Spectral Distribution of Light Scattered from Once-Broken Rods[1]

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ABSTRACT: The spectral distribution of light scattered from monodisperse, infinitely dilute solutions of optically isotropic, once-broken rods is calculated. It is assumed that the break occurs in the middle of the rod and that it acts as a universal joint about which the two segments independently undergo rotational diffusion with identical rotational diffusion coefficients. The integrated scattered intensity is calculated as well as the contributions to this intensity of the pure translational diffusion term and the first few terms whose spectral distribution depends on both the rotational and translational diffusion coefficients. The results are compared to those previously obtained for the rigid rod.

I. Introduction

The spectra of light scattered from optically isotropic rigid-rod[3] and Gaussian-coil macromolecules[4] have been studied in a previously published series of articles. It was shown in these articles that "intramolecular" motions contribute significantly to the scattered spectra when the molecules are large. Thus for rigid rods of the proper size, experimental study of the light-scattering spectrum would yield the rotational diffusion coefficient of the rod in addition to its translational diffusion coefficient. For the Gaussian coil, it was shown that the largest intramolecular relaxation times might be obtained from such experiments when the root-mean-square end-to-end distance of the coil is large. Experimental confirmation of these results has been obtained only for the rigid-rod case.[5] As yet no light-scattering experiments designed to observe the intramolecular motions in large flexible-coil macromolecules have been undertaken.

It is well known, however, that the rigid-rod and Gaussian coil models are limiting cases and that macromolecules in solution usually have more complex conformations and dynamics. Furthermore, many macromolecules undergo shape transitions from rodlike to flexible coil conformations when temperature or solution pH is varied. In fact theories of helix–coil transitions in polypeptide solutions contend that intermediate conformations containing helical rodlike regions alternating with flexible coil regions exist.[6]

In order to obtain a qualitative understanding of the light-scattering spectrum of this "intermediate" case, and to investigate the applicability of the light-scattering method to the study of such conformational transitions, we present here a calculation of the spectrum of the once-broken rod model recently considered by Yu and Stockmayer.[7] In fact, once-broken rod macromolecules have been synthesized, and their hydrodynamic properties studied.[8]

II. General Expressions

Consider a rod of total length L, broken in the middle. The break is considered to be a universal joint about which each portion of the rod is assumed to undergo rotational diffusion with identical rotational diffusion coefficients. In addition, it is assumed that the rotational motion of each portion of the rod is independent of the translational diffusion of the molecular center of mass. The rod is divided into $2n + 1$ optically isotropic segments. In a coordinate system with origin at the joint, the spherical polar coordinates of segment i on one side of the joint are $|i|b, \theta, \varphi$; those of segment j on the other side of the joint are $|j|b, \theta', \varphi'$, where $b = L/2n$. It is easy to show that the center of mass (cm) of the broken rod in this coordinate system is

$$\mathbf{r}_{\mathrm{cm}} = (nb/4)\{\hat{\imath}(\sin\theta\cos\varphi + \sin\theta'\cos\varphi') + \hat{\jmath}(\sin\theta\sin\varphi + \sin\theta'\sin\varphi') + \hat{k}(\cos\theta + \cos\theta'\} \quad (1)$$

Let $\mathbf{R}_{\mathrm{cm}}$ be the position of the center of mass of the broken rod in a laboratory coordinate system. Then the position of segment i in the laboratory system is

$$\mathbf{R}_i = \mathbf{R}_{\mathrm{cm}} + (\mathbf{r}_i - \mathbf{r}_{\mathrm{cm}}) \quad (2)$$

where $\mathbf{r}_i = (|i|b, \theta, \varphi)$.

The relative scattered light spectral density for this system is

$$S(\kappa, \omega) = \frac{1}{2\pi}\int \exp(-i\omega t)P(\kappa, t)\,\mathrm{d}t \quad (3)$$

where

$$P(\kappa, t) = \frac{1}{(2n)^2}\langle\sum_{i,j} \exp\{i\kappa\cdot[\mathbf{R}_i(0) - \mathbf{R}_j(t)]\}\rangle \quad (4)$$

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(5) T. J. Herbert, F. D. Carlson, and H. Z. Cummins, *Biophys. J.*, **8**, 95 (1968) (abstract TD-1).

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The length of κ depends on the scattering angle θ_s and light wavelength in the medium λ

$$\kappa = \frac{4\pi}{\lambda} \sin \frac{\theta_s}{2}$$

and ω is the frequency displacement of the scattered light frequency from that of the incident frequency.

Substituting eq 2 into eq 4, and assuming that translation of the molecular center of mass is independent of segmental rotation, we obtain

$$P(\kappa, t) = P_{\mathrm{I}}(\kappa, t)P_{\mathrm{D}}(\kappa, t) \tag{5}$$

where the first factor, the "intramolecular" factor, is given by

$$P_{\mathrm{I}}(\kappa, t) = \left\langle \frac{1}{(2n)^2} \sum_{i,j} \exp\{i\kappa\cdot[\mathbf{r}_{\mathrm{cm}}(t) - \mathbf{r}_{\mathrm{cm}}(0) + \mathbf{r}_i(0) - \mathbf{r}_j(t)]\} \right\rangle \tag{6}$$

and the second factor, the "translational diffusive" factor, is

$$P_{\mathrm{D}}(\kappa, t) = \langle \exp\{i\kappa\cdot[\mathbf{R}_{\mathrm{cm}}(0) - \mathbf{R}_{\mathrm{cm}}(t)]\}\rangle \tag{7}$$

$P_{\mathrm{D}}(\kappa, t)$ has been discussed in previous articles.[3,4] It depends upon the translational diffusion coefficient. D and is given by

$$P_{\mathrm{D}}(\kappa, t) = \exp(-\kappa^2 D|t|) \tag{8}$$

III. Calculation of the Integrated Relative Intensity

The integrated (over frequency) relative intensity is given by

$$P(\kappa L) \equiv \int S(\kappa, \omega)\, \mathrm{d}\omega = P(\kappa, 0) = \left\langle \frac{1}{(2n)^2} \sum_{i,j} \exp\{i\kappa\cdot[\mathbf{r}_i(0) - \mathbf{r}_j(0)]\} \right\rangle \tag{9}$$

The sum in eq 9 may be split into two sums—one over segments on the same side of the joint, and the other over segments on different sides of the joint

$$P(\kappa L) = \left\langle \frac{1}{(2n)^2} \sum_{\mathrm{same}} (\quad) \right\rangle + \left\langle \frac{1}{(2n)^2} \sum_{\mathrm{diff}} (\quad) \right\rangle \tag{10}$$

The first sum on the right-hand side of eq 10 is just one-half the standard relative intensity function, P_{rr}, for a rigid rod (rr) evaluated at $\kappa L/2$

$$\left\langle \frac{1}{(2n)^2} \sum_{\mathrm{same}} \right\rangle = {}^1\!/_2 P_{\mathrm{rr}}\left(\frac{\kappa L}{2}\right) \tag{11}$$

where

$$P_{\mathrm{rr}}\left(\frac{\kappa L}{2}\right) = \left[\frac{4}{\kappa L}\int_0^{\kappa L/2} \frac{\sin Z}{Z}\, \mathrm{d}Z - \left(\frac{4}{\kappa L} \sin \frac{\kappa L}{4}\right)^2\right] \tag{12}$$

The second sum on the right-hand side of eq 10 is also easy to evaluate since the orientations of the position vectors of segments on different sides of the rod are statistically uncorrelated. We find

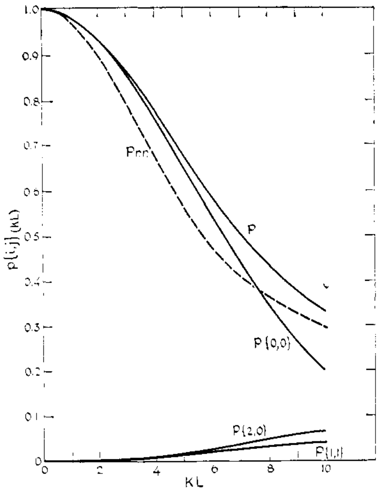

Figure 1. Plot of the integrated relative intensity functions of the once-broken rod, P, $P\{^{0,0}\}$, $P\{^{1,1}\}$, and $P\{^{2,2}\}$ *vs.* the scattering parameter $\kappa L = 4\pi(L/\lambda) \sin (\theta_s/2)$. For reference, the total integrated relative intensity function for a rigid rod P_{rr} (dashed curve) is also shown.

$$\left\langle \frac{1}{(2n)^2} \sum_{\mathrm{diff}} \right\rangle = {}^1\!/_2 \left(\frac{2}{\kappa L}\int_0^{\kappa L/2} \frac{\sin Z}{Z}\, \mathrm{d}Z\right)^2 \tag{13}$$

From eq 10–13, the total integrated intensity is

$$P(\kappa L) = {}^1\!/_2 \left[P_{\mathrm{rr}}\left(\frac{\kappa L}{2}\right) + \left(\frac{2}{\kappa L}\int_0^{\kappa L/2} \frac{\sin Z}{Z}\, \mathrm{d}Z\right)^2\right] \tag{14}$$

$P(\kappa L)$ is plotted in Figure 1 as well as $P_{\mathrm{rr}}(\kappa L)$. It is seen that $P(\kappa L)$ does not decrease as rapidly with increasing κL as $P_{\mathrm{rr}}(\kappa L)$. This is a result to be expected since the broken rod is more bunched up in solution and would therefore not give as much destructive intramolecular interference in light scattering. We also note that $P(0) = 1$ as it must.

IV. Calculation of $P(\kappa, t)$

$P_I(\kappa, t)$ may be evaluated by a method analogous to that used for rigid rods.[2] We break the sum in eq 6 for $P_{\mathrm{I}}(\kappa, t)$ into two sums—one in which the summation includes only segments on the same side of the joint $P_{\mathrm{I}}^{\mathrm{s}}$, and one in which summation includes only segments on different sides of the joint, $P_{\mathrm{I}}^{\mathrm{D}}$. Then

$$P_{\mathrm{I}}^{\mathrm{s}}(\kappa, t) = \left\langle \frac{1}{2n^2} \sum_{i,j}^{n} \exp\left\{i\kappa\cdot b\left[\left(1 - \frac{n}{4|i|}\right)\hat{r}(t)|i| - \left(1 - \frac{n}{4|j|}\right)\hat{r}(0)|j|\right]\right\}\right\rangle_{\theta,\varphi} \times \left\langle \exp\left\{- i\kappa\cdot\left[\frac{nb}{4}\hat{r}'(t) - \hat{r}'(0)\right]\right\}\right\rangle_{\theta',\varphi'} \tag{15}$$

and

$$P_{\mathrm{I}}^{\mathrm{D}}(\kappa, t) = \left\langle \frac{1}{2n^2} \sum_{i,j=0}^{n} \exp\left\{i\kappa\cdot b\left[\left(1 - \frac{n}{4|i|}\right)\hat{r}(t)|i| + \frac{n}{4}\hat{r}(0)\right]\right\}\right\rangle_{\theta,\varphi} \left\langle \sum_j \exp\left\{-i\kappa\cdot b\left[\left(1 - \frac{n}{4|j|}\right)\hat{r}'(0)|j| + \frac{n}{4}\hat{r}'(t)\right]\right\}\right\rangle_{\theta',\varphi'} \tag{16}$$

where $\hat{r}$ signifies a unit vector in the direction of $\mathbf{r}$ and $\langle\ \rangle_{\theta,\varphi}$ signifies an average over θ, φ. The averages are easily evaluated using the spherical harmonic expansion

$$\exp(i\kappa\cdot\mathbf{r}) = 4\pi\sum_l\sum_m i^l Y_l^{m*}(\Omega_r)Y_l^m(\Omega_k)j_l(\kappa r) \quad (17)$$

where Ω_r and Ω_k are the spherical polar coordinates of $\mathbf{r}$ and κ in some laboratory coordinate system and j_l is a spherical Bessel function of order l. Each segment of the rod has been assumed to obey the rotational diffusion equation

$$\frac{\partial J(\Omega - \Omega_0, t)}{\partial t} = \Theta\nabla^2 J(\Omega - \Omega_0, t) \quad (18)$$

where $J(\Omega - \Omega_0, t)$ is the probability that a segment is oriented in a direction between Ω and $\Omega + d\Omega$ at time t if it is oriented between Ω_0 and $\Omega_0 + d\Omega_0$ at time zero, and Θ is the rotational diffusion coefficient. The solution of eq 18 is

$$J(\Omega - \Omega_0, t) = \sum_l\sum_m Y_l^m(\Omega_{r_t})Y_l^{m*}(\Omega_{r_0}) \times \exp\{-\Theta(l)(l+1)|t|\} \quad (19)$$

From eq 15–19 and the orthonormality property of the spherical harmonics we obtain

$$P_{\mathrm{I}}^{\mathrm{s}}(\kappa, t) = \frac{1}{2n^2}\sum_{i,j}\sum_{l,l'}(2l+1) \times (2l'+1)\exp\{-\Theta[l(l+1) + l'(l'+1)]|t|\} \times i_l(\kappa\alpha_i)j_l(\kappa\alpha_j)j_{l'}{}^2\left(\frac{\kappa L}{8}\right) \quad (20)$$

and

$$P_{\mathrm{I}}^{\mathrm{D}}(\kappa, t) = \frac{1}{2n^2}\sum_{i,j}\sum_{l,l'} i^{2(l+l')}(2l+1)(2l'+1) \times \exp\{-\Theta[(l)(l+1) + l'(l'+1)]|t|\} \times j_l(\kappa\alpha_i)j_{l'}(\kappa\alpha_j)j_l\left(\frac{\kappa L}{8}\right)j_l\left(\frac{\kappa L}{8}\right) \quad (21)$$

where

$$a_i = b|i| - \frac{nb}{4} \quad (22)$$

Then, from eq 5, 8, 20 and 21

$$P(\kappa, t) = \exp[-\kappa^2 D|t|]\sum_{\{l,l\}} P_{\mathrm{I}}^{\{l,l'\}}(\kappa, t) \quad (23)$$

where

$$P_{\mathrm{I}}^{\{l,l'\}} = \begin{cases} P_{\mathrm{I}}^{(\boldsymbol{l},\boldsymbol{l'})} + P_{\mathrm{I}}^{(l,l')} & l \neq l' \\ P_{\mathrm{I}}^{(\boldsymbol{l},\boldsymbol{l'})} & l = l' \end{cases} \quad (24)$$

and

$$P_{\mathrm{I}}^{(l,l')}(\kappa, t) = \frac{1}{2n^2}(2l'+1)(2l+1)\exp\{-\Theta|t|[l(l+1) + l'(l'+1)]\}\sum_{i,j=0}^{n}\left\{j_l(\kappa\alpha_i)j_l(\kappa\alpha_j) \times j_{l'}{}^2\left(\frac{\kappa L}{8}\right) + i^{2(l+l')}j_l(\kappa\alpha_i)j_{l'}(\kappa\alpha_j)j_l\left(\frac{\kappa L}{8}\right)j_{l'}\left(\frac{\kappa L}{8}\right)\right\} \quad (25)$$

The double summations in eq 25 may be replaced by the squares of single summations, *e.g.*

$$\frac{1}{n^2}\sum_{i,j} j_l(\kappa\alpha_i)j_l(\kappa\alpha_j) = \left[\frac{1}{n}\sum_i j_l(\kappa\alpha_i)\right]^2 \quad (26)$$

The single summations may, in the limit of a continuous, distribution of segments, be replaced by integrations *e.g.*

$$\frac{1}{n}\sum_i j_l(\kappa\alpha_i) \rightarrow \frac{2}{\kappa L}\int_{-(\kappa L/8)}^{3\kappa L/8} j_l(Z)\,dZ \quad (27)$$

From eq 26 and 27, we find for the first few terms in the summation on the right-hand side of eq 23

$$P_{\mathrm{I}}^{\{0,0\}}(\kappa) = \left\{j_0\left(\frac{\kappa L}{8}\right)\left[\frac{2}{\kappa L}\int_{-\kappa L/8}^{3\kappa L/8} j_0(Z)\,dZ\right]\right\}^2 \quad (28)$$

$$P_{\mathrm{I}}^{\{1,0\}}(\kappa, t) = \frac{3}{2}\exp[-2\Theta|t|]\left\{j_1\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L} \times \int j_0(Z)\,dZ - j_0\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L}\int j_1(Z)\,dZ\right\}^2 \quad (29)$$

$$P_{\mathrm{I}}^{\{1,1\}}(\kappa, t) = 9\exp[-4\Theta|t|] \times \left\{j_1\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L}\int j_1(Z)\,dZ\right\}^2 \quad (30)$$

$$P_{\mathrm{I}}^{\{2,0\}}(\kappa, t) = \frac{5}{2}\exp[-6\Theta|t|] \times \left\{j_2\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L}\int j_0(Z)\,dZ + j_0\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L}\int j_2(Z)\,dZ\right\}^2 \quad (31)$$

$$P_{\mathrm{I}}^{\{2,1\}}(\kappa, t) = \frac{15}{2}\exp[-8\Theta|t|] \times \left\{j_1\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L}\int j_2(Z)\,dZ - j_2\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L}\int j_1(Z)\,dZ\right\}^2 \quad (32)$$

$$P_{\mathrm{I}}^{\{2,2\}}(\kappa, t) = 25\exp[-12\Theta|t|] \times \left\{j_2\left(\frac{\kappa L}{8}\right)\frac{2}{\kappa L}\int j_2(Z)\,dZ\right\}^2 \quad (33)$$

All integrals in eq 28–33 have lower integration limit $-(\kappa L/8)$ and upper limit $3\kappa L/8$. It is a simple matter to find higher $\{l, l'\}$ terms from eq 25.

We note that the spectrum of the $P_{\mathrm{I}}^{\{0,0\}}$ term will not depend on the segment rotational diffusion coefficient. This term will, when multiplied by $P_{\mathrm{D}}(\kappa, t)$, contribute a Lorentzian line with half-width

$$\Delta\nu_{1/2} = \frac{\kappa^2 D}{\pi} \quad (34)$$

and integrated intensity $P_{\mathrm{I}}^{\{0,0\}}$ to the scattered spectrum. We note that

$$\lim_{\kappa L \to 0} P^{\{l,l'\}}(\kappa L) = 0 \quad (35)$$

for $\{l, l'\} \neq \{0, 0\}$ where we have dropped the I subscript and use the convention that when t is not explicitly indicated it is equal to zero. This result is in accord with the rigid rod results and physical intuition.[2] In the limit of small rods and/or low κ rotations and intramolecular conformational changes will not contribute to the spectral width of the scattering from optically isotropic molecules. In this limit the spectrum consists of a single Lorentzian with half-width given by eq 34.

V. Numerical Results and Discussion

Calculations of $P(\kappa L)$ (eq 14) and $P^{\{l,l'\}}(\kappa L)$ for $\{l, l'\}$ from $\{0, 0\}$ to $\{2, 2\}$ (eq 28–33) have been carried out for values of κL between zero and ten. The difference

$$\Delta \equiv \frac{P(\kappa L) - P^{\{0,0\}}(\kappa L)}{P(\kappa L)} \times 100$$

is the per cent of the scattered intensity whose spectral width depends on the segmental rotational diffusion coefficient. The terms $P(\kappa L)$ and $P^{\{0,0\}}(\kappa L)$ are plotted in the graph. It may be seen from the graph that Δ is probably negligible for $\kappa L < 4$ (<2%). In this region measurement of the scattering spectrum would yield only the macromolecular translational diffusion coefficient. At $\kappa L = 7$, $\Delta \cong 13\%$; it rises to 40% at $\kappa L = 10$. Thus, in this region, the intramolecular effects are appreciable and should be detectable using standard laser techniques.[5]

Numerical calculation shows that $P^{\{1,0\}}(\kappa L)$, $P^{\{2,1\}}(\kappa L)$ and $P^{\{2,2\}}(\kappa L)$ are small compared to $P^{\{1,1\}}(\kappa L)$ and $P^{\{2,0\}}(\kappa L)$ over the range considered. Both $P^{\{1,1\}}(\kappa L)$ and $P^{\{2,0\}}(\kappa L)$ are plotted in the graph. The $P^{\{1,1\}}(\kappa L)$ term contributes a Lorentzian with half-width

$$\Delta\nu_{1/2} = \frac{D\kappa^2 + 4\Theta}{\pi} \quad (36)$$

to the scattered spectrum. Its total intensity ranges from 3% of $P(\kappa L)$ at $\kappa L = 6$ to 11% at $\kappa L = 10$. The $P^{\{2,0\}}(\kappa L)$ term contributes 4% at $\kappa L = 6$ and 18.6% at $\kappa L = 10$. Its spectral half-width is

$$\Delta\nu_{1/2} = \frac{D\kappa^2 + 6\Theta}{\pi} \quad (37)$$

The sum of the integrated intensities of all terms other than $\{0, 0\}$, $\{1, 1\}$ and $\{2, 0\}$ may be determined by subtraction.

$$P_s(\kappa L) = P(\kappa L) - [P^{\{0,0\}}(\kappa L) + P^{\{1,1\}}(\kappa L) + P^{\{2,0\}}(\kappa L)] \quad (38)$$

P_s is 1% of P at $\kappa L = 6$ and 9.4% of P at $\kappa L = 10$.

We have calculated the $\{1,0\}$, $\{2, 1\}$, and $\{2,2\}$ contributions to P_s. They are, however, each of the same order of magnitude and, as noted above, small compared to the $\{1, 1\}$ and $\{2,0\}$ terms. At $\kappa L = 8$, P_s is only 2% of P. We conclude that in the κL range from 7 to 8 at least 98% of the scattered intensity is given by the three Lorentzians with total intensities $P^{\{0,0\}}(\kappa L)$, $P^{\{1,1\}}(\kappa L)$ and $P^{\{2,0\}}(\kappa L)$ and widths given by eq 34, 36 and 37, respectively. The $\{1, 1\}$ and $\{2, 0\}$ terms are together about 18% of P at $\kappa L = 8$. For $\kappa L > 8$, the $P_s(\kappa L)$ terms should probably be considered in any experimental analysis.

These results should be compared with those obtained for the rigid rod.[3] As was noted in section III, the integrated relative intensity for the once-broken rod decreases more slowly with increasing κL than that for the rigid rod since the broken rod is, on the average, more compact in solution. Furthermore, the relative contributions of terms containing rotational diffusion coefficients to the total integrated intensity are less than those for the corresponding rigid rod at the same value of κL. On the other hand, over the κL range from 6 to 8, the broken rod spectrum will consist of a weighted sum of three Lorentzians while that for the rigid rod consists essentially of two Lorentzians.[3] If we further pursue the Yu–Stockmayer model, we note that Θ for the once-broken rod segment is twice that for the corresponding rigid rod. Thus the rotational diffusion coefficient contribution to the spectral widths, eq 36 and 37, will be larger than those for the rigid rod.[3]

If more breaks are made in the rod, we expect the intensities of the rotational terms to become smaller and smaller. In fact, a calculation of the scattered spectrum using the Rouse–Zimm Gaussian coil model shows that for "intramolecular" relaxation effects to be seen, the root-mean end-to-end distance, R, of the chain must be very large ($\kappa R > 4$). Since the coil is very compact in solution, the length along the chain (corresponding to our L) would be much larger than the root-mean-square end-to-end distance. Thus if a rigid rod with κL in the appropriate region undergoes a transition to a coil passing through a conformation resembling a once-broken rod, we expect the spectrum to change from the two-Lorentzian rod spectrum to the three-Lorentzian once-broken rod spectrum and then to the single Lorentzian translational diffusion spectrum predicted for rods with many breaks (or a Gaussian coil with $\kappa R > 4$). Of course if the spectrum were observed at low κL, it would initially be a single Lorentzian and remain so throughout the transition; however, its half-width would change due to variations of the translational diffusion coefficient with molecular shape.[9]

The mathematical techniques and methods of calculation presented here may be easily extended to the cases of rods with the break at points other than the center and, of course, to rods with many breaks as well as to systems in which the dynamics is more complex than simple rotational diffusion.

In addition these same techniques may be used to compute the depolarized spectrum for molecules composed of optically anisotropic segments.[10] In view of the limitation of the light-scattering method described above to very large molecules, we expect studies of the depolarized spectrum to be more useful than studies of the polarized spectrum. Calculations are now in progress on the depolarized spectrum of rigid and broken rods of arbitrary size.

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