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Determination of the Molecular Arrangement in Liquid Crystals. A New Method of Determining the Molecular Arrangement in Liquid Crystals by the Use of the Polarization of the Fluorescence

Sakumitsu SAKAGAMI, Akira TAKASE, Minoru NAKAMIZO, and Hitoo KAKIYAMA
National Industrial Research Institute, Kyushu, Tosu, Saga 841

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The molecular order in the liquid crystal states of *p*-*n*-octyloxybenzoic acid (OOBA) has been measured by means of a new method utilizing the polarization of the fluorescence. The polarized components of the fluorescence observed for the isotropic liquid state are independent of the rotation angle; this indicates that no molecular order exists in the liquid state. The polarized components of the fluorescence observed for the nematic state show that the molecular order of the aligned nematic state can be represented by a partially uniaxial orientation. The results observed for the nematic phase are also quantitatively discussed by the use of the uniaxial prolate ellipsoidal orientation pattern. On the other hand, the smectic state of OOBA is not affected by the surface action, and the observed patterns of the polarization of the fluorescence have very little angular dependence, in contrast with those for the nematic state. Furthermore, the molecular orientation for the crystal state of OOBA is briefly described.

It is well established that liquid crystals have properties similar to liquid in mobility, yet are crystal in structure, and that they can be classified into three basic types, *i.e.*, smectic, nematic, and cholesteric. These liquid crystal states are all characterized by a more or less complete orientation of the molecules with their long molecular axes parallel. In particular, the parallel orientation of the nematic state can usually be described by the degree of order: $S=(1/2)\cdot\langle 3\cos^2\theta-1\rangle_{av}$, where θ is the angle between a molecular axis and the preferred axis, which gives the average deviation of orientation of the molecular axes. Saupe and

Maier have shown that this degree of order can be determined by various experimental method[1-5] the principal refractive indices, the principal diamagnetic susceptibilities, the UV or IR dichroism, and the magnetic resonance.

In this paper, we wish to report a new method of determining the molecular order in the liquid crystalline states on the basis of the polarization of the fluorescence from molecules dispersed in liquid crystals. This method has the advantage that it is, in principle, possible to measure not only the extent of orientation, but also the type of orientation, because it utilizes the two-fold optical anisotropy of fluorescent molecules.

Theoretical

The theoretical background of this method has been given by Nishijima *et al.*[6-9] in their studies of molecular orientation in polymer solids; it consists of the application of a simple oscillator model of classical electrodynamics to the polarization phenomena of fluorescence on the assumption that the absorbing and emitting oscillators are linear oscillators whose directions coincide with a single molecular axis. The theory gives the intensities of the parallel and perpendicular components of the polarized fluorescence emitted from a system with a certain degree of optical anisotoropy, $I_{//}$ and $I_{\perp}$, whose electric vectors are, respectively, parallel and perpendicular to the direction of the electric vector of the linearly-polarized exciting light.

$$I_{//} = \frac{K}{2\pi}\int_0^{2\pi}\int_0^{\pi/2} N(\omega, \varphi)M_x^2M_x^2 \sin\omega d\omega d\varphi, \quad (1)$$

$$I_{\perp} = \frac{K}{2\pi}\int_0^{2\pi}\int_0^{\pi/2} N(\omega, \varphi)M_x^2M_z^2 \sin\omega d\omega d\varphi, \quad (2)$$

where K is the proportionality constant, where $N(\omega,\varphi)$ is an angular distribution function in the orientation coordinate system (a, b, c) fixed to the specimen, as is shown in Fig. 1, and where M_x and M_z are the components of the linear axis, **M**, of the fluorescent molecule in the directions of the X and Z axes in the optical coordinate system. The components in the optical coordinate system, M_x, M_y, and M_z, can easily be obtained from its components, M_a, M_b, and M_c, in the orientation coordinate system using a transformation matrix (T):

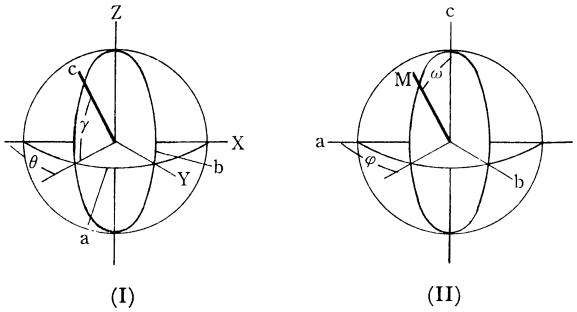

Fig. 1. Coordinate systems. (I): optical coordinate system, (II): orientation coordinate system.

$$\begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} = (T)\begin{pmatrix} M_a \\ M_b \\ M_c \end{pmatrix} \quad (3)$$

$$(T) = \begin{pmatrix} \cos\theta\sin\gamma & -\sin\theta & \cos\theta\cos\gamma \\ \sin\theta\sin\gamma & \cos\theta & \sin\theta\cos\gamma \\ -\cos\gamma & 0 & \sin\gamma \end{pmatrix} \quad (4)$$

The extent as well as the type of molecular orientation in the system can be obtained from measurements of the angular dependency of $I_{//}$ and $I_{\perp}$, and of the degree of polarization of fluorescence, P, which is defined by Eq. (5):

$$P = \frac{I_{//}-I_{\perp}}{I_{//}+I_{\perp}} \quad (5)$$

Experimental

Apparatus. The optical system used in this study is schematically illustrated in Fig. 2. The light of the 365 nm wavelength was separated from a mercury lamp using a monochromator, M, and was used as an exciting light; it illuminated fluorescent molecules dispersed in liquid crystals after passing through a polarizer, P. The wavelength of the exciting light coincides with that of the maximum of the principal absorption peak, which itself corresponds to the electronic transition between the ground and lowest excited states of the fluorescent molecules. The polarized components of the fluorescence intensity are measured by a photomultiplier, PM, through an analyzer, A, and a cut-off filter, CF, and are then recorded as the sample is being rotated through 360° on the rotating stage. The analyzer can also be rotated so that the direction of the electric vector of the fluorescent light lies either parallel ($I_{//}$) or perpendicular ($I_{\perp}$) to that of the exciting light. An ordinary polarizing microscope was modified as the optical system passed from the polarizer to the analyzer. The observed sample area is around 100 μm in diameter.

Materials. The liquid crystal compound used in this study is *p-n*-octyloxybenzoic acid (OOBA), which was purchased from the Tokyo Kasei Co.; it was recrystallized several

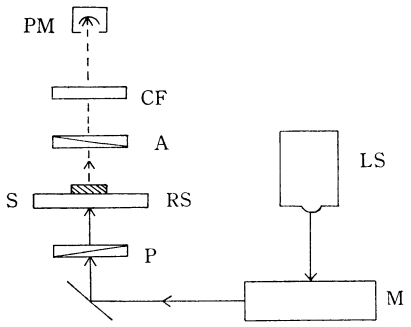

Fig. 2. Schematic diagram of the apparatus. LS: light source, M: monochromator, P: polarizer, RS: rotating stage, S: sample, A: analyzer, CF: cut-off filter, PM: photomultiplier.

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times from ethanol and benzene to insure a higher degree of purity. The phase transition of OOBA are:[10-12]

$$C_2 \overset{68^\circ C}{\longleftrightarrow} C_1 \overset{102^\circ C}{\longleftrightarrow} S_m(C) \overset{108^\circ C}{\longleftrightarrow} N \overset{145^\circ C}{\longleftrightarrow} I$$

1,6-Diphenyl-1,3,5-hexatriene was used as the fluorescent compound.[13] This fluorescent molecule can be considered to be an approximately perfect linear oscillator, because the measurement of the degree of the polarization of the fluorescence in various solvents with a wide range of viscosities has given the value of 0.5 at the extrapolation of $T/\eta=0$ theoretically anticipated by the perfect anisotropic molecule.

A mixture of the liquid crystal compound and fluorescent substances of about 10^{-3} wt% was dissolved in chloroform in order to obtain a uniformly-dispersed system, and then the solvent was removed by evaporation at room temperature under reduced pressure. The liquid crystal state was attained by heating this mixture to the isotropic state of the liquid crystal between a glass slide and a cover slip on a microscopic stage with a heating block, and by then slowly cooling it to the mesomorphic state. The sample thickness was approximately 5 μm. The aligned nematic state was obtained by the well-known method of rubbing the glass surface.[14-19]

Results and Discussion

The polarized components of the fluorescence intensity, $I_{//}$ and $I_{\perp}$, observed at each state are shown in Figs. 3 and 4 as a function of the angle of rotation, γ.

As is apparent from Fig. 3, in the isotropic state both $I_{//}$ and $I_{\perp}$ are independent of the angle, γ. This can easily be understood by considering that a molecular ordering in the liquid state is at random because of the

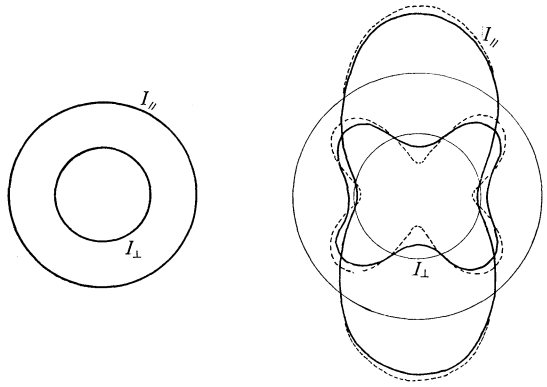

Fig. 3. Angular distributions of the polarized components of fluorescence observed in the aligned nematic state (N) and the isotropic liquid state (I). The dotted lines indicate the calculated intensities of the polarized components of fluorescence corresponding to $\alpha=5$ and $\theta=60°$.

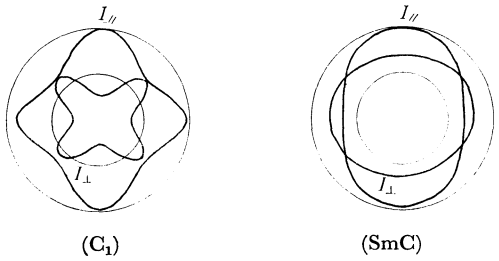

Fig. 4. Angular distributions of the polarized components of fluorescence observed in the smectic C state (S_mC) and the crystalline state (C_1).

vigorous thermal motion of the molecules. In the case of a completely random distribution, the intensity of the polarized component of fluorescence can be expressed by:

$$I_{//} = \frac{3}{15}K\Phi, \tag{6}$$

$$I_{\perp} = \frac{1}{15}K\Phi, \tag{7}$$

where K and Φ are independent of the angle of rotation and are correlated to the maximum probability of excitation and the quantum yield of the fluorescence respectively.[6,9] These equations indicate that the polarized components of the fluorescence for the completely random system are independent of the angle, γ, and that the intensity ratio of the fluorescence, $I_{//}/I_{\perp}$, is equal to 3. The observed polarized components of the fluorescence coincide entirely with those expected from the above equations so far as the angular dependence is concerned. However, the observed intensity ratio of the polarized components of the fluorescence is somewhat smaller than the ratio, $I_{//}/I_{\perp}=3$, theoretically expected from the above equations. This discrepancy is mainly attributable to the facts that the viscosity of the isotropic liquid state is low and that the molecules are very mobile in the liquid state.

At the phase transition from the liquid to the nematic, both $I_{//}$ and $I_{\perp}$ drastically change, as is illustrated in Fig. 3. Although the angular distribution of $I_{//}$ and $I_{\perp}$, in this nematic state, varied little with the measured place of the liquid crystal compound, the substantial features of angular dependence were the same as those shown in Fig. 3. In addition, no significant change in either $I_{//}$ or $I_{\perp}$ with the variation in the temperature was observed throughout the nematic state, except that the fluorescence intensity decreased slightly as the temperature decreased. As is shown in Fig. 3, $I_{//}$ has a maximum intensity at a definite angle of γ, whereas $I_{\perp}$ exhibits a fluorescence pattern with a four-leaf shape. It is evident from the angular dependence of $I_{//}$ and $I_{\perp}$ that the nematic state has a partially uniaxial molecular orientation.

The distribution function, $N(\omega,\varphi)$, is indispensable to explaining quantitatively the observed angular dependence of both $I_{//}$ and $I_{\perp}$. Taking account of the partially parallel molecular orientation in the nematic state, we assume that the molecular orientation for the nematic state can be expressed by the uniaxial prolate ellipsoidal pattern, as is illustrated in Fig. 5. Fur-

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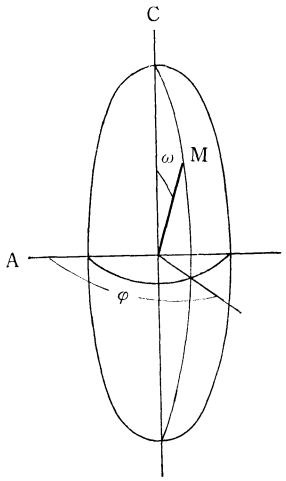

Fig. 5. Schematic representation of the distribution function $N(\omega, \varphi)$.

thermore, it seems quite reasonable to assume that the distribution function, $N(\omega,\varphi)$, is proportional to the cube of the distance from the center of the prolate ellipsoidal of rotation. $N(\omega,\varphi)$ is, then, given by:

$$N(\omega, \varphi) \propto \frac{1}{(\alpha^2 \sin^2 \omega + \cos^2 \omega)^{3/2}}, \quad (8)$$

where α is the axial ratio, C/A. The angular distribution of $I_{//}$ and $I_{\perp}$ can be straightforwardly computed by substituting this distribution function for $N(\omega,\varphi)$ in Eqs. (1) and (2). The final equations representing $I_{//}$ and $I_{\perp}$ include both γ and θ as parameters. The results of the calculations at $\alpha=5$ and $\theta=60°$ are shown by the dotted line in Fig. 3; these results agree well with the observed angular distributions of $I_{//}$ and $I_{\perp}$, aside from a very small difference in the intensity of $I_{\perp}$. This good accordance distinctly indicates that the molecular orientation in the nematic state lies essentially parallel and can be expressed by the uniaxial prolate ellipsoidal pattern, as has been discussed above. The fact that α is equal to 5 indicates that the molecules in the nematic state can be regarded as adopting an almost perfect parallel alignment over regions larger than the molecular dimensions. It is known that the molecular order of the nematic state is not seriously disturbed by the presence of a solute, but is clearly dependent on the molecular shape and size of a solute,[20] although it has thus far been assumed that the molecular order of the fluorescent molecules used as a probe is completely consistent with that of the nematic phase. Therefore, further detailed arguments concerning the molecular order in the nematic state are impossible.

The $I_{//}$ and $I_{\perp}$ observed for the smectic C state of OOBA are strikingly different from those for the nematic state, as is shown in Fig. 4. Both $I_{//}$ and $I_{\perp}$ are very little dependent upon the angle of rotation, γ, in contrast to those of the nematic state, with their sharp angular dependence. Furthermore, microscopic observations also indicate that this smectic C state exhibits the smectic schlieren texture[21,22] characteristic of the smectic C state, while the nematic state gives the pattern of the so-called aligned layers[14] due to the surface action. This suggests that the smectic C liquid crystal, unlike the nematic liquid crystal, is not easily aligned by rubbing glass surfaces.

It is well known that the smectic C state has such a layer structure that the long molecular axis is tilted to a layer and has optically biaxial properties.[23-27] Recently, the present authors have proposed, on the basis of optical observations,[28] twisted smectic layers for the molecular arrangements of the smectic C state. In these twisted smectic layers, the molecules are arranged in layers and have their long molecular axes successively twisted with respect to the normal layer. If this is the case, the observed $I_{//}$ and $I_{\perp}$, which are substantially independent of the rotation angle, are reasonable, since the molecular order in the twisted smectic layers is likely to be essentially distributed at random over the whole region where the polarization measurement of the fluorescence from the system is made.

The polarized fluorescence intensity decreases at the phase transition from the smectic to the crystalline state. The $I_{//}$ and $I_{\perp}$ for the crystalline state (C_1) are also significantly different from those observed for the nematic and smectic states, discussed above, in the angular dependence as well as in the intensity, as is shown in Fig. 4. The angular dependence of $I_{//}$ and $I_{\perp}$ suggests that the crystal state (C_1) of OOBA attained on cooling the smectic state has an approximately perfect biaxial molecular orientation, although a birefringence effect in the crystalline state must be considered for an accurate determination of the molecular orientation.[29]

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