

## Fast Hole Transport in a New Calamitic Liquid Crystal of 2-(4'-Heptyloxyphenyl)-6-Dodecylthiobenzothiazole

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The carrier transport in different phases of a new photoconductive calamitic liquid crystal, 2-(4'-heptyloxyphenyl)-6-dodecylthiobenzothiazole was studied by the time-of-flight technique: In the smectic *A* phase, a fast hole transient photocurrent was obtained in a nondispersive manner, in which the mobility was as high as  $5 \times 10^{-3}$  cm<sup>2</sup>/V s and independent of applied electric field; in the isotropic phase, however, slower carrier transport was observed, probably due to positive or negative ions, and their mobilities were as low as  $10^{-5}$  cm<sup>2</sup>/V s. These experimental results demonstrate the importance of local molecular alignment in creating the fast electronic conduction in calamitic liquid crystals. [S0031-9007(97)02729-4]

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The organic carrier transport materials such as molecularly doped polymers with a carrier transport material, e.g., triarylamine derivative, have been practically used as an indispensable component of the photoreceptor for xerographic copiers and laser beam printers [1]. The carrier mobilities of these materials, however, are typically on the order of  $10^{-6}$  cm<sup>2</sup>/V s which is smaller by 6 orders of magnitude than that of their single crystals [2–6], i.e., highly ordered molecular solids. In addition, these mobilities are both electric field and temperature dependent, attributed to the hopping conduction [1,7,8]. Thus, these practical materials are far from ideal in terms of the characteristics of carrier transport.

In the molecularly doped polymers, the carrier transport molecules are dispersed at random in a polymer matrix, so that the resulting hopping sites are distributed both spatially and energetically because of different microscopic circumstances of each molecule in the matrix [9,10]. Systematic studies based on the disorder formalism of carrier transport in various molecularly doped polymers lead to a recognition of dominant effects of carrier-dipole interaction on the carrier transport [11,12]. Then, a very high hole mobility of  $2 \times 10^{-3}$  cm<sup>2</sup>/V s at  $10^5$  V/cm as been achieved recently in a styrene-based block polymer doped with a bistritylamine derivative [13], according to the material design under this recognition.

On the other hand, there has been a considerable interest in carrier transport of the liquid crystalline mesophase in relation to the molecular crystal [14,15], in which the hopping sites are arranged orderly due to a self-organized molecular alignment of liquid crystalline molecules. In the 1980s, photoconductive behaviors of nematic liquid crystals were investigated in terms of carrier transport by Okamoto *et al.* and others [16–18] and more recently by Naito *et al.* [19–21]. They concluded that the ionic conduction was dominant, judging from viscosity-dependent slow mobilities in accordance with Walden's rule, which was attributed to ionic impurities or photogenerated ions [16–23].

Since then, the major interests have been focused on the discotic mesophase which exhibits relatively greater intermolecular order compared with calamitic liquid crystals, because of the discovery of mesomorphic benzenehexaalkanoate [24] followed by triphenylene and phthalocyanine derivatives [25–27].

Boden *et al.* and others characterized electrical properties in the discotic columnar phase of the doped triphenylene derivatives by ac and dc conductivity measurements [28,29] and phthalocyanine and porphyrin derivatives by microwave conductivity measurements, revealing a high mobility up to  $10^{-3}$  cm<sup>2</sup>/V s [30,31].

Recently Adam *et al.* have reported a fast carrier transport characterized by a high mobility of  $10^{-3}$  cm<sup>2</sup>/V s in a discotic hexagonal ( $D_h$ ) phase of hexapentyloxytriphenylene [32] and even higher one by  $0.1$  cm<sup>2</sup>/V s in more highly ordered helical (H) phase of hexahexylthiotriphenylene by the time-of-flight technique [33]. This fast mobility is understood in a framework of a pseudo-one-dimensional band conduction with shallow traps originated from ordering fluctuation of intracolumnar stacks of disk-shaped molecules arranged in a hexagonal lattice [34].

An important interest, however, still remains to be developed in the carrier transport of calamitic mesophase, because calamitic liquid crystals enjoy different degrees of molecularly ordered arrangement as is well known. In fact, smectic phases exhibit stronger intermolecular interaction than that of the nematic phase, resulting in a higher ordering in terms of the molecular alignment and in a higher viscosity. Both of them are quite beneficial to creation of the electronic conduction in the calamitic mesophase. The resulting electronic conduction could provide us with a new insight into a role of disorder in the characteristic carrier transport of disordered organic materials. With respect to electrical properties in smectic phase of liquid crystals, however, a few reports have been published recently without the quantitative characterization of carrier transport [35,36].

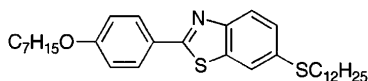


FIG. 1. Chemical structure of 2-(4'-heptyloxyphenyl)-6-dodecylthiobenzothiazole (7O-PBT-S12).

Our previous report described the molecular design of a new photoconductive calamitic liquid crystal, 2-(4'-heptyloxyphenyl)-6-dodecylthiobenzothiazole (7O-PBT-S12), whose chemical structure is shown in Fig. 1, and its photoconductive behaviors in smectic A (SmA) phase under steady-state uv light illumination. It suggests the first electric conduction in the calamitic mesophase [36].

7O-PBT-S12 was synthesized as reported elsewhere [36], which exhibits an absorption band in an ultraviolet region ( $\lambda_{\max} = 330$  nm,  $\epsilon = \sim 10^7$  cm<sup>2</sup>/mol) and the SmA phase between 90 and 100 °C. This material was purified by flush column chromatography and recrystallization just before use. The purified sample was capillary-filled into the cell consisting of two indiumtin oxide (ITO)-coated glass plates whose surfaces were rubbed mechanically so as to realize homogeneous alignment in the SmA phase. The cell thickness was varied in the range of 9 to 28  $\mu$ m by a polymer film spacer. The resulting mesophase consisted of polydomains, in which the homogeneous alignment stayed stable under applied electric fields. Each domain is similar in shape and size [36], whose diameter was 50–60  $\mu$ m and larger than the cell thickness.

In time of flight (TOF) measurements, the cell was mounted on a heater block of cryostat, whose temperature was controlled by a PID thermocontroller within the accuracy of 1 °C. The photoexcitation at the main absorption band of 7O-PBT-S12 was carried out with a N<sub>2</sub> laser ( $\lambda = 337$  nm, pulse width = 600 ps, illuminated area = 0.16 cm<sup>2</sup>). A penetration depth of the light was estimated to be less than 1  $\mu$ m from the interface between the illuminated electrode and the liquid crystal layer, so that the unipolar carrier transport should be dominant in all the transient photocurrents. The photocurrent was amplified by a preamplifier (Princeton Applied Research, model 115) and recorded with digital oscilloscope (Nicolet Pro92). The transit time of carriers was determined by an inflection point of the obtained transient photocurrent in a double linear plot [37].

In curves of Fig. 2, the transient photocurrents are shown in a linear plot for positive and negative (inset) carriers in the polycrystalline phase of 7O-PBT-S12. These exponential decays of the currents indicate an extinction process of photogenerated carriers in transit. This is probably because the carriers were trapped at deep levels derived from accumulated impurities and/or structural defects at grain boundaries of polycrystal.

In contrast to the deep trap-dominated transport in the polycrystalline state, a clear directional carrier transport was observed in the SmA phase as shown in the curves of Fig. 3. The curve shows a transient photocurrent for

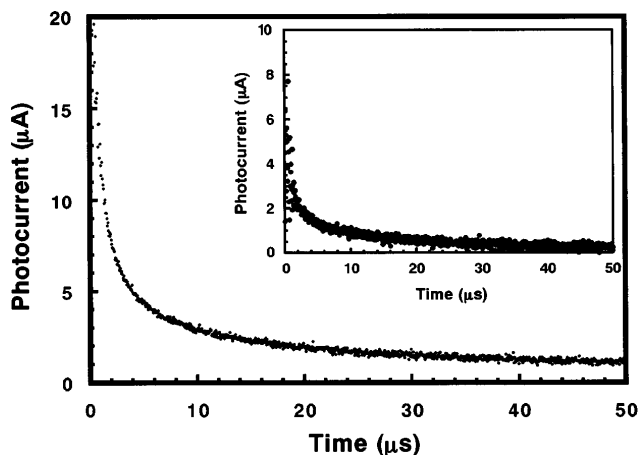


FIG. 2. Linear plot of typical transient photocurrents for positive carriers as a function of time, at an electric field of  $1 \times 10^5$  V/cm in polycrystalline phase at 50 °C; Inset: for negative carriers. Sample thickness was 28  $\mu$ m.

positively charged carriers exhibiting a fast nondispersive transport, where the current was proportional to the light intensity for the excitation; the collected charges (an integral of the transient photocurrent) was less than 10% of the accumulated charges estimated from a geometrical capacitance of the cell. The positive carrier mobility was found to be field independent, judging from a linear relation between  $1/t_T$  and  $V/d^2$  for different applied voltages of 50 to 200 V and cell thicknesses of 9 to 28  $\mu$ m. Thus, the mobility was determined to be  $5 \times 10^{-3}$  cm<sup>2</sup>/V s from the slope of the linear plot according to the equation of  $\mu = d^2/t_T V$ . This mobility is 1000 times larger than those of conventional polymeric or molecularly doped carrier transport materials as mentioned above, and even five times larger than that of hexapentyloxytriphenylene in the D<sub>h</sub> phase [32]. This fast nondispersive carrier transport

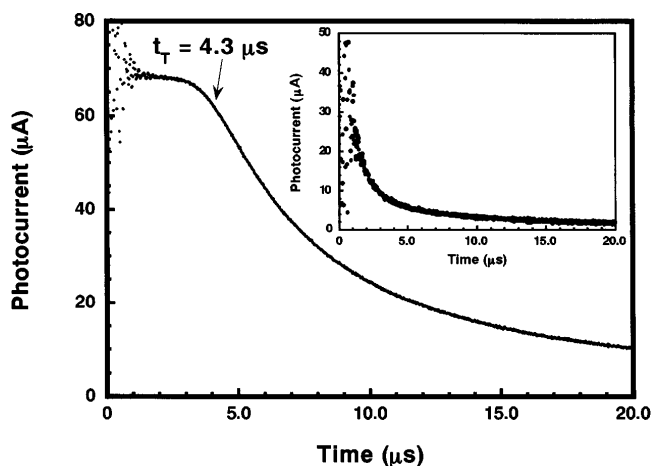


FIG. 3. Linear plot of typical transient photocurrents for positive carriers as a function of time, at an electric field of  $1 \times 10^5$  V/cm in SmA phase at 95 °C; Inset: for negative carriers. Sample thickness was 28  $\mu$ m.

is attributed to a large intermolecular electronic overlap of 7O-PBT-S12 molecules resulting from an orderly molecular alignment in the SmA phase. Within a framework of the disorder formalism [9], this could be explained by a narrowed distribution of hopping sites both in diagonal and off-diagonal disorders. The present field independence of the mobility is the same as the cases of discotic mesophase of triphenylene derivatives and molecular crystals in which the carrier transport process is bandlike [2–4,32,33]. This is in stark contrast to the field-dependent mobilities observed in most other polymeric systems.

For negatively charged carriers, however, only a small photocurrent decay was obtained in the SmA phase as shown by the curve in the inset of Fig. 3. This result was compatible with that from steady-state photocurrent measurement under the uv light illumination [36]. It is well explained by a low ionization potential for 7O-PBT-S12 favorable for the hole transport. This unipolar transport is a clear contrast to the  $D_h$  phase of the triphenylene derivative [32].

In the isotropic phase, however, ambipolar carrier transport was observed unexpectedly in the time range of a millisecond, while transient photocurrents were of a typical nondispersive form as shown in Fig. 4. Both of the transit times for positive and negative carriers were longer than that for holes in the mesophase by 2 orders of magnitude, giving mobilities of  $5 \times 10^{-5} \text{ cm}^2/\text{Vs}$ , irrespective of a polarity of carriers. Interestingly, these mobilities were temperature and electric field dependent.

The ionic conduction can be excluded in the SmA phase of 7O-PBT-S12 because a directional carrier transport with a minimal negative temperature dependence was observed as shown in Fig. 5. This is not the case of the ionic conduction, in which the carrier transport is ambipolar and characterized by a positive temperature-dependent mobility due to temperature-dependent viscos-

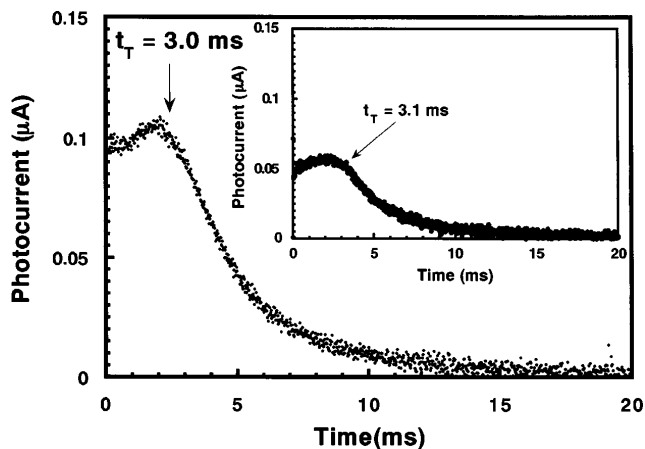


FIG. 4. Linear plot of typical transient photocurrents for positive carriers as a function of time at an electric field of  $8 \times 10^4 \text{ V/cm}$  in isotropic phase at  $110 \text{ }^\circ\text{C}$ ; Inset: for negative carriers. Sample thickness was  $28 \text{ }\mu\text{m}$ .

ity. This can be supported also by the estimation of viscosity in the SmA phase from Walden's rule which is valid for the ionic transport and expressed by the equation  $\mu\eta = e/6\pi r$ , where  $\eta$  is a viscosity of mesophase,  $r$  a radius of ions; assuming the ionic radius of 7O-PBT-S12 to be 1 nm, the observed  $\mu$  of  $5 \times 10^{-3} \text{ cm}^2/\text{Vs}$  yields  $1.6 \times 10^{-5} \text{ N s/m}^2$  for its viscosity  $\eta$ . This is quite unreasonable because the calculated viscosity is one order of magnitude smaller than that of water at  $20 \text{ }^\circ\text{C}$ . Thus, the present result is the first reported case of a confirmed electronic conduction in calamitic mesophase.

In contrast to a very viscous SmA phase, it is plausible that the ionic conduction is dominant in the isotropic phase which promotes the ionic transport because of the smaller viscosity. In fact, degraded the directional carrier transport was observed not only in this transient study but also in our previous steady-state one for the isotropic phase. In particular, the carrier transport for negatively charged carriers can be ionic probably and perhaps caused by extrinsic anionic species. For positively charged carriers, however, the conduction mechanism still remains uncertain whether it is ionic.

The abrupt mobility change by 2 orders of magnitude, as clearly shown in Fig. 5, can be due to the disappearance of molecular alignment caused by the phase transition from "smectic" to "isotropic." This fact indicates that the carrier transport process in the calamitic liquid crystal is governed decisively by a local molecular alignment, whose disorder makes it both difficult to realize the fast electronic conduction and easy to do the slow ionic conduction because of the resulting poor electronic overlap among each molecule and the lower viscosity in the isotropic phase. The negative temperature dependence on the mobility in the SmA phase, as shown in Fig. 5, can be explained by a thermal turbulence of molecular alignment unlike the case in the discotic system, in which hole mobility in  $D_h$  phase is

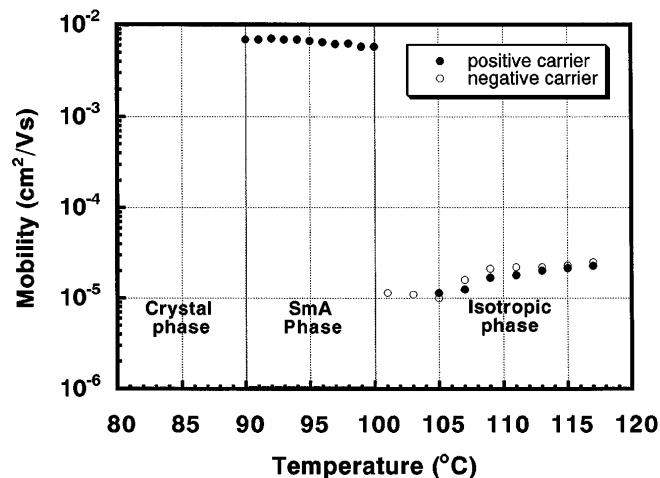


FIG. 5. Drift mobility of 7O-PBT-S12 as a function of temperature. The closed and open circles indicate mobilities for positively and negatively charged carriers, respectively.

constant over the range of 50 K [32]. This is a characteristic feature of a calamitic system with larger thermal fluctuation than the discotic mesophase.

In summary, the TOF study of carrier transport was carried out in the photoconductive calamitic liquid crystal 7O-PBT-S12, and its carrier transport properties in each phase were characterized. In the SmA phase, intrinsic and fast electronic transport was observed only for positively charged carriers, of which field-independent mobility was  $5 \times 10^{-3} \text{ cm}^2/\text{Vs}$ . This is the first establishment of electronic conduction in calamitic mesophase. In the isotropic phase, however, positively or negatively charged carriers were transported and their mobilities were on the order of  $10^{-5} \text{ cm}^2/\text{Vs}$ , suggesting a possible ionic conduction.

These experimental results indicate that the self-organized molecular alignment in the calamitic mesophase is quite effective to create electronic conduction in organic materials. The calamitic liquid crystals exhibit various molecular alignments with different degrees of ordering. Therefore, the electronic carrier transport in calamitic liquid crystals provides us with a new insight into understanding a role of disorder in the characteristic carrier transport in the disordered systems.

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