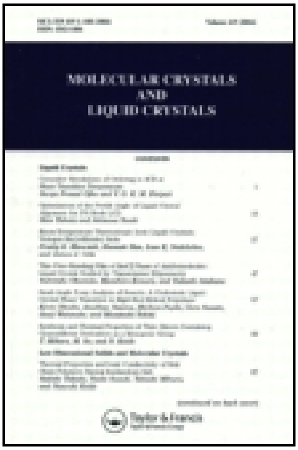

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One-Dimensional to Three-Dimensional Electronic Conduction in Liquid Crystalline Mesophases

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One-Dimensional to Three-Dimensional Electronic Conduction in Liquid Crystalline Mesophases

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We have established the electronic conduction in the nematic phase of a small molecule of a 2-phenylbenzothiazole derivative, i.e., 2-(4′-octyloxyphenyl)-6-butoxybenzothiazole (8O-PBT-O4). This gives a new insight into the quest for the electronic conduction in liquid crystals, which was initiated by Kusabayashi and Labes in late 1960s and had succeeded over several decades, leading it to the end. In addition, it is clarified that the ionic conduction often observed in less ordered mesophases is induced with trace amounts of chemical impurities due to its low viscosity. The present result indicates that the charge carrier transport in the mesophase is electronic in its intrinsic nature irrespective of mesophases and molecular sizes, i.e., 1D-electronic conduction in columnar phase, 2D-electronic conduction in smectic mesophases, and 3D-electronic conduction in the nematic phase.

Keywords: charge carrier transport; discotics; electronic conduction; ionic conduction; nematics; smectics

INTRODUCTION

Recent years, liquid crystals have attracted new attention as a new type of organic semiconductors exhibiting self-organization, which was initiated by discovery of electronic conduction in liquid crystals in 1990s [1,2]. The first attention to the electrical properties of liquid crystal, however, was paid in late 1960s by two groups: Heilmeier

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et al. reported ionic conduction in the nematic phase of *p*-azoxyaniole, which was associated with his invention of liquid crystal displays based on so-called dynamic scattering mode [3]; Kusabayashi and Labes extended their interest in the electrical properties of molecular crystals [4] to liquid crystals and reported those of various liquid crystals. Heilmeier's invention called high attention, so that the electrical properties of various calamitic, that is, rod-like liquid crystals were characterized in 1970s [5,6]. As a result, this led to a general recognition naturally that the charge carrier transport in liquid crystals was governed by ionic conduction. The liquid-like nature of liquid crystalline materials supports this idea easily.

After the synthesis of discotic liquid crystals in 1977 [7], the major interest in the electrical properties of liquid crystals was focused on the discotic liquid crystals such as triphenylene and porphirine derivatives because of their solid-like nature compared with calamitic liquid crystals. In late 1980s, Leeds university group indicated that the electronic conduction took place in columnar phase of a chemically doped triphenylene derivative by AC conductivity measurement [8], and Simon and his co-workers also suggested the electronic conduction in a columnar phase of porphirine derivative [9]. Finally, in 1993, the first electronic conduction was established in the hexagonal columnar phase of triphenylene derivative, H5T by evaluating carrier mobility by means of time-of-flight technique. Hole mobility was determined to be about $10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$, which is two to three orders of magnitudes higher than those of conventional amorphous semiconductor practically used [1].

After the discovery of electronic conduction in the discotic liquid crystals, however, the electrical conduction in the calamitic liquid crystals had been still believed to be ionic as a result of historical studies in 1970s and 1980s [10,11]. In 1995, we found that fast hole conduction took place in the smectic phase of 2-phenylbenzothiazole derivative as well [2,12], and since then the electronic conduction have been reported in the smectic mesophases of various calamitic liquid crystals including phenylnaphthalene, terthiophene, biphenyl, and so on [13–15].

The electronic conduction has been reported also in solid-like or highly viscous nematic phases such as liquid crystalline polymers including polyfluorenes [16,17] and the nematic glasses including oligofluorenes [18]. However, as for the low viscous nematic phase of small molecules, the charge carrier transport has been considered to be ionic so far, as a result of historical studies in 1970s and 1980s. In fact, the ionic conduction was reported in the nematic phase of 4,4′-cyanopentylbiphenyl (5CB) and 4,4′-cyanooctylbiphenyl (8CB) recently [19,20]. Furthermore, in a recent report that describes electronic conduction in the cholesteric phase of phenyl-substituted quaterthiophene derivative, it is emphasized that a large π-conjugated moiety of phenyl-substituted quaterthiophene favors hopping conduction over ionic conduction due to an increase in the intermolecular transfer integral [21].

In fact, the ionic conduction in the nematic phase is suspected to be extrinsic due to contamination of ionic impurities, but it has not been clarified yet what the intrinsic charge carrier transport properties is in the low viscous nematic phase of small molecules.

In this report, in order to answer this question, we have carefully investigated the charge carrier transport properties in the nematic phase of small molecules, e.g., 2-phenylbenzothiazole derivatives exhibiting the nematic phase.

EXPERIMENTAL

We selected a 2-phenylbenzothiazole derivatives of 2-(4′-octyloxyphenyl)-6-butoxybenzothiazole(8O-PBT-O4(**6**) in Fig. 1), as a model nematic liquid crystal because of our accumulated experience in purification of this type of materials and synthesized it according to a synthetic route as shown in Figure 1: We synthesized 2-(4′-octyloxyphenyl)-6-butoxybenzothiazole(8O-PBT-O4) (**6**) with a condensation reaction of 2-amino-6-butoxybenzenethiole(**5**) prepared from p-nitrophenol (**1**) in 4 steps as described in the synthetic scheme in Figure 1, with p-octyloxybenzaldehyde in DMSO at 150°C in 72% yield.

8O-PBT-O4 was purified by flush chromatography and recrystallization from ethanol and n-hexane several times. The phase transition-behavior was determined by differential scanning calorimetry (DSC, Shimazu DSC-60) and X-ray diffraction (XRD, RigakuRAD-2B diffractometer with Cu Kα radiation) studies. The charge carrier

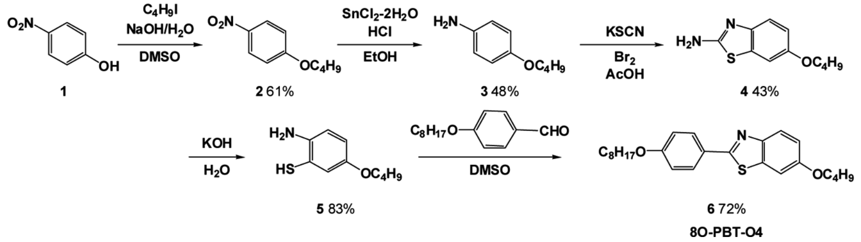

FIGURE 1 Synthetic route of 2-(4′-octyloxyphenyl)-6-butoxybenzothiazole (8O-PBT-O4(**6**)).

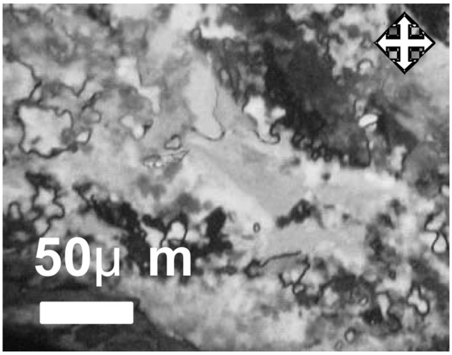

FIGURE 2 Texture images under polarized optical microscope in nematic phase.

transport properties were studied by time-of-flight experiments. The purified 8O-PBT-O4 was capillary-filled into liquid crystal cells having transparent ITO electrodes without a alighment layer. The resulting liquid crystal cells exhibited a polydomain texture of homogeneous alignment. A typical cell thickness was 10 μm. The cell was set on a sample stage maintained at a constant temperature with a PID controller. The transient photocurrents were measured by the conventional time-of-flight set-up equipped with a nitrogen laser ($\lambda = 337$ nm, pulse duration. 600 ps) as an excitation light and recorded by a digital oscilloscope (Nicolet Pro92. The bias voltage was applied to the sample with a power supply unit (Keithley 237). The transit time of carriers, τ_T, was determined from a kink point of the transient photocurrent measured.

RESULT AND DISCUSSION

The phase transition behavior of 8O-PBT-O4 was identified by the observation of optical texture under polarized microscope and Xray diffraction study. 8O-PBT-O4 exhibited a nematic phase (N phase) between 101°C and 124°C. Figure 2 shows a typical texture of 8O-PBT-O4 at the temperature range described above, indicating a very texture of the nematic phase. As shown in Figure 3, an X-ray diffraction pattern of 8O-PBT-O4 shows no sharp peak at entire diffraction angles measured, supporting the nematic phase.

Figure 4 shows the transient photocurrents observed in the nematic phase of samples in different purification steps at 115°C: in the sample “not purified enough”, the transient photocurrent shows a shoulder

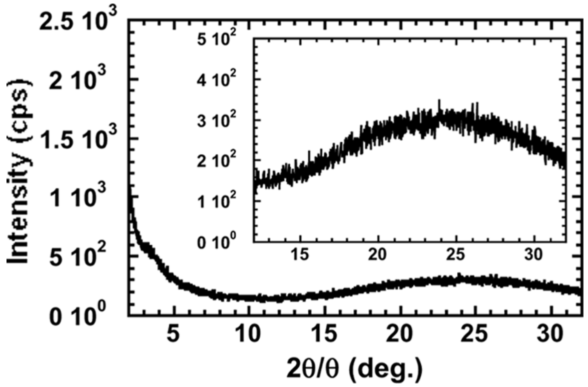

FIGURE 3 XRD patterns of 8O-PBT-O4 in nematic phase.

indicating slow transit of positive carriers at around 548.1 μs as shown in Figure 4(c), which corresponds to a slow mobility of $10^{-5}\,\mathrm{cm^2/Vs}$; in a "moderately purified" sample as shown in Figure 4(b), the photocurrent shows two shoulders at different time ranges of 76.4 μs and 546.4 μs, which correspond to the slow and fast mobilities of $10^{-5}\,\mathrm{cm^2/Vs}$ and $10^{-4}\,\mathrm{cm^2/Vs}$; in an "extensively purified" sample, the photocurrent

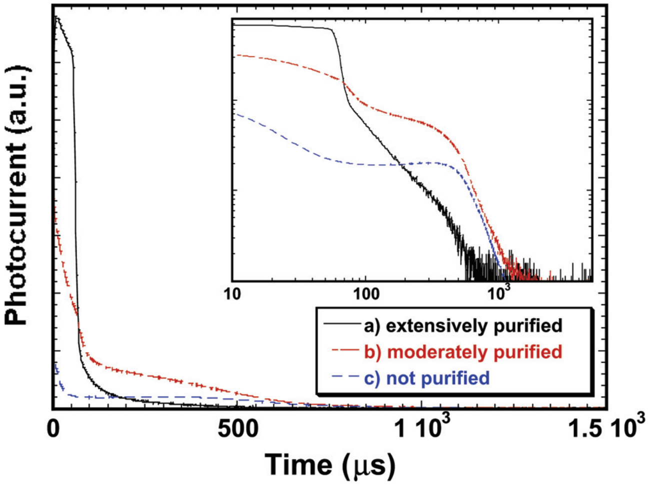

FIGURE 4 Transient photocurrents for positive carriers in the nematic phase of 8O-PBT-O4 at 115°C and $1 \times 10^5\,\mathrm{V/cm}$. The cell thickness was 10 μm.

shows a fast transit at around 57.8 μs as shown in Figure 4(a), which is the same as the fast transit as shown in Figure 4(b) and corresponds to a high mobility of 10^{-4} cm^2/Vs. The mobility of 10^{-4} cm^2/Vs that we found in the nematic phase of 8O-PBT-O4 is rather fast, comparable to those of less ordered smectic mesophases such as SmA and SmC phases [12,13], while it is one order of magnitude higher than those of ions in the nematic phases reported to be 10^{-5} to 10^{-6} cm^2/Vs.

As for the negative carriers, we observed a fast transit of carriers accompanied by a slow transit only when 8O-PBT-O4 was further purified and a thinner cell of 4.8 μm was employed for the measurements. The mobility for the fast transit was estimated to be 9.5×10^{-5} cm^2/Vs close to the fast mobility of positive carriers, while the mobility for the slow transit was to be 5.0×10^{-5} cm^2/Vs.

In order to clarify the origin of the fast and slow mobilities, we conducted TOF experiments in diluted samples with a low viscous solvent such as *n*-tetradecane (n-$C_{14}H_{30}$) freshly distilled. At the concentrations of *n*-tetradecane up to 12.5 mol%, neither macrophase separation of *n*-tetradecane in the diluted samples nor any significant change of phase transition temperatures was observed, which was confirmed by texture observation under a polarized optical microscope : the phase transition temperature of 5 mol% and 10 mol% diluted 8O-PBT-O4 with *n*-tetradecane were at c.a. 122.1°C and 120.7°C in cooling, which was not so big difference from 124°C in non-doped 8O-PBT-O4 in cooling. In a diluted sample, the mobility becomes higher compared with that of non-diluted sample, indicating that the conduction mechanism is ionic as is expected in the Walden rule [22]. On the other hand, the carrier mobility for the fast transit becomes smaller in the diluted samples, indicating that the conduction mechanism is electronic as is expected in the hopping transport within smectic layers. Table 1 shows the summary of the transit times and mobilities in non-diluted and diluted samples "moderately purified". It is very clear that the fast transit time becomes longer with an increase in the concentration of *n*-tetradecane, while the slow transit

TABLE 1 The Charge Carrier Mobility for Fast and Slow Positive Carriers in Non-Diluted and Diluted 8O-PBT-O4 at 5 and 10 mol% with *n*-tetradecane

	n-tetradecane non-diluted	*n*-tetradecane 5 mol%	*n*-tetradecane 10 mol%
Fast transit time (μsec)	76.4	82.4	89.2
Fast mobility (cm^2/Vs)	1.31×10^{-4}	1.21×10^{-4}	1.12×10^{-4}
Slow transit time (μ sec)	546.4	526.4	500.2
Slow mobility (cm^2/Vs)	1.83×10^{-5}	1.90×10^{-5}	1.99×10^{-5}

time becomes shorter. That is, the fast mobility is decreased from $1.31 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{Vs}$ to $1.12 \times 10^{-4}\,\mathrm{cm}^2/\mathrm{Vs}$, while the slow mobility is increased from $1.83 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{Vs}$ to $1.99 \times 10^{-5}\,\mathrm{cm}^2/\mathrm{Vs}$. These results support that the fast mobility is attributed to the electronic conduction, and the slow mobility to the ionic conduction. According to the present results, it is concluded that the nematic phase of small molecules exhibits ambipolar electronic conduction in its intrinsic nature, irrespective of viscosity and a size of π-conjugated system in the core moiety.

The ionic conduction is often observed in low viscous liquid crystals. According to our previous studies on the impurity effect on the charge carrier transport in the smectic mesophases, we indicate that the ionic species responsible for the ionic conduction are not always ionic impurities, but ionized impurity molecules are most possible, which are formed by photo-ionization of impurity molecules and/or their carrier trapping. It should be noted that the electronic conduction in mesophases is extremely sensitive to chemical impurities responsible for carrier traps and trace amounts of them, e.g., tens ppm, are good enough to destroy the electronic conduction in the mesophases. In addition, there is another reason why the ionic conduction takes place so easily in the mesophases. That is a microphase-separated structure of mesophase: in the columnar and smectic mesophases, the microphase-separated structure provides two conduction channels; one is a solid-like region consisting of stacked π-conjugated core moieties for hole and electrons and the other is a liquid-like region consisting of flexible hydrocarbon chains for ions [23,24]. As for the nematic phase, it is due to its low viscosity that favors the ionic conduction.

In the electronic conduction of mesophases, the conduction becomes anisotropic because of microphase separated structure of the mesophases: in discotic columnar phases, stacked core moieties having aromatic π-conjugate systems of a column, which is responsible for charge carrier transport of electrons and holes, are separated with long hydrocarbon chains from neighboring columns, so that inter-columnar conduction of the charge carriers is negligible compared with intra-columnar conduction of them because of a big difference in the transfer integral of neighboring molecules for intra- and inter-colums; this is true for the smectic mesophases also, and inter-smectic layer conduction of charge carriers is quite negligible compared with the intra-smectic layer conduction of them. Therefore, the electronic conduction become one dimensional for the discotic columnar phases and two dimensional for smectic mesophases, as illustrated in Figure 5. In fact, it was demonstrated by various experiments [8,25,26].

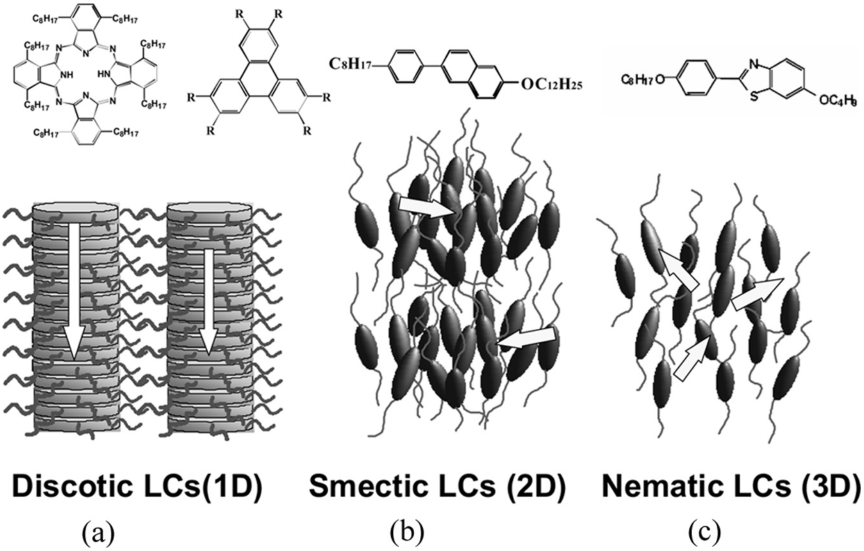

FIGURE 5 The carrier transport properties in various liquid crystal phases (a) discotic phase (b) smectic phase, (c) nematic phase. An intermolecular distance in neighboring molecules dominates a hopping rate of carriers in mesophase. Therefore, the dimension of conduction in mesophases is decided by anisotropy of the intermolecular distance in each mesophase: therefore, it becomes one-dimension for discotics, two-dimension for smectics, and three-dimension for nematics.

For the electronic conduction in the nematic phase, however, the anisotropy of conduction is considered to be considerably small, especially in small molecules compared with those for columnar and smectic mesophases, because of moleculare alignment of nematic phase, i.e., no positional order and a low order parameter. Therefore, it is quite plausible that the conduction is three dimensional as in the case of that in the amorphous solids. This should be confirmed by comparison of the charge carrier mobilities in the homogeneous and homeotropic alignment cells.

CONCLUSION

We investigated the charge carrier transport in the nematic phase of small molecules such as 2-phenylbenzothiazole derivatives by time-of-flight experiments. As a result, we revealed that the intrinsic conduction mechanism was electronic and ambipolar irrespective of molecular size, and its mobility was around $10^{-4}\,\mathrm{cm}^2/\mathrm{Vs}$ for electrons and holes. This discovery gives a new insight into the quest for the electronic conduction in liquid crystals after continuous efforts to clarify the intrinsic conduction mechanism in liquid crystals over several decades, leading it to the end.

In conclusion, the intrinsic charge carrier transport in liquid crystals is electronic and ambipolar irrespective of mesophases and molecular sizes, which is one dimensional in columnar phases, two-dimensional in smectic phases, and three-dimensional in nematic phases.

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