Carrier Transport Properties of Calamitic Liquid Crystalline Photoconductors

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Abstract

Carrier transport properties of a calamitic liquid crystalline photoconductor (Calamitic LCPC), 2-phenynaphthalene derivatives were investigated by steady state and transient photocurrent measurements. These materials exhibited calamitic mesophases such as nematic (N), smectic A (SmA), smectic B (SmB), and smectic E (SmE) phases, which depended on hydrocarbon chains attached to a core moiety of 2-phenylnaphthalene. A large photoconductive anisotropic ratio over 50 was observed under light illumination due to molecular alignment. The transient photocurrents from time-of-flight measurements exhibited non-dispersive and ambipolar carrier transits in all the mesophases, whereas only small current decays were observed in polycrystalline phase.

The carrier transport in the smectic phases was electronic, while the ionic conduction was dominant in both of isotropic and nematic phases. The mobility was increased stepwise when the phase transition took place with a decrease in temperature. The mobility for smectic phases was independent of temperature and applied electric field, while those in isotropic and N phases depended on temperature positively. The highest mobility of 10^{-2} cm^2/Vs was obtained for both electrons and holes in SmE, which was four orders of magnitude faster than those of the conventional disordered photoconductors.

These results indicate how effective the molecular alignment is in order to upgrade the carrier transport in spite of a small π-conjugate core moiety of 2-phenylnaphthalene.

Introduction

Organic photoconductors have been utilized in photoreceptors for xerographic copiers and laser printers[1], and more recently in active components of electroluminescent devices. These applications require large-area uniformity in thin films, so that the materials practically used are amorphous and prepared either by polymerization, vacuum evaporation, or molecular doping into polymer films, of photoconductive small molecules. The electrical properties of resulting amorphous films, however, are degraded significantly compared with their own molecular crystals: the carrier mobilities are decreased down to 10^{-6}~ 10^{-5} cm^2/Vs and depend on both electric field and temperature. In addition, traps play serious role for determining the response time, which are caused by impurities and carrier–dipole interactions in the disordered photoconductors. These limit their practical applications. The considerable improvement of mobility has been achieved up to 10^{-3} cm^2/Vs by utilizing less polar polymer matrices for the molecularly doped polymers in order to reduce the carrier-dipole interaction[2]. However, there still remains a serious problem of the field and temperature dependence.

In order to relax the present limitation of the organic photoconductors in device application, a new material exhibiting a high mobility independent of electric field and temperature and few deep defect density has to be realized. From this viewpoint, we had paid our attention to the liquid crystalline materials exhibiting fluidity and the self-organized molecular alignment. This is because the liquid crystalline photoconductors meet the requirement of large-area uniformity due to their fluidity and at the same time give a high potential of realizing the enhanced carrier transport due to their self-organized molecular alignment.

The first result came from Haarer's group at Bayreuth University in 1993[3]: they discovered the fast electronic conduction on the order of 10^{-3} cm^2/Vs in the discotic columnar phase of triphenylene derivatives. The second one from us[4,5,6,7]: we found that the calamitic, i.e., rod-like liquid crystals also exhibit the fast electronic carrier transport comparable to the discotic ones, whose electrical conduction had been thought to be ionic due to ionic impurities and/or their own ionized species since the first report of Heilmeier. 2-Phenylbenzothiazole and 2-phenylnaphthalene derivatives are typical examples, which exhibit smectic phases and are more liquid-like compared with the discotic ones.

In this report, we overview the electrical properties of 2-phenylnaphthalene liquid crystals characterized by steady state and transient photocurrent measurements.

Experimental

2-phenyl naphthalene derivatives, 5-PNPO1, 8-PNP-O4, and 8-PNP-O12 were easily synthesized with Suzuki coupling reaction catalyzed by $Pd(PPh_3)_4$ between corresponding 4-alkylphenylboric acids and 2-bromo-6-alkoxynaphthalenes in dimethoxyethane in the presence of aqueous Na_2CO_3 solution and recrystallized from hexane before use. The chemical structures are shown in Fig.1.

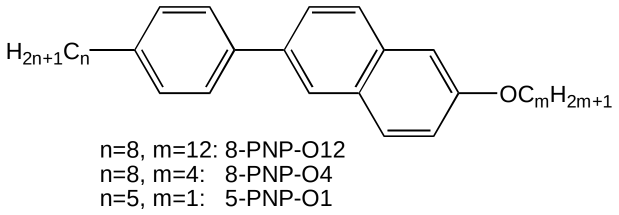


Figure 1. Chemical structure of phenynaphthalene photo-conductive liquid crystals.

Phase characterization was carried out by observation of micrographic textures under polarization microscopy and a miscibility test between these phenyl naphthalene derivatives and a standard material such as 4-hexyl-4-heptyloxybiphenyl. The phase transition characteristics are summarized in Table 1.

Table 1. Phase Characteristics of 2-Phenylnaphthalene Derivatives

Materials	Phase transition characteristics
5-PNP-O1 (n=5, m=1•	**K** -121°C-**N**-128°C-**Iso**
8-PNP-O4 (n=8, m=4)	**K**-50°C-**SmE**-123°C-**SmA**-128°C-**Iso**
8-PNP-O12 (n=8, m=12)	**K**-79°C-**SmB**-103°C-**SmA**-120°C-**Iso**

The n and m indicate a number of carbons in the chemical structure shown in Fig.1, respectively.

Liquid crystal cells were prepared from two ITO-coated glass plates or Al-evaporated glass plates spaced with silica particles. In TOF measurements for positive carriers, the Al-evaporated electrodes were used, and the ITO electrodes for negative carriers. This is because of minimizing the interface effects of electrodes on carrier trapping of photo-generated carriers. The liquid crystalline materials were capillary-filled into the cells. The liquid crystalline materials were easily aligned homogeneously, whose molecular axis is parallel to the substrate surface. The resulting homogenous alignment consisted of fan-like textures of 10~40 μm in diameter and were stable against electric fields applied. For the homeotropic cells, in which the molecular axis aligned perpendicular to the substrate surface, was prepared by chemical modification of the pre-formed SiO_2 surface (<600A) on ITO electrodes with triethoxydecyl silane.

For steady-state photocurrent measurements, Xe lamp (500W) equipped with a band pass filter (UV33DS, Toshiba Glass Co.Ltd) was used for UV illumination (300 ~ 380 nm). The light intensity was 2.5 mW/cm^2. The liquid crystal cell was mounted on the hot stage in which the temperature was controlled by PID thermocontroller within an accuracy of 0.1 K. The photocurrent was recorded with a source measurement unit.

For transient photocurrent measurements, conventional time-of -flight set-up was used with a N_2 laser (37nm, 40 J/pulse, pulse width: 600ps). The signals were pre-amplified and recorded by a digital oscilloscope (Model Pro92, Nicolet Co.Ltd.). The transit time of photo-generated carriers was determined from an inflection point in a double logarithmic plot of transient photocurrent as a function of time. With this transit time, carrier mobility was calculated from the equation,

$$\mu = d^2/V\, \tau \tag{1}$$

where μ is a carrier mobility, d a sample thickness, V an applied voltage, and τ_T a transit time.

Results and Discussions

The phenynaphthalene derivatives exhibited light absorption peak around at 300nm and their penetration depth was estimated to be less than 1μm for 337 nm of N_2 laser. Therefore, in all the transient photocurrent measurements, one carrier condition was established for a carrier transit. Typical transient photocurrents for positive and negative carriers in different phases for phenynaphthalene derivatives are shown in Fig. 2 (a) and (b), respectively.

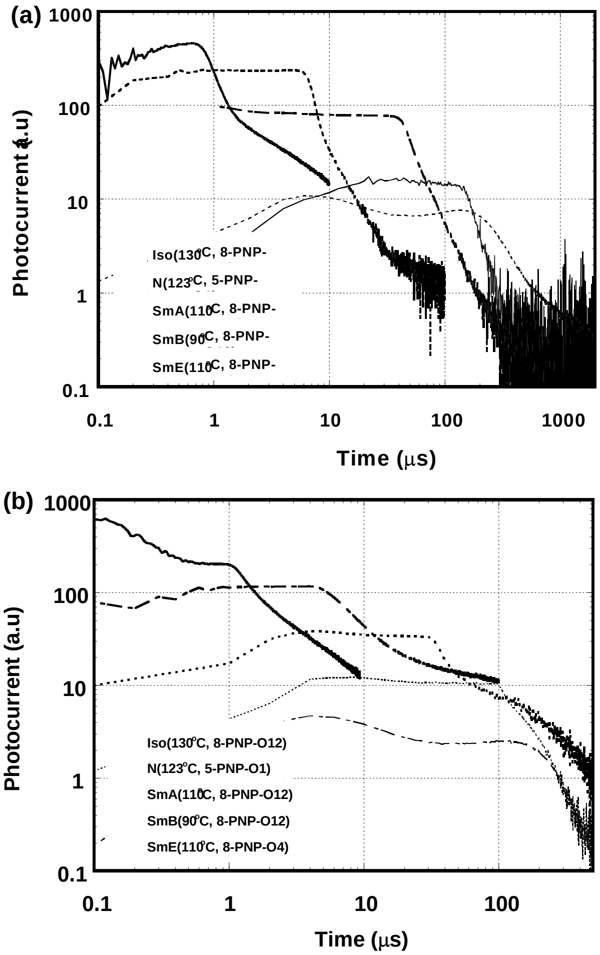


Figure 2. Typical transient photocurrents in different phases of phenynaphthalene derivatives for positive carriers (a) and for negative carriers (b).

1. Isotropic Phase

All the materials, 5-PNP-O1, 8-PNP-O4, and 8-PNP-O12, exhibited ambipolar non-dispersive transient photocurrents at a range of 120°C to 130°C in isotropic phase. The carrier transport did not depend on applied electric field, but did on temperature positively. The carrier mobilities were determined to be on the order of 10^{-5} cm^2/Vs, which is a typical value for the ionic conduction in liquids. The Arrhenius plot for the mobilities gave 0.3 e V as an activation energy in good agreement with a typical value for the ionic transport in liquids. We did two additional tests to determine the conduction mechanism which will be reported elsewhere: one was to check the effect of dilution with hydrocarbon on the mobility, which causes a smaller viscosity compared with pure materials; the other was to check the effect of electronic impurity on the carrier transport. Thus, the carrier transport in this phase was concluded to be ionic.

2. Nematic Phase

Only 5-PNP-O1 exhibited N phase in 2-pheny naphthalene derivatives synthesized so far. The carrier transport was non-dispersive and ambipolar. The carrier mobilities showed no significant difference from the isotropic phase and were on the same order of 10^{-5} cm^2/Vs.

The calamitic liquid crystals had been regarded to be a kind of liquid insulator and their carrier transport also to be ionic due to ionic impurities for a long time. In fact, there are many reports on the ionic conduction in nematic liquid crystals[8,9]. However, there remains a question whether the intrinsic carrier transport is ionic because the most of liquid crystals were azomethyne type of nematic liquid crystals that are very unstable in the ambient atmosphere. On contrary, the 5-PNP-O1 is a very stable compound, so that we can exclude the impurity effect on the carrier transport in this material. Thus, we concluded that the carrier transport in N phase of 5-PNP-O1 is ionic on the same basis as in the isotropic phase discussed in the previous section.

3. Smectic A and B Phases

In SmA phases of 8-PNP-O4 and 8-PNP-O12, non-dispersive and ambipolar transient photocurrents were obtained as in isotropic and N phases as shown in Fig.2. The mobilities were on the order of 10^{-4} cm^2/Vs that was one order of magnitude faster than those in isotropic and N phases, which did not depend on neither temperature nor electric field. Even faster carrier transport was observed in SmB phase of 8-PNP-O12, whose mobilities were on the order of 10^{-3} cm^2/Vs.

In these phases, the electronic conduction was confirmed by testing Walden's rule with the present high mobility of 10^{-4}~10^{-3} cm^2/Vs and large viscosity of these phases. That is, it gave the answer that ionized species can not move in a viscous media of the smectic phase with such a high mobility over 10^{-4} cm^2/Vs.

4. Smectic E Phase [10]

8-PNP-O4 exhibited a more highly ordered phase of SmE, where the molecules sit a rectangular lattice with a molecular flipping motion around the molecular axis. The domains in SmA phase were maintained but more defective, when the phase transition takes place from SmA to SmE. This was obvious in the observation of these phase by polarization microscopy. As shown Fig.3, nice non-dispersive carrier transits for both electrons and holes, however, were observed at shorter time range of a few μ seconds, compared with those in previous SmB phase.

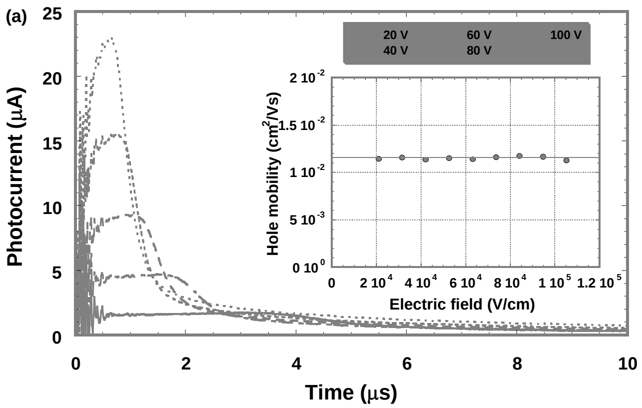
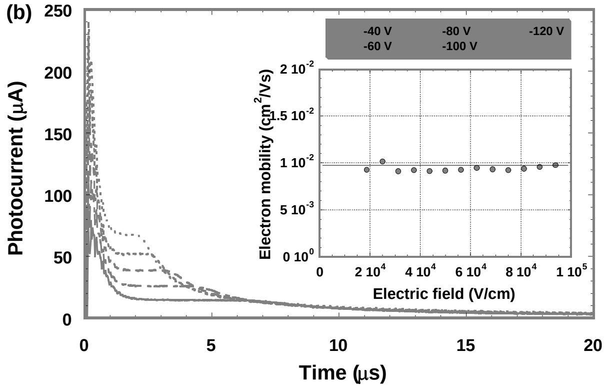


Figure 3. Typical transient photocurrents obtained for positive carriers (a) and for negative carriers (b) in SmE phase of 8-PNP-O4 at 110 °C. The cell thickness was 10 μm. for (a) and 16 μm for (b), respectively.



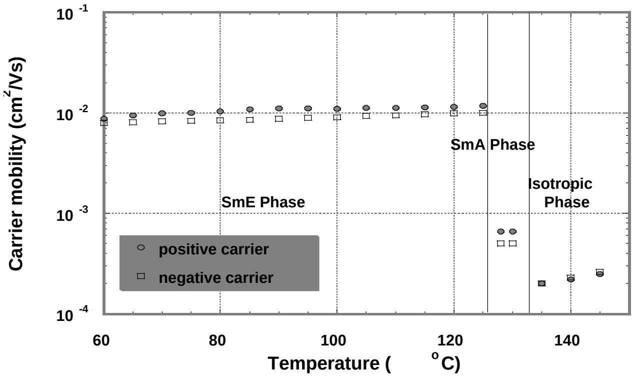


Figure 4. Mobilities of 8-PNP-O4 in different phases as a function of temperature

The ambipolar mobility was on the order of 10^{-2} cm^2/Vs independent of electric fields, but depended slightly on the temperature. This is not the case in SmA and SmB phases. The activation energy was estimated to be about 0.1 eV.

5. Crystal Phase

In crystal phases of all the materials, 5-PNP-O1, 8-PNP-O4, and 8-PNP-O12, only small photocurrent decays were observed irrespective of carrier signs, which indicate the extinction of photo-generated carriers during the transit. It is plausible that deep defects were formed at the grain boundaries and the bulk in the crystal phases. For example, the domains in SmE phase were degraded into small micrograins when the phase transition took place from SmE to crystal phase. This is a clear contrast to the phase transition between smectic phases such as from SmA to SmB and from SmA to SmE, which is probably due to the structural flexibility, i.e., “soft” structure, in mesophase responsible for a structural relaxation of accumulated distortion at the phase transition. This is another aspect of liquid crystalline materials in terms of structural defect formations.

Conclusion

The carrier transport properties in smectic liquid crystals of 2-phenylnaphthalene derivatives are summarized as follows:

1. The carrier transport in isotropic and N phases was governed by the ionic conduction, whose ambipolar mobilities were on the order of 10^{-5} cm^2/Vs.
2. In smectic phases, the electronic conduction was dominant, whose ambipolar mobilities were independent of electric field and increased stepwise according to molecular alignment: a typical mobility was 10^{-4}~10^{-3} cm^2/Vs in SmA and SmB phases, and 10^{-2} cm^2/Vs in SmE phase.
3. In crystal phase, the deep defects deteriorated the carrier transport properties, resulting in the range-limited photoconductive behavior.

References

1. P. M. Borsenberger and D. S. Weiss, *“Organic Photoreceptors for Xerography”*, Maecel Dekker, Inc. New York (1998)
2. P. M. Borsenberger, W. T. Gruebaum, L. J. Serriero, and N. Zumbulyadis, *Jpn. J. Appl. Phys*., **34**, L1597 (1995)
3. D. Adam, F. Closs, T. Frey D. Funhoff, D. Haarer, H. Ringsdorf, P. Schumacher, and K. Siemensmeyer, *Phys. Rev. Lett.*, **70**, 457 (1993)
4. M. Funahashi and J. Hanna, *Jpn. J. Appl. Phys.* **35**, L703 (1996)
5. M. Funahashi and J. Hanna, *Phys. Rev. Lett.*, **78**, 2184 (1997)
6. M. Funahashi and J. Hanna, *Mol. Cryst. Liq. Cryst*., **304**, 429 (1997)
7. M. Funahashi and J. Hanna, *Appl. Phys. Lett*., **71**, No.5, 602 (1997).
8. G. H. Heilmeir and P. M. Heyman, *Phys. Rev. Lett*., **18** 583 (1967)
9. K. Okamoto, S. Nakajima, M. Ueda, A. Itaya, and S. Kusabayashi, *Bull.Chem.Soc.Jpn*., **56** 3545 and 3830 (1983)
10. M. Funahashi and J. Hanna, submitted to *Appl. Phys. Lett.*, (1998)

Biography

Jun-ichi Hanna received his B.S. and M.S. in Chemistry from Tokyo Institute of Technology in 1974 and 1976, respectively, and his Dr. of Engineering in Imaging Science and Engineering from the same Institute in 1982. Dr. Hanna joined the present laboratory in Tokyo Institute of Technology in 1977. Since then, he has studied imaging materials and their application to new imaging systems. And now he is a professor in his organization. His current interests are in large-area electronic materials including low-temperature CVD poly-Si thin films and liquid crystalline semiconductors for imaging devices.

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