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Charge-carrier Transport in Nematic 2-(*p*-Decyloxybenzylideneamino)-9-Fluorenone

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2-(*p*-Decyloxybenzylideneamino)-9-fluorenone (DBAF), with a large π-electronic group, showed a transient photocurrent induced by the strongly-absorbed light from a N_2 gas laser in the nematic, monotropic smectic, and isotropic liquid states. This photocurrent seemed to be due to the space-charge-limited current. The drift mobilities of the positive and negative charge carriers (μ_p and μ_n respectively) were determined from the peak time. The μ_n was ten times larger than μ_p, while the activation energies were identical. The modified Walden rule was valid in the nematic state ranging from 90 °C to 135 °C. The nematic mixtures of DBAF and *N*-(*p*-methoxybenzylidene)-*p*-butylaniline also showed a similar transient photocurrent, the magnitude of which increased significantly with an increase in the DBAF content. The mobilities were independent of the DBAF content and were nearly equal to those in nematic DBAF at the same viscosity, η: that is, $\mu_n = 3\times10^{-5}$, and $\mu_p = 2.5\times10^{-6}$ cm^2/V s at $\eta = 0.026$ Pa s. These facts indicate that the nature of the carrier transport of the photoconduction is not electronic, but ionic. The O_2^- and the cation radical of DBAF are proposed as the ionic carrier species for both nematic DBAF and the nematic mixtures.

Charge-carrier transport in liquid crystals has been extensively studied over the last ten years and has been found to be of an ionic nature.[1—10] In most of the studies, either the voltage-pulse-injection method[1—4] or the polarity-inversion method[5,6] has been used to measure the carrier mobility. These methods, however, give no direct information as to the sign of the carriers. Yamashita and Amemiya have measured the drift mobility of the positive charge carriers photoinjected from an amorphous Se layer in nematic *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA).[8] To our knowledge, this is the only case where the sign of the carriers migrating in a liquid crystal has been identified. On the contrary, the drift mobility in many organic solids has been measured separately for the positive and negative charge carriers. This is because the time-of-flight method is easily applied to the organic solids where the pulse-photocurrent is caused by pulsed strongly-absorbed light. Unfortunately, the liquid crystals investigated to date have not been photoconductive.

In the previous paper,[11] we found that nematic 2-(*p*-decyloxybenzylideneamino)-9-fluorenone (DBAF), which has a relatively large π-electronic group, showed photoconduction in its absorption region. In the present investigation, we measured the transient photocurrent induced by pulsed strongly-absorbed light to determine the drift mobility. We believe that this is the first report in which the drift mobilities have been determined separately for the positive and negative charge carriers in a liquid crystal.

Experimental

The DBAF was prepared as has been described previously.[11] The MBBA was obtained commercially and was purified with vacuum distillation. The sample was sandwiched between two nesa-coated glass electrodes with a Myler spacer 20—100 μm thick. Cells with a homogeneous alignment were prepared by means of the rubbing technique of the glass electrodes.[11] Caution was taken in preparing the cells so as not to heat the DBAF sample above 95 °C. The effective area of the cells was typically 1 cm^2. A nitrogen-gas laser (3 ns in pulse width) was irradiated on a cell set in a cryostat with an argon atmosphere. The induced photocurrent was observed through a series load resistor by means of a storage oscilloscope. Before the measurement, the dark current was cancelled out by means of a compensation circuit. The viscosity was measured with an Ostwald viscometer calibrated by using MBBA[12] and hexadecane[13] as standard samples.

Results and Discussion

Typical traces of the transient photocurrent are shown in Fig. 1. The attenuation coefficient of a nematic DBAF sample was evaluated to be 1.2×10^5 cm^{-1} at 337 nm from the molar extinction coefficient of its benzene solution (2.2×10^4 M^{-1} cm^{-1}). This value indicates that the exciting light is absorbed within the surface layer to a depth of less than 0.5 μm. The original photocarriers, which are supposed to be the cation radical of DBAF and the anion radical of either DBAF or an electron-acceptor impurity,[11] are generated in this surface layer. When the front electrode is

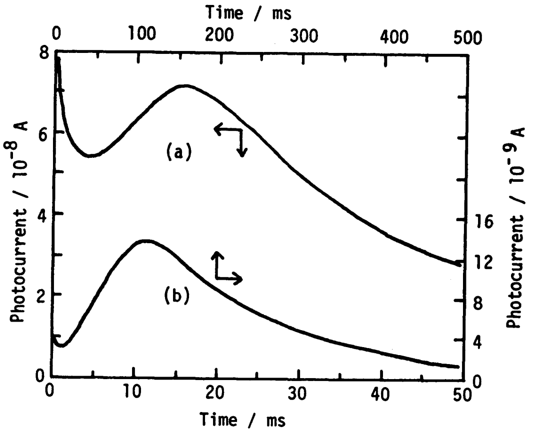

Fig. 1. Typical traces of transient photocurrent in nematic DBAF. (a) and (b): Negative- and positive-electrode illuminations, respectively. Applied voltage: 34 V, sample thickness: 30 μm, temperature: 97 °C.

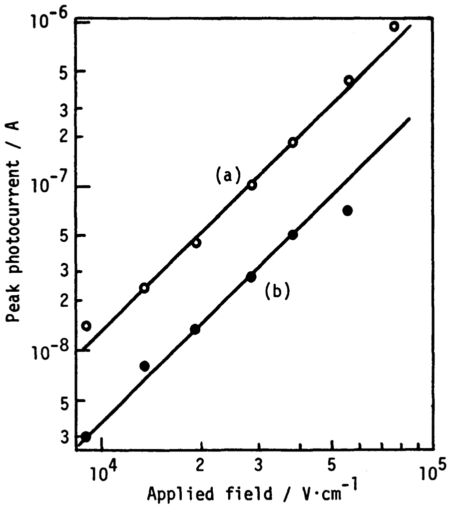

Fig. 2. Dependence of peak photocurrent on applied electric field. (a) and (b): Negative- and positive-electrode illuminations. Sample thickness: 50 μm, temperature: 97 °C.

positively biased, the positive-charge carriers can drift toward the back electrode, and *vice versa*. Thus, the transient photocurrent observed for the positive- or negative-electrode illumination is due to the positive- or negative-charge carriers respectively.

The transient photocurrent showed a peak, as may be seen in Fig. 1. The peak photocurrent was proportional to the square of the applied field, as shown in Fig. 2. It was roughly proportional to the inverse cube of the sample thickness. Judging from these facts, the observed transient photocurrent seems to be to the space-charge-limited current. The drift mobility, μ, was calculated from the peak time, t_p, according to Eq. 1;(14)

$$\mu = 0.79\,d^2/t_p\,V, \qquad (1)$$

where d is the sample thickness, and V, the applied voltage. Thus, the drift mobilities of the positive- and negative-charge carriers were determined separately and labelled μ_p and μ_n respectively.

The mobilities in nematic DBAF were independent of the sample thickness, but they were dependent on the applied electric field, as shown in Fig. 3. The μ_n was roughly proportional to the root of the field, while the μ_p increased at a much slower rate with an increase in the field. It has been suggested that the ionic mobility measured in high electric fields is probably overestimated because of the effect of the electrohydrodynamic (EHD) flow.(8,9) This suggests that the mobility in liquid crystals may be dependent on the field. The mobility in liquid crystals has, however, been reported to be independent of the field,(1–3,5–9) except in only one report.(4) Both μ_n and μ_p in the nematic mixtures of MBBA and DBAF, which will be mentioned below, were independent of the field, as shown in Fig. 3. The EHD flow was observed for both nematic DBAF and nematic mixtures of DBAF and MBBA in fields higher than about 2×10^3 V/cm. These facts suggest that the field dependence of the mobility in nematic DBAF is not due to the effect of the EHD flow. At present, though, we have no explanation for this field dependence.

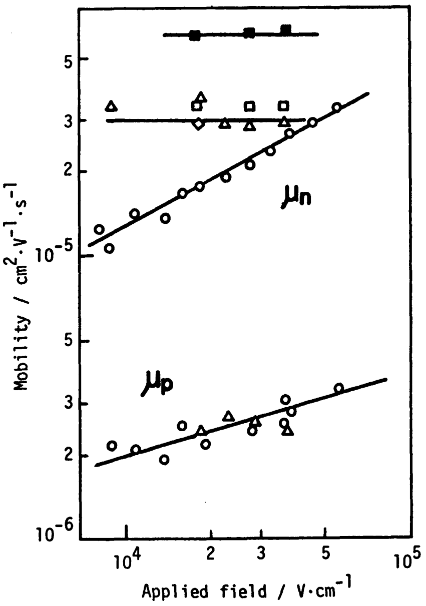

Fig. 3. Dependence of drift mobility on applied electric field.

DBAF: ○, at 97 °C. Nematic mixtures of MBBA and DBAF: △, 30 mol% of DBAF at 55 °C; □, 20 mol% of DBAF at 55 °C; ◇; 10 mol% of DBAF at 35 °C; ■, 20 mol% of DBAF in isotropic liquid state at 68.5 °C.

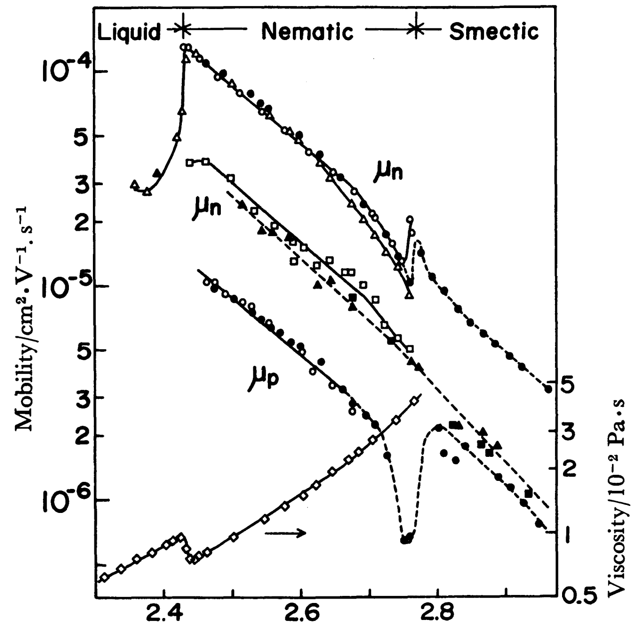

Fig. 4. Temperature dependence of drift mobilities and viscosity.

○, △, and □: 1st, 2nd, and 3rd heating runs, respectively. ●, ▲, and ■: 1st, 2nd, and 3rd cooling runs, respectively.

The temperature dependence of the mobilities at the field of 3.66×10^4 V/cm is shown in Fig. 4. The mobility data were reproducible unless the cell was heated up to the isotropic liquid state. In the nematic state, both

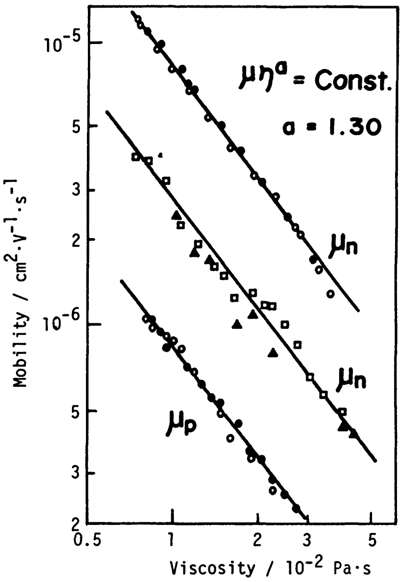

Fig. 5. Viscosity dependence of drift mobility in nematic state. Keys are identical with those in Fig. 4.

μ_n and μ_p had the same activation energy of *ca.* 0.54 eV. On the cooling runs, the mobilities showed a discrete change at the transition from the nematic phase to the smectic phase (88.7 °C), while their activation energies in the smectic state were nearly equal to those in the nematic state. The μ_n decreased abruptly and irreversibly at the transition from the nematic to the isotropic phase (138.7 °C). Once the cell was heated up to the isotropic liquid state, the μ_n in the nematic state as well as in the smectic one decreased to a third of its original value, as shown in Fig. 4, while the activation energy practically did not change.

The temperature dependence of the viscosity is also shown in Fig. 4. The activation energy of the viscosity was *ca.* 0.40 eV for both nematic and isotropic liquid states.

If the carrier transport is of an ionic nature, Walden's rule (Eq. 2) or its modification (Eq. 3) should be valid:[15]

$$\mu\eta = e/6r, \tag{2}$$

$$\mu\eta^a = \text{constant}, \tag{3}$$

where e is the electronic charge; r, the effective radius of the ionic carrier species, and a, an experimental constant close to unity. The mobility data for the nematic state shown in Fig. 4 were replotted against the viscosity in the bilogarithmic form according to Eq. 3. As shown in Fig. 5, straight lines with the same slope were obtained: they gave the a value as 1.3. It should also be noted that the modified Walden's rule is valid in the nematic state over the wide range from 90 °C to 135 °C.

The transient photocurrent in the nematic mixtures of MBBA and DBAF was also measured at the temperatures where the viscosity of the mixtures was roughly equal to that of DBAF at 97 °C (2.6×10^{-2} Pa s). Nematic MBBA did not show the transient photocurrent, although it absorbed the exciting light strongly. The nematic mixtures containing more than 10 mol% of DBAF showed a transient photocurrent similar to that shown in Fig. 1. The peak photocurrent increased about ten times with an increase in the DBAF content from 10 mol% to 30 mol%, indicating that the photocarriers were generated from the excited state of DBAF. On the other hand, the drift mobilities in the nematic mixtures were independent of the DBAF content and were nearly equal to those in nematic DBAF, as shown in Fig. 3; that is, $\mu_n=3\times10^{-5}$ and $\mu_p=2.5\times10^{-6}$ cm²/V s at $\eta=2.6\times10^{-2}$ Pa s. This important fact indicates that the photocarriers do not migrate in nematic media by means of the electronic hopping process, but by means of the ionic process, and that the ionic carrier species are identical between nematic DBAF and the nematic mixtures of MBBA and DBAF.

In both nematic DBAF and the nematic mixtures of MBBA and DBAF, the effective radii of the negative ionic carriers were estimated from Eq. 2 to be *ca.* 1.1 Å. This value is quite small. In MBBA and 4,4′-azoxyanisole the radii of the ionic carriers have been estimated to be 2.1 and 1.1 Å respectively, and O^{2-} has been proposed as the negative carrier species.[3,7] The O_2^-, however, is the most probable negative carrier species in the present case for the following reasons. First, O_2 has the gaseous electron affinity of 0.44 eV,[16] which may be sufficient to accept an electron from the original negative photocarrier or the DBAF anion radical. Secondary, the effective radius of O_2^- has been reported to be 1.54 Å[17] or 1.4 Å.[18] These values are in fair agreement with the estimated value (1.1 Å). Third, it is well known that the carrier transport in liquid hydrocarbons changes from an electronic nature to an ionic one in the presence of only an extremely small amount of O_2.[19]

Once the cells were heated up to the isotropic liquid state with applying the electric field, the estimated radius of the negative ionic species changed from 1.1 Å to 4.1 Å. This suggests that an unknown degradation product acts as an electron trap instead of O_2.

In both nematic DBAF and the nematic mixtures of MBBA and DBAF, the radii of the positive ionic carriers were estimated from Eq. 2 to be 12.6 Å. This value is about ten times larger than that for the negative ones. 2-Amino-9-fluorenone, a probable impurity, is a candidate for the positive carrier species, because it may have an ionization potential sufficient to release an electron to the original positive photocarrier or the DBAF cation radical. It is, however, not probable that the 2-amino-9-fluorenone cation radical has an effective radius as large as 12.6 Å. Therefore, the DBAF cation radical itself seems to be the positive carrier species, actually migrating in the nematic media. For nematic MBBA, Yamashita and Amemiya have reported small μ_p values of (6—9)$\times10^{-6}$ cm²/V s and proposed the MBBA cation radical as the positive carrier species.[8] Even in the nematic mixtures of MBBA and DBAF, the DBAF cation radical seems to be the positive carrier species, because the ionization potential of DBAF is smaller than that of MBBA.

It should be noted that μ_n is much larger than μ_p in the nematic state of MBBA,[3,8] DBAF, and their mixtures. A similar result was obtained for *N*-methyl-2-(*p*-hexyloxybenzylideneamino)-carbazole, which has a large π-electronic group;[20] that is, $\mu_n=1\times10^{-4}$ cm²/V s and $\mu_p = 1 \times 10^{-5}$ cm^2/V s in the nematic state at 122 °C. This is due to the significant difference in the effective radius of the carrier species between O_2^- and the corresponding cation radicals of the liquid crystal molecules. It may be considered that doping with an electron donor of a small molecular size increases μ_p appreciably.

Although being necessary to the occurrence of photoconduction, the presence of a π-electronic group in a liquid crystal molecule can not change the nature of carrier transport from ionic to electronic, as mentioned above. This can be explained as follows. For example, a DBAF molecule is composed of two parts. One is a fluorenone moiety which might serve as a hopping site. The other, a phenyl group with a long alkyloxy chain, is necessary to the presence of liquid crystal states. The latter part, which occupies the predominant space in the molecule, significantly reduces the electronic interaction between the large π-electronic groups. This is supported by the fact that the molecules having only the former part show electronic hopping transport in the liquid state, as has been reported for 2,4,7-trinitro-9-fluorenone[21] and benzene.[22]

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