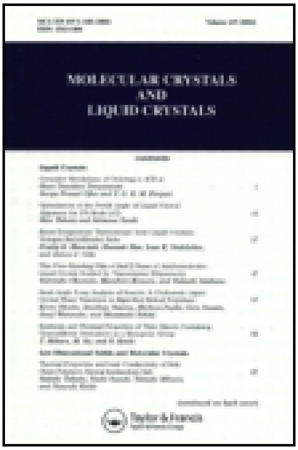

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Orientational Characteristics of nCB(n =5,6,7) Liquid Crystals by Means of Fluorescence Probe Method

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Orientational Characteristics of *n*CB(*n* = 5,6,7) Liquid Crystals by Means of Fluorescence Probe Method

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Three kinds of fluorescence depolarization ratios (R_1, R_2 and R_3) of 4-amino-4′-nitrobiphenyl have been measured in the liquid crystalline state of 5CB, 6CB and 7CB. It was found that these three ratios depend to a certain extent on the sample thicknesses. The dependence was studied in detail by using three kinds of cells of different thickness for each sample. The 2nd orientational order parameter $\overline{P}_2$, evaluated analytically from R_1, R_2 and R_3 were found to be thickness independent. Several methods to estimate the fourth orientational order parameter $\overline{P}_4$ of the solute from the above $\overline{P}_2$ or from that of a neat sample were examined on the basis of Marcelja's type mean field theory. The temperature dependence of two correlation times of rotational Brownian motion have been evaluated and interpreted on the basis of a reorientational diffusion model.

1. INTRODUCTION

The study of orientational order parameters and molecular dynamics of liquid crystals has been of primary importance in understanding various aspects of the physics of liquid crystals.[1] Experimental determination of order parameters has been carried out extensively by a wide variety of spectroscopic methods, but few of them are practically capable of providing information on the molecular dynamics in liquid crystals. Among them, the fluorescence method is versatile in principle, since fluorescence depolarization contains both information on 2nd and 4th orientational order parameters ($\overline{P}_2$ and $\overline{P}_4$), and molecular reorientational relaxation times (τ_{00} and τ_{20}) in the liquid crystalline state.[2] However, in practice, the above quantities are not able to be determined merely from fluorescence depolarization ratios unless a relation between these quantities is known.[3] This difficulty had been avoided in previous works by neglecting the contribution of reorientational motions on depolarization ratios,[4] or by assuming $\tau_{00} = \tau_{20}$.[5] In a recent work,[6] an indirect

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relation between τ_{00} and τ_{20} was derived on the basis of a mean field theory. But it seems at present rather difficult to make reliable predictions for dynamical properties of liquid crystalline states such as τ_{00} and τ_{20}.

In the present work, we measured three kinds of fluorescence depolarization ratios (R_1, R_2 and R_3) of 4-amino-4'-nitrobiphenyl(ANB) embedded in 4-*n*-alkyl-4'-cyanobiphenyl (*n*CB; $n = 5, 6, 7$) liquid crystals.

Sample cells of three different thicknesses were used to study the thickness dependence of fluorescence depolarization ratios for each homogeneously and homeotropically aligned sample. Three ratios were found to depend systematically on sample thicknesses to some extent. Nevertheless, $\overline{P}_2$, evaluated analytically from R_1, R_2 and R_3 was found to hardly depend on sample thicknesses. To get other quantities, a relation between $\overline{P}_2$ and $\overline{P}_4$ was derived on the basis of the mean field theory of Marcelja's type[7,8] in which the solute-solvent interaction was taken explicitly into consideration. $\overline{P}_4$, and the ratio of reorientational correlation times (τ_{00}, τ_{20}) on fluorescence lifetime (τ_F) were deduced simultaneously by using the above relation. Another relation between $\overline{P}_2$ and $\overline{P}_4$ was also examined. The remarkably different temperature dependence between τ_{00}/τ_F and τ_{20}/τ_F were obtained and were exploited reasonably on the basis of a rotational diffusion model of the molecular reorientational motion.[9,10]

EXPERIMENTAL

ANB/*n*CB samples were prepared in the same way as before.[3] Three depolarization ratios R_1, R_2 and R_3 were measured in a forward arrangement shown in Figure 1. The 436 nm line of a high pressure Hg lamp, which was isolated by using interference and $Cu(NH_3)_4SO_4$ solution filters, was used as an excitation source. Linear polarization of light was attained by means of a Glam-Thompson prism. The optical setup was carefully adjusted before the measurement so that the Z and X polarized excitation light (Figure 1) gave the same fluorescence spectrum for a sample in the isotropic phase. Because we observed the dependence of fluorescence depolarization ratios on the sample thickness, sample cells of three different thicknesses, 12 μm, 25 μm and 38 μm were used for each homogeneously and homeotropically aligned sample.

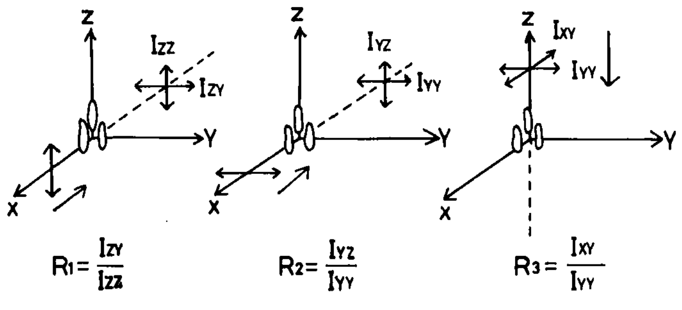

FIGURE 1 Experimental geometries for measuring the fluorescence depolarization ratios (R_1, R_2 and R_3) by the forward arrangement.

RESULTS AND DISCUSSION

Observed depolarization ratios (R_i^{obs}) were corrected for various optically anisotropic effects.[11,12] Supposing an isotropic local field to apply, the corrected depolarization ratios (R_i^{obs}) are written, as a whole,

$$R_1^{corr} = R_1^{obs}/C, \qquad R_2^{corr} = CR_2^{obs}, \qquad R_3^{corr} = R_3^{obs}$$
$$C = (n_e + n_o)^2/(n_o + n_g)^2 \tag{1}$$

where n_e and n_o are the refractive indices of extraordinary and ordinary light at the measured wavelength of fluorescence depolarization ratios and n_g is the refractive index of the glass. The n_e and n_o were obtained by interpolating the reported values[13,14] to our measured wavelength using the dispersion formula, $n_{e,o} = 1 + A_e, \lambda^2/(\lambda^2 - B_{e,o})$. The corrections described above are all thickness-independent. We observed that fluorescence depolarization ratios R_1^{obs}, R_2^{obs} and R_3^{obs}, depend to some extent on the sample thickness for every ANB/5CB, 6CB and 7CB sample. These thickness dependences were rather unexpected findings, because there have been few comprehensive references about them in the literature. Hence, we have measured R_1, R_2 and R_3 minutely using sample cells of three different thicknesses, 12 μm, 25 μm and 38 μm, for each of the homogeneously and homeotropically aligned 5CB, 6CB and 7CB samples. Figures 2–4 clearly show that depolarization ratios depend systematically on sample thicknesses. The thickness dependence of R_2 is more noticeable than that of R_1 and R_3. It is noted that the sign of thickness dependence $dR_2/dl > 0$ observed here (where l is the sample thickness) is opposite to that of the corresponding R_2 in the resonance Raman measurement.[15–17]

Since both the absorption and emission transition dipole moments are parallel in this experimental situation to the molecular long axis of ANB, $\overline{P}_2$ is expressed analytically in terms of R_1, R_2 and R_3, as[3]

$$\overline{P}_2 = \frac{R_2\,(1 + R_1) - R_1\,(1 + R_3)}{R_2\,(1 + 4R_1) + 2R_1\,(1 + R_3)} \tag{2}$$

Figures 5–7 show unexpected results in that $\overline{P}_2$ evaluated from Equation 2 by substituting the fully corrected depolarization ratios of Equation 1 do not show any recognizable thickness dependence. This behavior of $\overline{P}_2$ is remarkably contrastive with that in the polarized Raman measurement. In the latter, not only depolarization ratios, but also $\overline{P}_2$ depend on sample thicknesses. In Figure 5, $\overline{P}_2$ of the ANB/5CB sample obtained here is compared with that in the previous work.[3]

Applying Zannoni's theory,[3,4] fluorescence depolarization ratios are written as:

$$R_1 = \frac{1 + \overline{P}_2 - 2R_{00}}{1 + 4\overline{P}_2 + 4R_{00}}, \qquad R_2 = \frac{1 + \overline{P}_2 - 2R_{00}}{1 - 2\overline{P}_2 + R_{00} + 3R_{20}},$$
$$R_3 = \frac{1 - 2\overline{P}_2 + R_{00} - 3R_{20}}{1 - 2\overline{P}_2 + R_{00} + 3R_{20}} \tag{3}$$

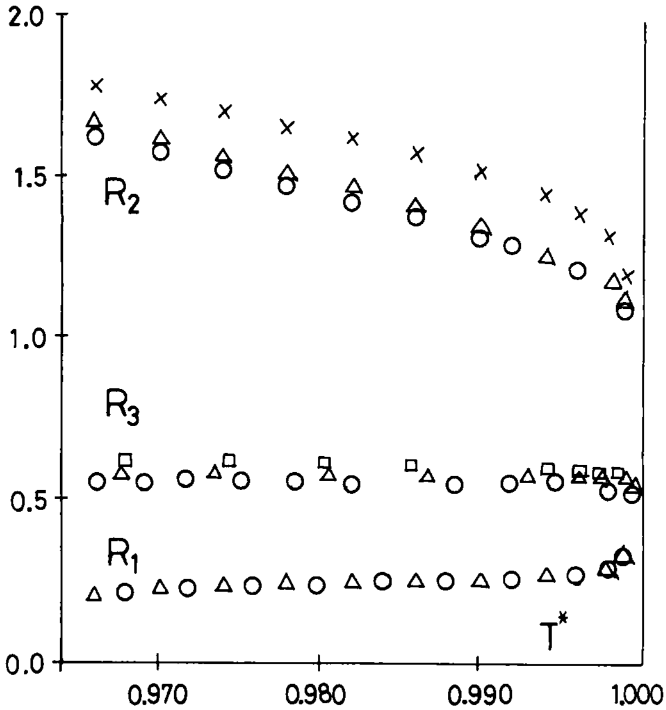

FIGURE 2 The temperature and thickness dependence of the fluorescence depolarization ratios of the ANB/5CB sample —○—○—○, 12 μm; —△—△—△—, 25 μm; —□—□—□—, 38 μm; —×—×—×—, 50 μm.

where

$$R_{k0} = (1/\tau_F) \int_0^\infty \overline{D^{(2)}_{k0}(\Omega(0)D^{(2)}_{k0}(\Omega(A))} \exp(-t/\tau_F)\, dt \tag{4}$$

represents the extent of rotational Brownian motions during the fluorescence lifetime (τ_F), and are written on the assumption of the single exponential decay of the orientational correlation functions with correlation time τ_{00} and τ_{20} for $D^{(2)}_{00}(\Omega(t))D^{(2)}_{00}(\Omega(0))$ and $D^{(2)}_{20}(\Omega(t))D^{(2)}_{20}(\Omega(0))$, as;

$$\begin{aligned} R_{00} &= (\overline{P_2^2} - (\overline{P}_2)^2)\tau_{00}/(\tau_{00} + \tau_F) + (\overline{P}_2)^2 \\ R_{20} &= (1/5 - (2/7)\overline{P}_2 + (3/35)\overline{P}_4)(\tau_{20}/(\tau_F + \tau_{20})) \end{aligned} \tag{5}$$

It should be noted that the quantities we can determine directly from R_1, R_2 and R_3 are $\overline{P}_2$, R_{00} and R_{20}, as can be seen in Equation 4. Because R_{00} and R_{20} are functions of four quantities, $\overline{P}_2$, $\overline{P}_4$, τ_F/τ_{00} and τ_F/τ_{20}, we can not uniquely determine these quantities merely from depolarization ratios, unless a relation is known be-

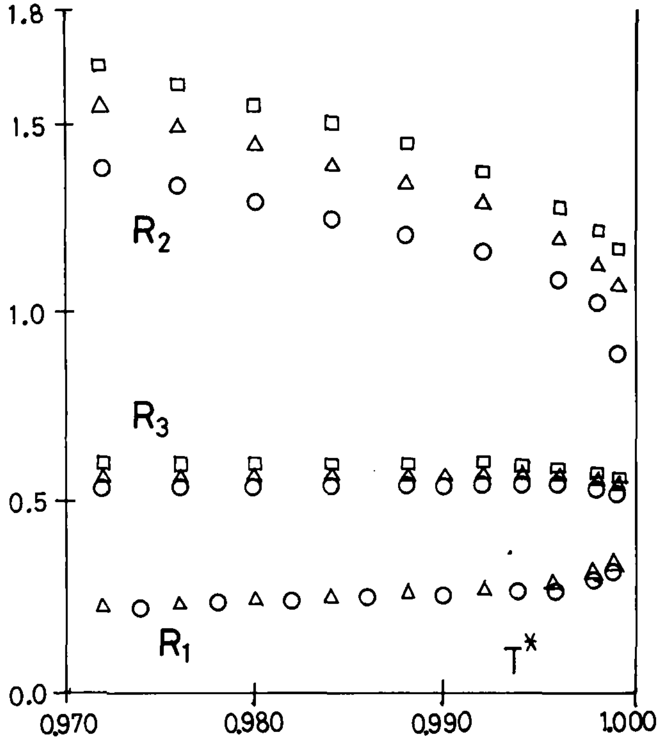

FIGURE 3 The temperature and thickness dependence of the fluorescence depolarization ratios of the ANB/6CB sample —○—○—○, 12 μm; —△—△—△—, 25 μm; —□—□—□—, 38 μm.

tween these quantities. In the previous paper,[3] a relation between critical order parameters had been used to elucidate these quantities. But accurate determination of depolarization ratios prerequisited to use this method is sometimes rather difficult, because these quantities change rather rapidly near transition temperature (T_N). In this work, we invoked a mean field to derive a relation between $\overline{P}_2$ and $\overline{P}_4$ of solute ANB. To this end, Marcelja's theory[7,8] was extended so as to be applicable to binary systems taking the solute-solvent interaction explicitly into consideration.

The molecular field experienced by a nematic molecule (A) and a solute molecule (B), X_A and X_B respectively, can be written as;

$$\begin{aligned} -X_A &= \phi_A \nu_{AA} \overline{P}_{2,A} + \phi_B \nu_{BA} \overline{P}_{2,B} \\ -X_B &= \phi_A \nu_{AB} \overline{P}_{2,A} + \phi_B \nu_{BB} \overline{P}_{2,B} \end{aligned} \tag{6}$$

where ϕ_A and ϕ_B denote the volume fractions of A and B and where $\overline{P}_{2,A}$ and $\overline{P}_{2,B}$ are the 2nd order parameters of A and B respectively. The ν_{AB} etc. represent the strength of anisotropic interaction between A and B molecules, ν_{BB} being zero in this case because ANB is non-nematogenic. $\overline{P}_{2,B}$ can be written, from the require-

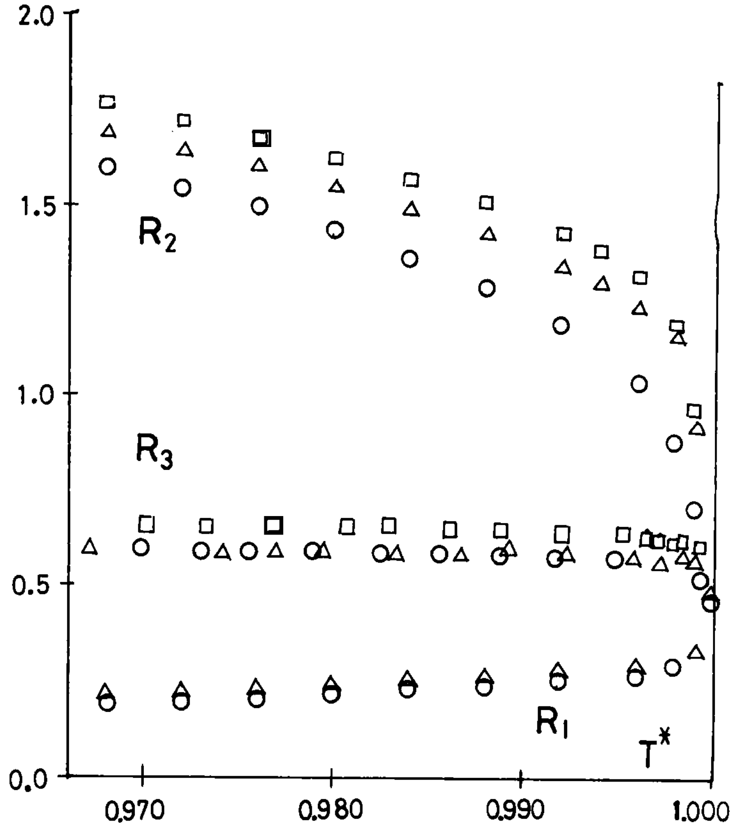

FIGURE 4 The temperature and thickness dependence of the fluorescence depolarization ratios of the ANB/7CB sample —○—○—○, 12 μm; —△—△—△—, 25 μm; —□—□—□—, 38 μm.

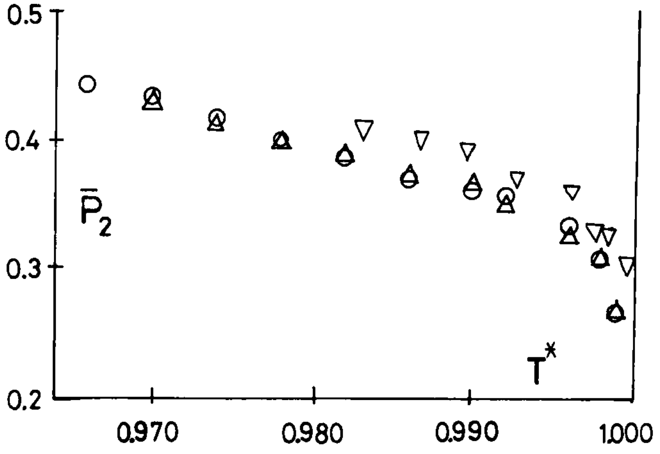

FIGURE 5 $\bar{P}_2$ of the ANB/5CB sample evaluated from Equation 2. ○—○—○, 12 μm; —△—△—△—, 25 μm.

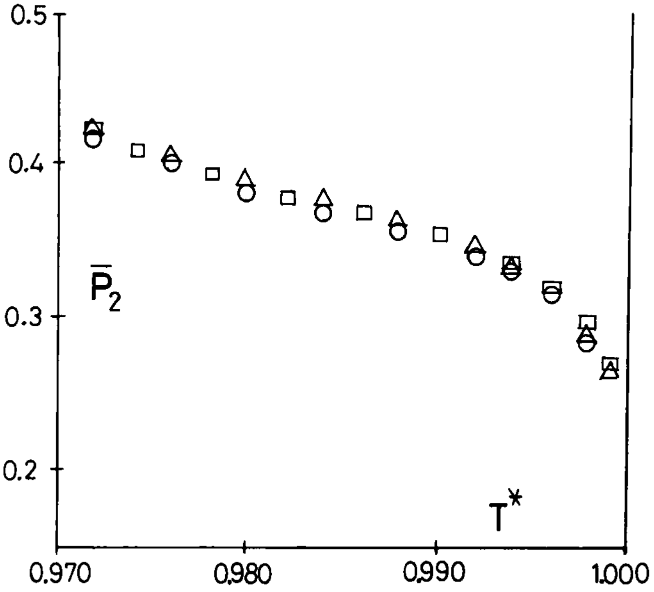

FIGURE 6 $\bar{P}_2$ of the ANB/6CB sample evaluated from Equation 2. —○—○—, 12 μm; —△—△—, 25 μm; —□—□—□—, 38 μm.

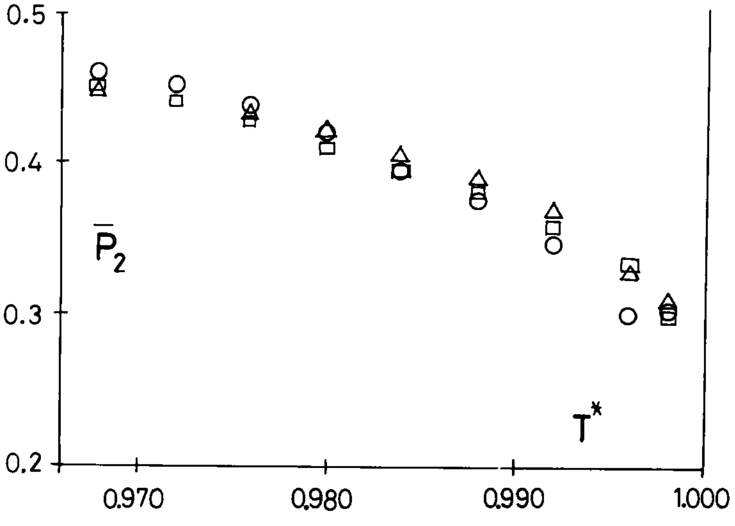

FIGURE 7 $\bar{P}_2$ of the ANB/7CB sample evaluated from Equation 2. —○—○—, 12 μm; —△—△—, 25 μm; —□—□—□—, 38 μm.

ment of self-consistency, as

$$\overline{P}_{2,\mathrm{B}} = \frac{\int_0^1 P_2(x)\exp\{(\nu_{\mathrm{AB}}/\nu_{\mathrm{AA}})(\overline{P}_{2,\mathrm{A}}/0.22019\mathrm{T}^*)P_2(x)\}\,dx}{\int_0^1 \exp\{(\nu_{\mathrm{AB}}/\nu_{\mathrm{AA}})(\overline{P}_{2,\mathrm{A}}/0.22019\mathrm{T}^*)P_2(x)\}\,dx} \tag{7}$$

where T* is the reduced temperature, and $\nu_{\mathrm{AB}}/\nu_{\mathrm{AA}}$ is a measure of the strength of solute–solvent interaction relative to that of solute–solute. Substituting $\overline{P}_2$ obtained by the resonance Raman method for the order parameter of the host, $\overline{P}_{2,\mathrm{A}}$,[18] the ratio $\nu_{\mathrm{AB}}/\nu_{\mathrm{AA}}$ was determined so as to reproduce the order parameter of the solute, $\overline{P}_{2,\mathrm{B}}$ of Equation 7. It was found that the value of $\nu_{\mathrm{AB}}/\nu_{\mathrm{AA}} \doteqdot 0.7$ reproduced as a whole $\overline{P}_{2,\mathrm{B}}$ of ANB for all 5CB, 6CB and 7CB. It is interesting to note that this ratio is nearly equal to the ratio of the length of the ANB molecule to the *n*CB molecules. Using this ratio, $\overline{P}_{4,\mathrm{B}}$ were evaluated as usual, consequently τ_F/τ_{00} and τ_F/τ_{20} were determined from Equations 3, 5. The $\overline{P}_4$ thus derived were found to be very small for all ANB/*n*CB systems throughout the entire nematic range of measurement, being in harmony with the previous results.[3]

In addition, the method proposed by Bradshaw and Tough[19] was examined. We found that $\overline{P}_4$ obtained from resonance Raman method by using β-carotene as a probe[18] can be reproduced surprisingly well by the equation,

$$\overline{P}_4 = \frac{\int_0^1 P_4(x)\exp\{(\gamma\overline{P}_2/0.22019\mathrm{T}^*)P_2(x)\}\,dx}{\int_0^1 \exp\{(\gamma\overline{P}_2/0.22019\mathrm{T}^*)P_2(x)\}\,dx} \tag{8}$$

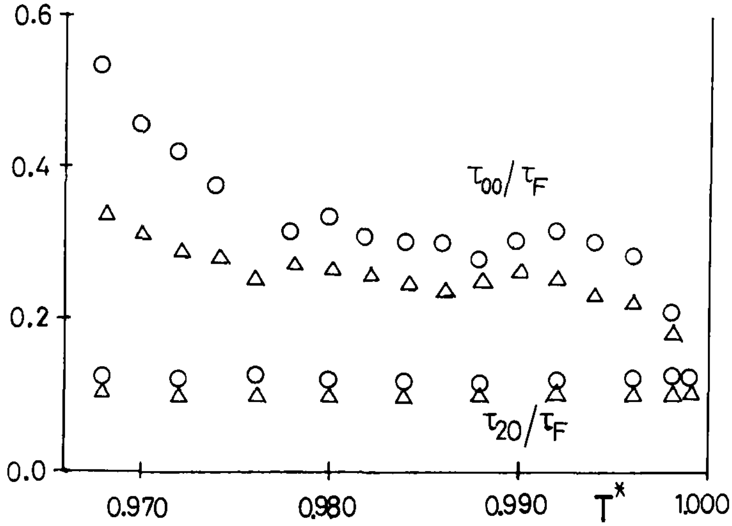

FIGURE 8 The temperature and thickness dependence of τ_{00}/τ_F and τ_{20}/τ_F of the ANB/5CB sample. —O—O—, 12 μm; —Δ—Δ—, 25 μm.

with $\gamma = 1.25$ for 7CB, $\gamma = 1.33$ for 5CB and 6CB. Assuming that the same γ values are applicable to the ANB probe molecule, $\overline{P}_{4,B}$ were calculated from $\overline{P}_{2,B}$. The $\overline{P}_{4,B}$ thus obtained were very small for all ANB/*n*CB systems, in harmony with the preceding results.

Figures 8–10 show clearly that τ_{00}/τ_F and τ_{20}/τ_F thus evaluated depend on sample thicknesses, reflecting the thickness dependence of depolarization ratios. The thickness dependence of τ_{00}/τ_F is more striking than that of τ_{20}/τ_F, and both are larger for a thinner sample. The origin of the thickness dependence of fluorescence depolarization ratios is not simply ascribed to multiple scattering by bulk liquid crystals. The surface effect is deemed also to have an important contribution. But quantitative explanation of the effect is not clear at present, nor is that of Raman depolarization ratios, and would be an interesting future study.

As regards temperature dependence of τ_{00}/τ_F and τ_{20}/τ_F, Figure 8 shows that τ_{20}/τ_F is almost temperature independent over the entire nematic range, whereas τ_{00}/τ_F is somewhat larger than τ_{20}/τ_F and decreases rapidly as the temperature is raised. In the isotropic phase, both were observed to be approximately equal as they should be so theoretically. The approximate constancy of τ_{20}/τ_F on temperature obtained here is in harmony with the assumption made in the previous work.[3] On the other hand, the temperature dependence of τ_{00}/τ_F is a new finding. The decreasing trend of τ_{00}/τ_F indicates that τ_{00} decreases with increase in temperature,

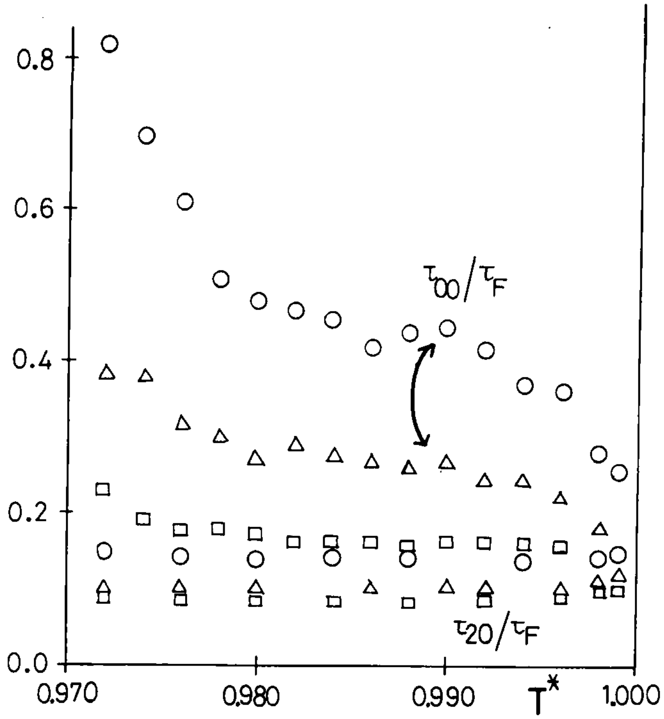

FIGURE 9 The temperature and thickness dependence of τ_{00}/τ_F and τ_{20}/τ_F of the ANB/6CB sample. —○—○—, 12 μm; —△—△—, 25 μm; —□—□—□—, 38 μm.

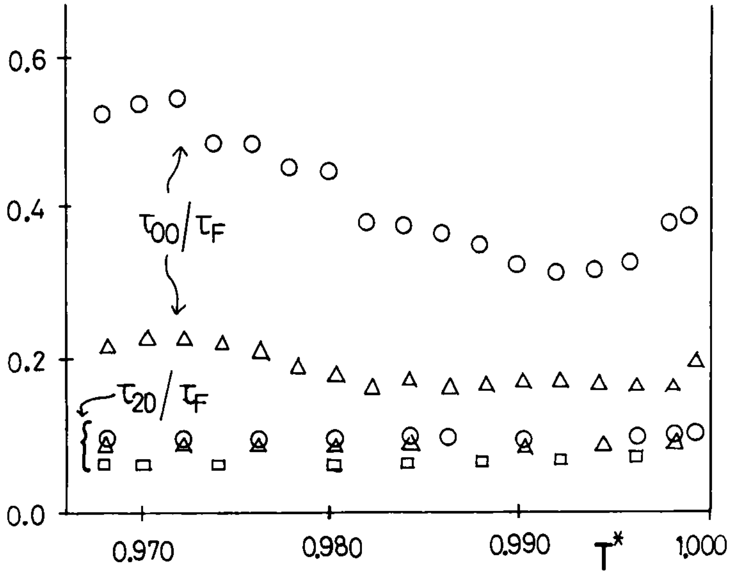

FIGURE 10 The temperature and thickness dependence of τ_{00}/τ_F and τ_{20}/τ_F of the ANB/7CB sample. —○—○—, 12 μm; —△—△—, 25 μm; —□—□—□—, 38 μm.

considering the slightly decreasing behavior of τ_F with increasing temperature which has been reported recently.[20] The τ_{00} is deemed to be inversely proportional to the rotational diffusion constant. The decreasing behavior of τ_{00} with temperature increase obtained here is consistent with the recent remarkable observation that $D_\perp$ increases with temperature rise. The approximate constancy of τ_{20}/τ_F on temperature would be reasonably explained by the model depicted in Figure 11. This model is based on the fact that the orientational correlation function relevant to τ_{20}/τ_F is written, on the assumption of the statistical independence of the azimuthal

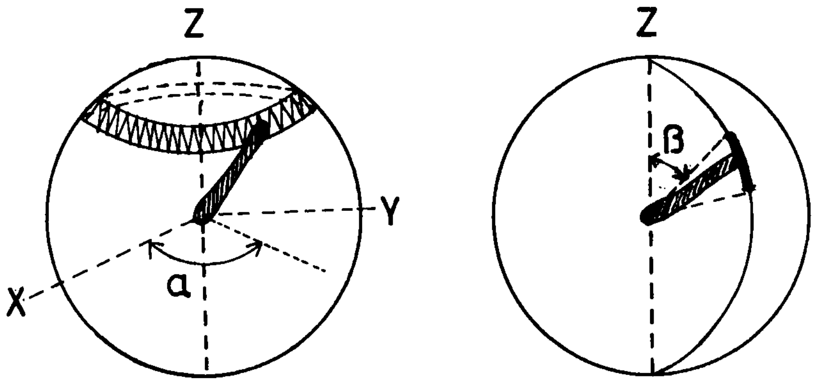

FIGURE 11 A rotational diffusion model for Φ_{20} and Φ_{00}.

and polar angle, as;

$$\begin{aligned}\overline{D^{(2)}_{20}(\Omega(t))D^{(2)}_{20}(\Omega(0))} &= \{\overline{P_2\,(\cos\beta(t))P_2\,(\cos\beta\;(0))} - 2\overline{P}_2 + 1\} \\ &\quad \times \overline{\exp\,\{2i\;\alpha(t) - \alpha(0)\}}\end{aligned} \tag{9}$$

The fluctuation of the azimuth angle α would more easily occur and be more rapid than that of the polar angle β, because it can be occurred without the change of order parameters. By means of the same reasoning, τ_{20} would be nearly temperature-independent, as was obtained here.

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