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Carrier Transport in Calamitic Mesophases of Liquid Crystalline Photoconductor 2-Phenylnaphthalene Derivatives

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We have characterized carrier transport in mesophases of 2-phenyl-naphthalene derivatives by transient photocurrent measurements. In contrast to ionic conduction of isotropic and nematic (N) phase, electronic and ambipolar carrier transport was observed in smectic A (SmA), smectic B (SmB), and smectic E (SmE) phases. In particular, anomalous large mobilities on the order of 10^{-2}cm^2/Vs were obtained in SmE phase. Carrier mobilities in mesophases of 2-phenynaphthalene derivatives were increased stepwise corresponding to sophistication of molecular ordering from N to SmE. This indicated a dominant effect of molecular ordering on the carrier transport of calamitic mesophases.

Keywords: calamitic mesophase; photoconductivity; semiconductor; smectic A; smectic B; smectic E

INTRODUCTION

The behaviors of ionized molecules in an organic material play an essential role in electrical conduction under electric field. The ionic conduction takes place when the ionized molecules move along the electric field, which is usual in liquids[1]. On the other hand, the electronic conduction takes place when the charges in ionized molecules migrate to the nearest neighbor. This happens often certain organic solids including polymeric materials and amorphous solids[2]. In the latter case, the charge transport is well illustrated as a

continuous hopping of charge carriers, i.e., electrons and holes, between molecules[2]. Therefore, the enhanced carrier transport is reasonably expected in molecularly ordered materials such as molecular crystals. Indeed, the charge carriers can move very fast in the molecular crystals whose chemical structure allows the charged state energetically, by 3 to 6 orders of magnitudes faster than in the disordered materials[3, 4].

This is true even for liquid crystals. The first electronic conduction was found in a discotc columnar phases of triphenylene derivatives, which exhibited quite high mobilities from 10^{-3} to 10^{-1} cm^2/Vs[7, 8, 9, 10]. More recently, the electronic conduction was revealed even in calamitic liquid crystals whose electrical conduction had been considered to be ionic and attributed to ionic impurities or their own ionized species[5, 6]. 2-phenylbenzothiazole[11, 12, 13] and 2-phenylnaphthalene derivatives[14] are typical examples, which exhibit high mobilities over 10^{-3} cm^2/Vs comparable to those in the discotic ones. Interestingly, naphthalene derivatives are ambipolar, that is, electrons and holes are transported at the same speed. Those are the first materials that exhibit ambipolar mobilities over 10^{-3} cm^2/Vs[14] except some aromatic molecular crystals.

In this paper, we will compare carrier transport properties in isotropic and Nematic, and various smectic phases of three 2-phenyl naphthalene derivatives with TOF technique, and clarify the effect of molecular ordering on the carrier transport.

EXPERIMENTAL

We synthesized three materials, 2-(4'-octylphenyl)-6-dodecyloxy-naphthalene (8-PNP-O12: K 79℃ SmB 101℃ SmA 120℃ Iso), 2-(4'-octylphenyl)-6-butyloxynaphthalene (8-PNP-O4: K 50℃ SmE 123℃ SmA 128℃ Iso), and 2-(4'-pentylphenyl)-6-methoxynaphthalene (5-PNP-O1: K

121℃ N 128℃ Iso), for comparison between isotropic, nematic, SmA, SmB, and SmE phases in which the axes of the liquid crystal molecules are perpendicular to the smectic layers. These molecular structures are described in Figure 1.

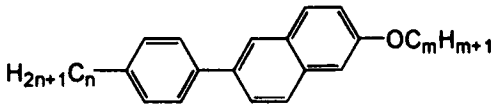

FIGURE 1 Molecular structures of 2-phenylnaphthalene derivatives

These materials were purified with recrystallization from *n*-hexane. The purified samples were capillary-filled into the cells which consisted of two ITO or semitransparent Al electrodes spaced by silica particles. We could not achieve mono-domain alignment, however, the resulting molecular alignment was homogeneous in each domain, whose size is sufficiently larger than sample thickness. So it is likely that there should be no domain boundaries along the path of carriers, perpendicular to the electrodes, in each domain.

In TOF measurement, the liquid crystal cell was fixed on a hot stage whose temperature was controlled by a thermocontroller within accuracy of 0.1 degree. Photoexcitation in main absorption band of these compounds was carried out with N_2-pulse laser (λ = 337 nm, pulse width = 600 ps, Intensity = 40 μJ/pulse), whose penetration depths were estimated from their absorption coefficient to be less than 1 μm. The transient signals were amplified with a preamplifier and recorded by a digital oscilloscope. The transit time was determined by a kink point in a double logarithmic plot of the resulting transient photocurrent curve as a function of time. The carrier mobility, μ is given by a slope of $1/t_T$ as a function of V/d^2 according to the relation of $\mu = d^2/Vt_T$, where d is a cell thickness, V an applied voltage, and t_T a transit time[5].

RESULTS AND DISCUSSION

We could obtain transient photocurrents exhibiting same mobility both for positive and negative carrier in all phases, as shown in Figure 2.

In isotropic phase of these three materials and nematic phase of 8-PNP-O1, both carrier mobilities were determined to be on the order of 10^{-5} cm^2/Vs in the temperature range between 120℃ and 130℃. These carrier mobilities were independent of electric field, however exhibited positive temperature-dependence, due to thermally activated process. This positive temperature-dependence of carrier mobility is probably caused by ionic conduction, in which carrier mobility is controlled by temperature-dependent viscosity. And this ionic nature of carrier transport in these two phases were also confirmed by the effect of addition of carrier trapping materials, as described elsewhere[16].

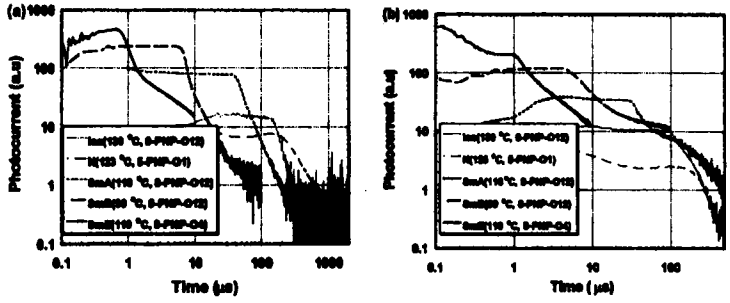

FIGURE 2 Transient photocurrent curves in various phases for (a) positive carrier and (b) negative carrier. The sample thickness was 9 μm, applied voltage 100 V.

In SmA and SmB phases of 8-PNP-O12[14], and SmA phase of 8-PNP-O4, non-dispersive transient photocurrent curves were obtained for both carriers, giving field- and temperature-independent mobilities on the order of 10^{-4} cm^2/Vs

in SmA phase, and 10^{-3} cm^2/Vs in SmB phase, respectively. They increased stepwise at phase transitions with decreasing temperature.

We can determine whether carrier transport mechanism is ionic or electronic from an estimation of viscosity based on Walden's rule, which is valid for ionic transport and expressed by an equation, $\mu\eta = e/6\pi r$, where η is a viscosity, r a radius of ions[12, 13]. Photo-ionized liquid crystal molecules with a size of 10 ~ 20 A would not drift across these viscous smectic phases with such a high carrier mobility on the order of 10^{-4} ~ 10^{-3} cm^2/Vs. Thus we can conclude that the carrier transport is electronic in the smectic phases. The carrier transport characteristics in these smectic phases resemble more those of aromatic molecular crystals, rather than conventional organic amorphous solid, in which carrier mobility depends strongly upon electric field and temperature. Such characteristics are probably caused by crystal-like nature of smectic phases.

In addition, we can conclude that carrier mobility and conduction mechanism depend upon molecular packing and ordering in each mesophase. Electronic conduction is dominant in smectic phases, whereas ionic conduction is favored in isotropic and nematic phases because of low viscosities and small intermolecular electronic correlation. Thus higher carrier mobility can be expected in more highly ordered smectic phases such as SmE, which is considered to be more crystal-like among various mesophases.

In SmE phase of 8-PNP-O4, anomalous high carrier mobilities of $1X10^{-2}$ cm^2/Vs for both positive and negative carriers were obtained, as shown in Figure 3, which is two orders of magnitude larger than that in the SmA phase of this material and 8-PNP-O12, and one order of magnitude larger than that in the SmB phase of 8-PNP-O12. In SmE phase, molecular positions are fixed at rectangular lattice formed by contraction of the hexagonal or pseudo-hexagonal lattice in SmB or SmA phase, and only flipping movement around molecular axis is allowed[15]. This high mobility on the order of 10^{-2} cm^2/Vs thus indicates that

closer molecular packing and smaller disorder in molecular alignment of SmE phase promote carrier transport within smectic layers. As far as the hole mobility is concerned, it is comparable to that of hydrogenated a-Si. And the electron mobility is highest among organic materials except some aromatic molecular crystals.

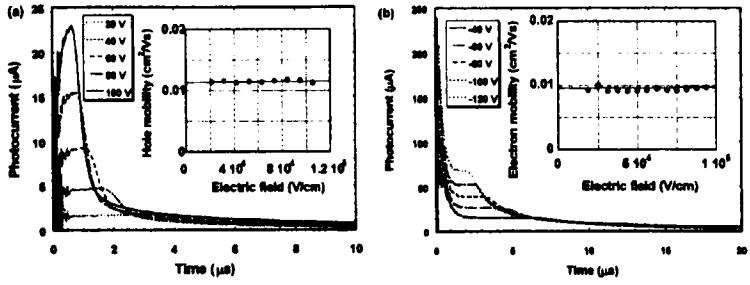

FIGURE 3 Transient photocurrent curves in SmE phase for (a) holes and (b) electrons. The insets show the dependence of carrier mobilities upon electric field. The effective illuminated area was 1 cm^2, and sample thickness is 10 μm for (a) and 16 μm for (b).

This ambipolar carrier mobility was independent of electric field and exhibited a small dependence upon temperature as shown in Figure 4, although the activation energies for both carriers were on the order of 0.1 eV. These features were universal for electronic carrier transport in smectic phases and molecular single crystals.

However, only a small photocurrent decay was obtained in these crystal phases, in spite of highly ordered molecular alignment. This is probably because photo-generated carriers were captured by deep defects formed at grain boundaries in polycrystals. Basic domain structure formed in SmA phase, in which domain size was about 20 - 40 μm, was maintained in SmE phase,

although many dislocation lines were caused in each domain by shrinkage from pseudo-hexagonal lattice to rectangular one when the phase transition took place from SmA to SmE. In contrast to SmE phase, domain structures were destroyed, affording many smaller grains and more defects in polycrystalline phase. This SmE phase should be characterized as a plastic crystal phase with flipping motion around the molecular axis fixed at a rectangular lattice, rather than a liquid crystal phase. However, in terms of carrier transport, SmE phase is not crystal-like but more liquid-like, and should be distinguished from a molecular crystal phase. This is probably because distortion caused at phase transition can relax in SmE phase due to its structural flexibility derived from freedoms of molecular motion.

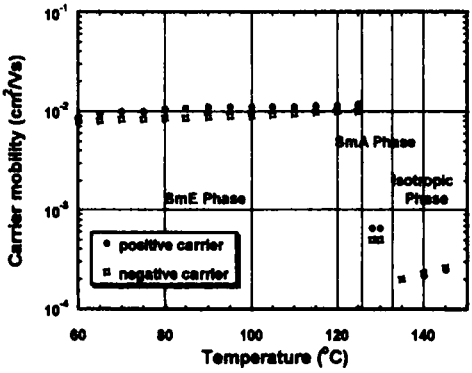

FIGURE 4 Temperature-dependence of carrier mobilities of 8-PNP-O4

In summary, the carrier transport characteristics in isotropic phase, nematic phase, and various smectic phases of 2-phenylnaphthalene derivatives were investigated by TOF technique. In contrast to isotropic and nematic phases, in which ionic conduction is dominant, field- and temperature-independent electronic ambipolar transport was exhibited in smectic phases. The electronic

carrier mobility was increased stepwise when the phase transition took place with a decrease in temperature. In particular, anomalous high carrier mobilities for both carriers on the order of 10^{-2} cm^2/Vs were observed in SmE phase, which were the highest ambipolar mobilities ever observed except for the molecular crystals of aromatic compounds.

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