chains are assumed to be randomly distributed over the azimuthal angle, ϕ. Imposing the symmetry condition that $f(\theta) = f(\pi - \theta)$, one has[5]

$$f(\theta) = \sum_{\substack{l=0 \\ \text{even}}}^{\infty} c_l P_l(\cos\theta) \tag{1}$$

where the coefficients c_l are given by:

$$c_l = \frac{2l+1}{2}\langle P_l\rangle \tag{2}$$

$\langle P_l\rangle$ is the average of the lth Legendre polynomial defined through:

$$\langle P_l\rangle = \int_{-1}^{1} P_l(\cos\theta) f(\theta)\,\mathrm{d}(\cos\theta) \tag{3}$$

The first few Legendre polynomials in the series are:

$$P_0 = 1 \qquad P_2 = [3\cos^2\theta - 1]/2$$
$$P_4 = \tfrac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3) \tag{4}$$

The experimental quantities are thus $\langle P_l\rangle$ which are obtained using eq 3 and 4 in terms of the measurable moment averages of the distribution $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$. Thus

$$\langle P_0\rangle = 1 \qquad \langle P_2\rangle = [3\langle\cos^2\theta\rangle - 1]/2$$
$$\langle P_4\rangle = \tfrac{1}{8}(35\langle\cos^4\theta\rangle - 30\langle\cos^2\theta\rangle + 3) \tag{5}$$

The parameter $\langle P_2\rangle$, often referred to as the orientation factor,[6] has long been used to estimate degrees of order in fiber materials. For perfect order $\langle\cos^2\theta\rangle = 1$ and $\langle P_2\rangle = 1$. For complete disorder, i.e., a random distribution with $f(\theta)$ = constant, one has an isotropic state where $\langle\cos^2\theta\rangle = {}^1/_3$ and hence $\langle P_2\rangle = 0$. Opitcal birefringence; infrared, visible, and ultraviolet dichroic absorption measurements; and magnetic resonance techniques are the most frequently cited means of determining the degree of order.[7] The optical methods are inherently limited to yield only a measure of $\langle\cos^2\theta\rangle$. For very highly ordered systems $\langle P_2\rangle \rightarrow 1$, and one loses experimental sensitivity in discerning relative differences in these types of samples. Since $\langle\cos^2\theta\rangle \geq \langle\cos^4\theta\rangle$, the next term in the series expansion, $\langle P_4\rangle$, will provide additional sensitivity to characterize samples with high degree of order as is the case here. In addition, since $\langle\cos^4\theta\rangle \geq \langle\cos^2\theta\rangle^2$, one can estimate the breadth of the distribution: the equality will hold for a Dirac type distribution while the inequality will become more pronounced as the distribution broadens. Both the second and fourth moments are available from a suitable analysis of magnetic resonance data and from polarized Raman and fluorescent emission spectra of active sites (embedded probes or sensitive molecular elements) in the array. In this work, we have employed the fluorescence polarization method on Kevlar 49 fibers in a manner similar to that used to calculate $\langle P_2\rangle$ and $\langle P_4\rangle$ in a low molecular weight nematic liquid crystal.[8,9]

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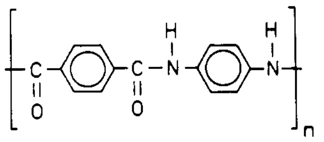

Figure 1. The chemical structure (repeat unit) of Kevlar 49.

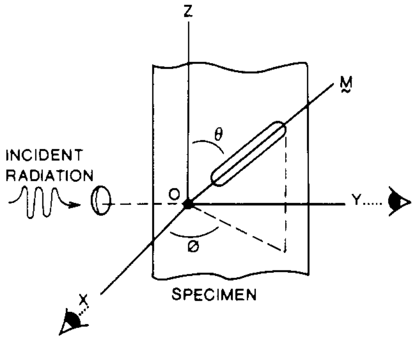

Figure 2. Orientation of a representative fiber segment with long axis M in the laboratory frame 0-XYZ. The specimen is assumed to lie with its major symmetry axis along Z. Incident radiation enters from the left and travels along the Y axis. The condition of observation is the right angle geometry along the X axis as indicated.

Some workers have proposed model forms for the distribution function with one or more adjustable parameters used to fit data of some experimental property sensitive to an average over $f(\theta)$. These attempts are open to the criticism of reasonableness and uniqueness of the chosen approximation to $f(\theta)$. The use of eq 1 is unambiguous in as only uniaxial symmetry need be assumed.

The Fluorescence Depolarization Experiment as Applied to Kevlar 49.[7-9] Kevlar 49 is a highly oriented uniaxial fiber material which is extruded from solution in the liquid crystalline state and then treated using a sophisticated technological process so as to freeze in the high level of macromolecular orientation in the finished fiber. It was, thus, not possible for us to introduce an external probe which would be sensitive to the orientation of the polymer chain as we have previously done with a low molecular weight nematic liquid crystal.[9] As a result of the highly aromatic nature of the polymer chain, it was observed, however, that Kevlar 49 was naturally fluorescent as received. This high concentration of fluorophores, however, presented the possibility that energy transfer might contribute in a significant fashion to the emission depolarization. This problem will be dealt with separately in the next section.

The fluorescent emission intensity from an immobile ensemble of fluorophores observed through a polarization analyzer placed directly along a laboratory polarization axis j, resulting from light absorbed from an excitation source polarized directly along laboratory axis i, is given by:[10]

$$I_{ij} = \langle M_{\mathbf{a}i}{}^2 M_{\mathbf{e}j}{}^2 \rangle \tag{6}$$

where $M_{\mathbf{a}i}{}^2$ and $M_{\mathbf{e}j}{}^2$ are the squares of the absorption and emission oscillators, **a** and **e** respectively, projected on to the laboratory axes i and j (see Figures 2 and 3). The indicated average is analogous to that in eq 3 and thus produces the second and fourth cosine moment averages which are required in the analysis.

The extent to which the emission is polarized is frequently quoted in terms of r, the emission anisotropy, defined through:

$$r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \tag{7}$$

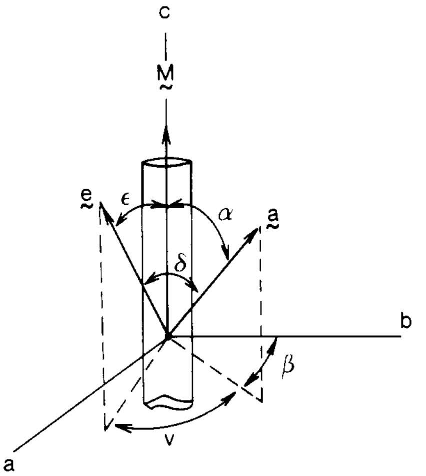

Figure 3. Orientation of absorption and emission oscillators of a polymer chain segment **a** and **e**, respectively, in the molecular frame 0-abc.

where $I_{\parallel}$ and $I_{\perp}$ are the emission intensities in a right-angle experimental geometry with polars positioned parallel and perpendicular, respectively. I_{ij} are reduced intensities including instrumental, concentration, and volume factors which thus cancel due to the ratio form of eq 7. Many definitions of r are possible because of the matrix form of the intensities, I_{ij}. For a simultaneous determination of $\langle \cos^2 \theta \rangle$ and $\langle \cos^4 \theta \rangle$, two independent determinations of r are required:

$$r' = \frac{I_{zz} - GI_{zy}}{I_{zz} + 2GI_{zy}} \tag{8}$$

$$r'' = \frac{I_{xz} - GI_{xy}}{I_{xz} + 2GI_{xy}} \tag{9}$$

where $G = I_{xz}/I_{xy}$. The factor G is used to correct for detector anisotropy and would be equal to 1 for an isotropic random sample with an ideal detector.[11]

Making the appropriate substitution with the intensity matrix elements[9,10] for a long axis polarized excitation transition as is the case here (see Appendix), i.e., $\alpha = 0$ in Figure 3, one has

$$r' = \frac{9\langle \cos^4 \theta \rangle - 3\langle \cos^2 \theta \rangle}{6\langle \cos^2 \theta \rangle} P_2(\cos \delta) \tag{10}$$

$$r'' = \{[6\langle \cos^2 \theta \rangle - 5\langle \cos^4 \theta \rangle - 1]/[(5 - 6\langle \cos^2 \theta \rangle + \langle \cos^4 \theta \rangle) + (6\langle \cos^2 \theta \rangle - 3\langle \cos^4 \theta \rangle - 3) \cos^2 \delta]\} P_2(\cos \delta) \tag{11}$$

where δ is the angle between the absorption and emission oscillators as shown in Figure 3. For r' the excitation polarization is normal to the base plane and parallel to the major symmetry axis of the sample, while for r'' the excitation polarization is parallel to the base plane and normal to major symmetry axis of the sample. The spectroscopic parameter (intramolecular energy transfer angle) δ may be determined by measuring the polarization in a dilute random glass, i.e., in the limit $T/\eta \rightarrow 0$, $\langle \cos^2 \theta \rangle = {}^1/_3$, $\langle \cos^4 \theta \rangle = {}^1/_5$, where T is the absolute temperature and η is the viscosity. Under this condition r' reduces to:

$$r_0' = {}^2\!/_5 P_2(\cos \delta) \tag{12}$$

A "dilute" glass is required to minimize the depolarization effects caused by intermolecular energy-transfer processes.

Since Kevlar 49 is insoluble in all common solvents, it is not possible to prepare such a dilute random glass, and this determination must thus await the preparation of suitable model compounds, such as low molecular weight analogues of the polymer. We regard this as being an extensive project beyond the scope of the present study, however, due to the fact that it is not at all clear as to how many monomeric units constitute an effective fluorophore.

Complications Due to Energy Transfer. As previously noted, Kevlar 49 was fluorescent as received and it was not possible for us to introduce additional probes. The naturally occurring fluorescence of the fibers was however utilized in these depolarization studies. The high concentration of fluorophores can lead to intermolecular energy transfer by a coupled oscillator mechanism as mathematically described by Weber:[12]

$$\frac{r}{(r)_{c\downarrow 0}} = (1 + 3/2\langle \sin^2 \Psi \rangle \langle n \rangle)^{-1} \quad (13)$$

where Ψ is the angle between emission oscillators, n is the number of transfers which have taken place, and $(r)_{c\downarrow 0}$ is the emission anisotropy in the limit of infinite dilution of fluorophores. Weber found that the depolarization caused by concentration induced energy transfer for an isotropic solution was given by:

$$r = \frac{(r)_{c\downarrow 0}}{1 + \frac{\pi}{30} M (R/a)^6} \quad (14)$$

where M is the number of molecules in 1 cm^3, a is the effective molecular radius, and R is the distance at which the probability of emission equals that of transfer for parallel oscillators. For an anisotropic medium, Weber's formalism can be readily extended to give:

$$r = \frac{(r)_{c\downarrow 0}}{1 + \frac{\pi}{4} M (R/a)^6 (\langle \cos^2 \theta \rangle - \langle \cos^4 \theta \rangle)} \quad (15)$$

Note that for the random values of $\langle \cos^2 \theta \rangle = {}^1/_3$ and $\langle \cos^4 \theta \rangle = {}^1/_5$, eq 15 reduces to eq 14. More important, however, in this connection, for highly ordered systems when $\langle \cos^2 \theta \rangle \simeq \langle \cos^4 \theta \rangle$, there is no concentration induced depolarization. It is on this basis that we justify the use of the intrinsic fluorescence of Kevlar 49 in the determination of polymer chain order.

Experimental Section

The intensity measurements were performed as previously described[9] using a Perkin-Elmer MPF-2A spectrofluorimeter with a Solartron 1860 "time domain analyzer", a computing digital voltmeter which averaged the intensity, in real time t, according to the following algorithm:

$$I = \frac{1}{t_0} \int_0^{t_0} i(t) \, dt \quad (16)$$

The use of precise intensity measurements in the calculation of the emission anisotropy cannot be overemphasized since small differences between large numbers can be involved. The measured intensities are the primary experimental quantities which are used in eq 8 and 9. The samples were excited at 370 nm and intensities were noted at 475 nm, the midpoint of a broad featureless emission band, as shown in Figure 4. Slits of 10 nm were employed and the sample temperature was maintained at 25 °C. A considerable amount of Rayleigh scattering was observed, but this did not prove to be a problem because of the large red shift of the emission relative to the excitation. A UV-D25 cutoff filter (supplied with the instrument) was used to prevent stray radiation from the excitation monochromator in excess of 380 nm from impinging upon the sample, where it could be scattered into the path of the detector, giving an erroneous contribution to the measured signal. This problem is especially severe for weakly fluorescing solid polymers. The fibers were mounted on a wire hanger so as to be parallel to the Z axis.

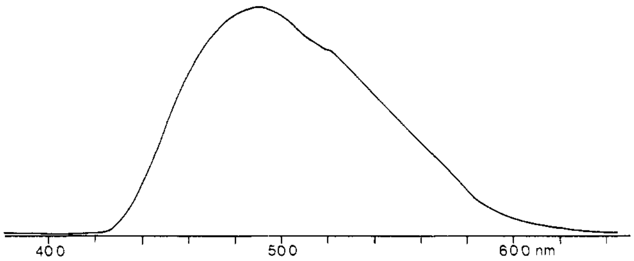

Figure 4. The broad featureless emission spectrum for Kevlar 49, when excited at 370 nm with the excitation and emission slits set at 8 and 2 nm, respectively.

Table I
Polarization Data for an Isotropic Film of Kevlar 49

determination	G^a	r_0' after eq 8
1	0.761	0.0222
2	0.750	0.0155
3	0.746	0.0196
4	0.747	0.0186
5	0.751	0.0178
6	0.744	0.0185
	av 0.750	0.0187

[a] Detector anisotropy.

The nature of the emission spectrum was essentially independent of excitation wavelength over the range 300–410 nm. For wavelengths less than 380 nm, the UV-D25 cutoff filter was employed in the excitation beam. At higher wavelengths, narrow band interference filters were used.

In addition, an isotropic film was prepared by dissolving the fibers in concentrated sulfuric acid, pouring the viscous solution onto a glass plate, and then slowly immersing the plate into a water bath. The isotropic nature of the film was confirmed by its appearance in a polarization microscope: 1. It darkened considerably when observed between crossed polars. The darkened areas were not affected by rotation of the sample relative to the axis of the crossed polars. This is indicative of unoriented amorphous material. 2. Small birefringent regions, assumed to be microcrystallites, were similarly unaffected by sample rotation. This indicates that the crystallite axes are randomly distributed relative to the film plane, which for the purposes here is equivalent to having an isotropic sample. The relative amounts of the crystalline and amorphous phases varied considerably for different parts of the film.

Results and Discussion

Isotropic Film. The results for the emission anisotropy for the isotropic film as well as the detector anisotropy correction are given in Table I. The factor G is subsequently used for calculating r' and r'' for the oriented fibers. The quantity r_0' is very small, i.e., the emission is highly depolarized. From eq 12, one could thus estimate a value of $P_2(\cos \delta) = 0.0468$ giving $\delta = 52.86°$. This represents, however, only a lower limit for the true value of $P_2(\cos \delta)$, in as much as considerable depolarization is to be expected from the effects of intermolecular energy transfer in a bulk *isotropic* sample, as a result of the high concentration of fluorophores in this polymer.

It has been pointed out[13] that for some systems concentration induced energy transfer and the accompanying depolarization disappear when excitation is performed on the red edge of the absorption spectrum. By this means, one could in principle obtain the limiting value of the emission anisotropy, r_0', and hence $P_2(\cos \delta)$ from measurements on the isotropic film. Unfortunately, this phenomenon was not operative for Kevlar 49 as shown by the data in Figure 5, where the emission anisotropy is

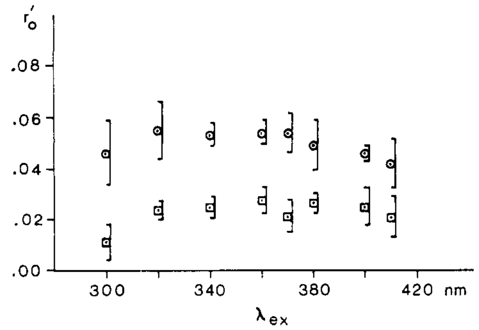

Figure 5. The emission anisotropy, r_0', as measured on the isotropic film as a function of the excitation wavelength, λ_{ex}. The measurements were performed at 475 nm. The error bars are the 95% confidence limits. The symbols □ and ○ denote two different sample positions for which data were taken.

Table II
Polarization Data for Kevlar 49 Fibers

determination	r' sample I	r' sample II	r'' sample I	r'' sample II
1	0.1344	0.1138	0.1444	0.1178
2	0.1216	0.1080	0.1393	0.1190
3	0.1190	0.1028	0.1374	0.1127
4	0.1198	0.1042	0.1350	0.1161
5	0.1211	0.1043	0.1387	0.1160
6	0.1201	0.1058	0.1377	0.1155
	av 0.1227	0.1065	0.1388	0.1162
av I + II	0.114_6		0.127_5	

found to be independent of excitation wavelength over the range 300–410 nm.

It can also be seen from the data in Figure 5 that the magnitude of r_0' depends on the placement of the sample in the spectrophotometer. This is presumably related to the fact that the energy transfer induced depolarization is related to the degree of crystallinity in the portion of the sample under observation. The range of values for $P_2(\cos\delta)$ thus obtained were from nil, complete depolarization due to energy transfer, to 0.13, the value determined in the next section by an alternate procedure. It is not unreasonable to speculate that energy transfer in a highly crystalline region would lead to less depolarization than in an amorphous region.

Oriented Fibers. The data for the oriented fibers are shown in Table II. It is seen that values for the emission anisotropy of the ordered system are an order of magnitude greater than that of the isotropic film. From these data, it is also clear that the mounting of the fiber leads to a greater systematic uncertainty in the measurement than the random error introduced by taking repeated measurements on the same sample. The values of r' and r'' can be substituted in eq 10 and 11 which then can be simultaneously solved for $\langle\cos^2\theta\rangle$ and $\langle\cos^4\theta\rangle$. Such a calculation requires, however, a knowledge of δ, the angle between the absorption and emission oscillators. As has been previously discussed, an accurate direct determination of δ is not yet possible. Fortunately, for the purposes of the calculation here, the value of $\langle\cos^2\theta\rangle$ has been obtained from X-ray diffraction data[4] which gave a value of θ fixed at approximately 5°, implying $\langle\cos^2\theta\rangle = 0.992_6$ for this fiber. Equations 10 and 11 can then be solved simultaneously, giving $\langle\cos^4\theta\rangle = 0.984_6$ and $P_2(\cos\delta) = 0.116$. The latter corresponds to an angle $\delta = 50.15°$, and the value of $\langle\cos^4\theta\rangle$ yields a most probable angle θ of 5.0°. From these results we conclude the following:

(1) The value of $P_2(\cos\delta) = 0.116$ determined from the highly oriented fiber is always greater or equal to that obtained for the isotropic film. This is in agreement with theoretical considerations based on intermolecular energy transfer, eq 13–15, which predict an enhanced depolarization in an isotropic medium when the concentration of fluorophores is high.

(2) $\langle\cos^2\theta\rangle \simeq \langle\cos^4\theta\rangle$ thus justifying the computational approach employed here, i.e., intermolecular energy transfer for the oriented fibers can be ignored according to eq 15.

(3) The identical most probable value of θ as obtained from the second and fourth moment averages shows that in addition to having the molecular chains highly oriented along the fiber axis, the distribution of orientations is very narrow.

The orientational distribution function, $f(\theta)$, for Kevlar 49 can now be calculated by using eq 1–5 and is shown in Figure 6. For this calculation, $\langle P_2(\cos\theta)\rangle = 0.988_9$ and $\langle P_4(\cos\theta)\rangle = 0.960_4$ so that both the first- and second-order terms are contributing significantly to the expansion, eq

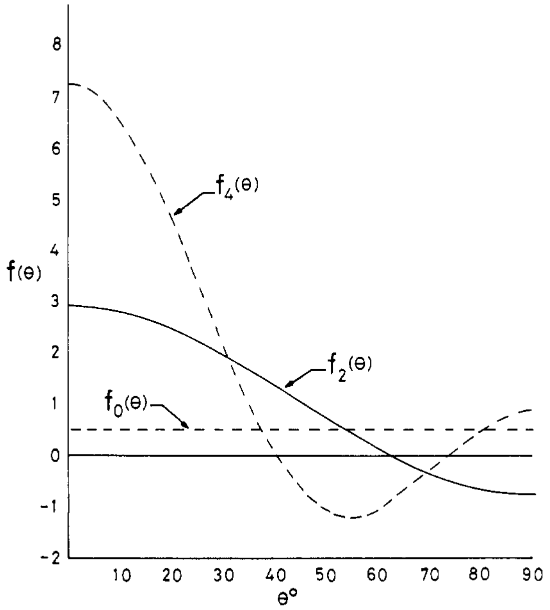

Figure 6. The orientational distribution function, $f(\theta)$, for Kevlar 49 as calculated from eq 1. The subscript on $f(\theta)$ refers to the highest Legendre polynomial employed in the truncated representation of eq 1.

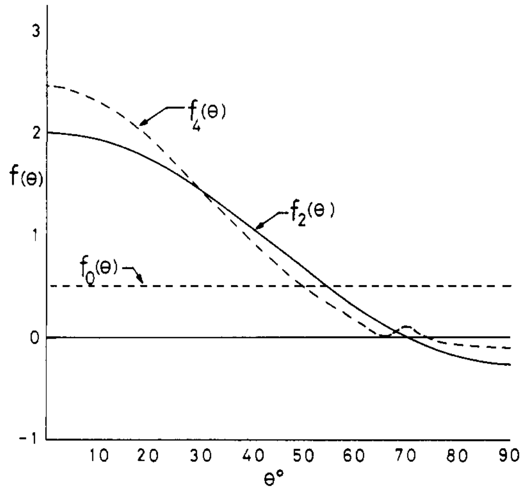

Figure 7. The orientational distribution function, $f(\theta)$, for a low molecular weight nematic liquid crystal N-(p-methoxybenzylidene)-p-n-butylaniline (MBBA). The subscripts on $f(\theta)$ are as in Figure 4. For this calculation, $\langle P_2\rangle$ is taken as 0.6 and $\langle P_4\rangle$ as 0.1.

1. Note the sharp increase at lower angles in $f(\theta)$ that is obtained by the inclusion of the P_4 term. This is in contrast to the case shown in Figure 7 for the low molecular weight nematic liquid crystal *N*-(*p*-methoxybenzylidene)-*p*-*n*-butylaniline, MBBA, where $\langle P_2(\cos\theta)\rangle >> \langle P_4(\cos\theta)\rangle$, and reinforces our initial postulate that for highly ordered systems, it would be necessary to experimentally obtain information about the higher order terms in eq 1 in order to obtain a valid picture of the orientational distribution function, $f(\theta)$. The negative values of $f(\theta)$ obtained at some angles are presumably due to the truncation of the series expansion. Information about the higher moments of the distribution would be necessary to faithfully reproduce the form of $f(\theta)$ for all θ.

Finally, the fact that the above determinations can be performed on a naturally fluorescent polymer precludes a valid criticism often leveled at probe studies: namely, that the presence of the probe might create a significant local perturbation of the structure and that ensemble averages for the probe do not adequately reflect those of the polymer chains, the real subject of study.

Conclusion

It is possible to use the fluorescence depolarization method to obtain the orientational distribution function to second order for highly oriented ultrahigh-modulus fibers.

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Appendix

The Polarization of the Absorption Transition Moment in Kevlar 49. The justification for assuming that the transition for Kevlar 49 is long-axis polarized, i.e., $\alpha = 0°$, lies in the fact that a reasonable and self-consistent numerical solution to the equations for r' and r'' is readily deduced. If the transition were short-axis polarized, i.e., $\alpha = 90°$, the following set of equations analogous to eq 10 and 11 derived from the tensor elements of ref 14 would apply:

$$r' = \frac{3(2x+1)\langle\cos^4\theta\rangle - 2(6x+1)\langle\cos^2\theta\rangle + (6x-1)}{8(1-\langle\cos^2\theta\rangle)} \tag{A1}$$

$$r'' = \frac{5(2x+1)\langle\cos^4\theta\rangle - 6(6x-5)\langle\cos^2\theta\rangle + (10x-11)}{2(2x+1)\langle\cos^4\theta\rangle + 12(2x-3)\langle\cos^2\theta\rangle + (4x-14)} \tag{A2}$$

where $x = \cos^2\delta$.

One can readily see that $r'' < 0$ for highly oriented fiber samples, i.e., small values of θ. For perfect orientation, $\theta \equiv 0$, $r'' = -^1/_2$. Note that the data here clearly show that $r'' > 0$. Additionally, an attempt to solve eq A1 and A2 using the experimentally determined values of r' and r'' shows that it is impossible irrespective of the choices of δ to obtain θ equal to a small angle as indicated from the X-ray results[4] and the generally accepted physics of these materials.

References and Notes

(1) J. Preston, *Polym. Eng. Sci.*, **15** (3), 199 (1975).
(2) H. Mark, *Macromolecules*, **10** (5), 881 (1977).
(3) G. Alfonso, E. Bianchi, A. Ciferri, S. Russo, F. Salaris, and B. Valenti, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **18** (1), 179 (1977).
(4) M. G. Dobb, D. J. Johnson, and B. P. Saville, *J. Polym. Sci., Part A-2*, **15**, 2201 (1977).
(5) E. B. Priestly, P. J. Wojtowicz and Ping Sheng, Eds., "Introduction to Liquid Crystals", Plenum Press, New York, 1974, Chapter 6.
(6) P. H. Hermans, "Contribution to the Physics of Cellulose Fibers", Elsevier, Amsterdam, 1946, p 195ff.
(7) I. M. Ward, "Structure and Properties of Oriented Polymers", Applied Science, London, 1975.
(8) L. L. Chapoy and D. B. DuPrê, *J. Chem. Phys.*, **69**, 519 (1978).
(9) L. L. Chapoy and D. B. DuPré, *J. Chem. Phys.*, **70**, 2550 (1979).
(10) L. L. Chapoy and D. B. DuPrê, "Experimental Methods of Physics: Polymer Physics", R. A. Fava, Ed., Academic Press, in press.
(11) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **57**, 2413 (1962).
(12) G. Weber, *Trans. Faraday Soc.*, **50**, 552 (1954).
(13) G. Weber and M. Shinitzky, *Proc. Natl. Acad. Sci. U.S.A.*, **65** (4), 823 (1970).
(14) J. H. Nobbs, D. I. Bower, I. M. Ward, and D. Patterson, *Polymer*, **15**, 287 (1974).

Quasielastic Light Scattering from Entangled Polymer Solutions

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ABSTRACT: The theoretical interpretation of the quasielastic light scattering properties of entangled polymer solutions is discussed. A modified version of the theory of Brochard and deGennes, based on an entanglement network with finite lifetime, is found to be in accord with recent experimental results on certain macroion solutions. This leads to the suggestion that an intermediate regime of hydrodynamic properties exists between that concentration corresponding to the onset of entanglements, described by the "congested diffusion" model of Lee et al., and the characteristic concentration defined by Klein in which a cooperative transition to a reptative diffusion mode occurs. The analysis described here appears to have potential for a more detailed interpretation of the hydrodynamic structure of entangled polymer solutions from light scattering experiments.

Following the theoretical treatment by deGennes[1,2] of the hydrodynamic properties of entangled solutions of flexible polymers in good solvents, there has been recent interest in experimental tests of the accuracy of the theoretical predictions utilizing quasielastic light scattering techniques.[3-5] In summary, the deGennes theory[1,2] concludes that, at concentrations below c^*, a critical value at which interchain entanglements are manifest, the relaxation of concentration fluctuations proceeds by the usual Fickian mechanism, characterized by the mutual trans-

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