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Electronic conduction in nematic phase of small molecules

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We investigated charge-carrier transport in the nematic phase of small molecules such as 2-phenylbenzothiazoles by time-of-flight experiments, in which the conduction mechanism has been considered to be ionic. As a result, we established the hole and electron transports in the nematic phase of highly purified samples: we found that there were two transits, namely, fast and slow transits, in less pure samples; the slow transit was attributed to ionic conduction originating from trace amounts of impurities and the fast transit was attributed to electronic conduction whose attribution was elucidated by mobility changes in the diluted samples with a hydrocarbon of n-tetradecane (n-$C_{14}H_{30}$). From these results, we conclude that the intrinsic conduction mechanism in the nematic phase of small molecules is ambipolar and electronic, irrespective of the size of the π-conjugate system of the core moiety. Thus, they provide a new insight into the conduction mechanism in fluidic materials.

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Recently, liquid crystals have attracted additional attention as a new type of organic semiconductor exhibiting self-organization, which was initiated in the 1990's by the discovery of electronic conduction in both discotic and smectic liquid crystals.[1,2] However, the electrical properties of liquid crystals have attracted interest since the late 1960's. Heilmeier *et al.*[3] reported that ionic conduction occurs in the nematic phase of p-azoxyanisole, which was used by them to develop a liquid-crystal display based on the so-called dynamic scattering mode, whereas Kusabayashi and Labes[4] extended their interests from the electrical properties of molecular crystals to those of liquid crystals. Thus, in 1970's, the electrical properties of liquid crystals were one of the major interests in the studies of liquid crystals. As a result, the electrical properties of various calamitic, that is, rodlike liquid crystals, have been characterized,[4,5] and the results naturally led to a general recognition that the charge-carrier transport in liquid crystals is governed by ionic conduction. The liquidlike nature of liquid-crystalline materials supports this idea easily.

After the synthesis of discotic liquid crystals in 1977,[6] there was a shift in focus from the electrical properties of calamitic liquid crystals to those of discotic liquid crystals such as triphenylene derivatives. In 1993, hole conduction was established first in a columnar phase of hexapentyloxytriphenylene (H5T).[1] The electronic conduction was discovered also in smectic liquid crystals such as phenylbenzothiazole and phenylnaphthalene derivatives.[2,7,8] These discoveries gave an answer to a historical quest for electronic conduction in liquid crystals, generating a new interest in liquid crystals as described above.

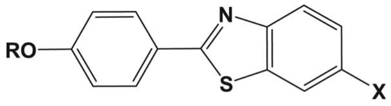
Charge-carrier transport in the nematic phase of small molecules, however, has been considered to be ionic so far as a result of historical studies in 1970's, while electronic conduction has been observed in viscous solid nematic phases such as nematic glasses[9] and the nematic phase of polymers having aromatic π-conjugated mesogens.[10,11] In fact, papers published after the discovery of electronic conduction describe the ionic nature of electrical properties in the nematic phases of 4,4′-cyanopentylbiphenyl (5CB) and 4,4′-cyanooctylbiphenyl (8CB).[12,13] Furthermore, in a recent report that describes electronic conduction in phenyl-substituted quaterthiophene derivatives, it is emphasized that a large π-conjugated core moiety of phenylquaterthiophene favors hopping conduction over ionic conduction due to an increase in the intermolecular transfer integral.[14]

When a small molecule is ionized in its fluidic states such as nematic and isotropic phases in a given electric field, a charge transfer to a neighboring molecule and drift of the ionized molecule can be competitive. Either of the two events would occur depending on the balance between the fluidic viscosity that affects the ion drift and the charge-transfer rate determined by both the intermolecular transfer integral of molecular orbitals and an energy difference between the molecular levels responsible for the charge transfer. This holds true only for the material without electronically active impurities, i.e., chemical impurities responsible for deep trapping states of carriers. However, we have to be careful in reality for the chemical impurities especially in fluidic states. In fact, extrinsic conduction often dominates these competitive processes in mesophase materials.[15–17]

We have investigated charge-carrier transport in the nematic phase of small molecules, i.e., 2-phenylbenzothiazole derivatives of 2-(4′-octyloxyphenyl)-6-butoxybenzothiazole and 2-(4′-pentyloxyphenyl)-6-dodecylbenzothiazole (referred to as 8O-PBT-O4 and 5O-PBT-12, respectively) as shown in Fig. 1. These compounds were selected as reference materials since we had immense experience on their purification.[8]

The 2-phenylbenzothiazoles were synthesized as reported elsewhere.[18] Isolated 2-phenylbenzothiazoles were repeatedly and carefully purified by silica column chromatography and recrystallization from ethanol and hexane.[19]

Their phase-transition behaviors were determined by differential scanning calorimetry (DSC) (Shimazu DSC-60) and x-ray diffraction (XRD) (Rigaku RAD-2B diffractometer with Cu K_{α} radiation, $\lambda = 1.54$ Å) studies. The properties of charge-carrier transport were studied by time-of-flight (TOF)



8O-PBT-O4(R=C_8H_{17}, X=OC_4H_9)
5O-PBT-12(R=C_5H_{11}, X=$C_{12}H_{25}$)

FIG. 1. Molecular structures of 2-(4′-octyloxyphenyl)-6-butoxybenzothiazole and 2-(4′-pentyloxyphenyl)-6-dodecyl benzothiazole (referred to as 8O-PBT-O4 and 5O-PBT-12, respectively).

experiments whose setup is described elsewhere.[20] The samples for TOF experiments were prepared by filling 2-phenylbenzothiazole derivatives by capillary action into liquid-crystal cells having two In_2O_3-SnO_2 (ITO) electrodes in their isotropic phases. The resulting molecular alignment of mesophases in the cells was homogeneous, where the long axis of liquid-crystalline molecules was parallel to the substrate. This alignment was stable in all the electric fields. On the other hand, homeotropic alignment, where the long axis of liquid-crystalline molecules is perpendicular to the substrate, was achieved only when the surface of the substrate was chemically modified with a silane coupling reagent such as octadecyltriethoxysilane. However, this alignment was highly unstable even at a low electric field of 1×10^4 V/cm, and it easily transformed into the homogeneous alignment because the molecular dipole was perpendicular to the long molecular axis (negative dielectric anisotropy).

8O-PBT-O4 exhibited three phase transitions, as shown in the DSC chart of Fig. 2. The phase that was observed at temperatures from 123.9 to 100.8 °C on cooling and from 102.3 to 125.2 °C on heating had typical threadlike texture, as shown in the polarized optical microscope image (a) in Fig. 2. 8O-PBT-O4 also exhibited a smectic C (SmC) phase from 100.8 to 68.3 °C on cooling whose texture is shown in the polarized microscope image (b) in Fig. 2 and a crystal phase adjacent to the SmC phase at temperatures below 68.3 °C.

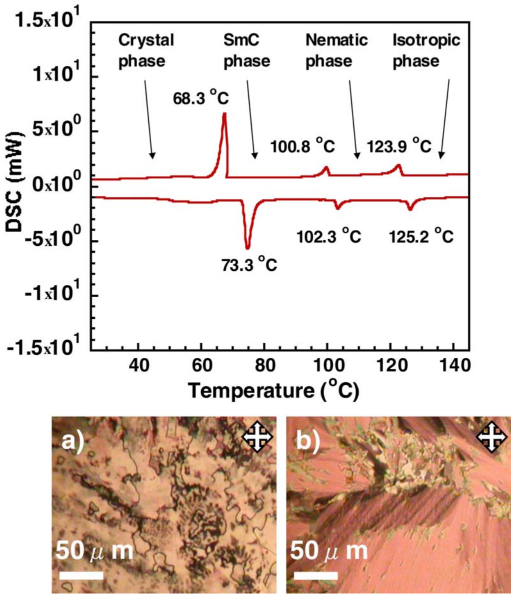


FIG. 2. (Color online) DSC chart of 8O-PBT-O4 obtained at a cooling rate of 10 °C/min and a heating rate of 10 °C/min, and texture images obtained using a polarized optical microscope at (a) 110 and (b) 90 °C.

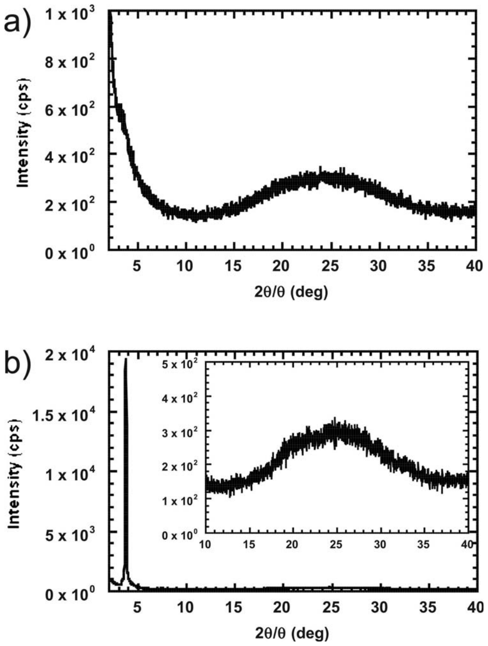


FIG. 3. XRD patterns of 8O-PBT-O4: (a) nematic phase at 110 °C and (b) smectic C phase at 90 °C.

Figure 3 shows a typical XRD pattern of 8O-PBT-O4 at 110 °C. This pattern does not show any sharp peak at all the measured diffraction angles; therefore, it is similar to a typical XRD pattern of the nematic phase. 5O-PBT-12 exhibited the nematic phase in a very narrow temperature range of 79.2–86.4 °C and the SmA phase from 59.3 to 79.2 °C on cooling.

We characterized the charge-carrier transport properties for the nematic phase from 100 to 120 °C by TOF experiments. All the measured transient photocurrents were nondispersive for positive and negative carriers. When 8O-PBT-O4 was not sufficiently purified, we observed a clear shoulder in the transient photocurrent curve for positive carriers, as shown in Fig. 4(a), indicating the transit time of carriers arriving at the counter electrode. This transit time corresponds to a mobility of 1×10^{-5} cm^2/V s. In contrast, in the case of 8O-PBT-O4 that was highly purified, we observed a well-defined transit time at a shorter time range by 1 order of magnitude as shown in Fig. 4(c), which corresponded to a mobility of 1×10^{-4} cm^2/V s. In the case of 8O-PBT-O4 that was moderately purified, we observed two transits in the same time ranges mentioned above, as shown in Fig. 4(b), which corresponded to the mobilities described above, respectively.

We observed a fast transit of negative carriers accompanying a slow transit as shown in Fig. 5, only when 8O-PBT-O4 was further purified and a cell of thickness 4.8 μm was employed in the TOF experiments. Otherwise, the transient photocurrent showed only one shoulder corresponding to the slow transit. The mobility in the fast transit was esti-

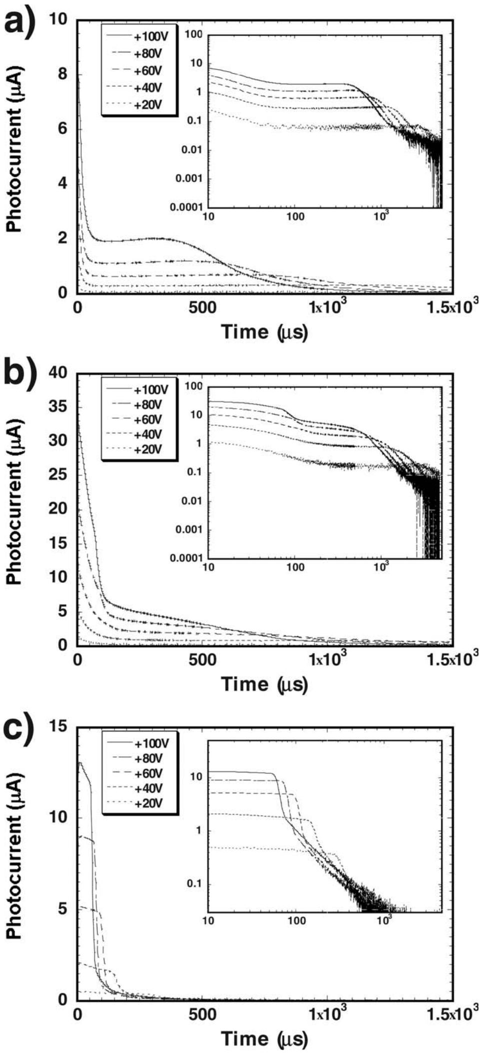


FIG. 4. Positive transient photocurrents measured by applying various voltages at 115 °C. The cell thickness was 10 μm. (a) Insufficiently purified 8O-PBT-O4, (b) moderately purified 8O-PBT-O4, and (c) highly purified 8O-PBT-O4.

mated to be 9.5×10^{-5} cm^2/V s, which was close to the high mobility of positive carriers, while the mobility in the slow transit was 5.0×10^{-5} cm^2/V s. This is very similar to the case of positive carrier transport in this material.

We did not succeed in characterizing the charge-carrier transport properties of the nematic phase in the homeotropic alignment because we could not maintain this alignment at electric fields higher than 1×10^4 V/cm, where we could observe a transient photocurrent with a high signal-to-noise ratio.

In order to clarify the origin of the two transits in the nematic phase, we studied the change in carrier transport in 8O-PBT-O4 when it was diluted with a freshly distilled hydrocarbon of *n*-tetradecane (n-C$_{14}$H$_{30}$), which was electrically inert and had low viscosity. At concentrations of *n*-tetradecane up to 12.5 mol %, we observed neither the macrophase separation of *n*-tetradecane in diluted 8O-PBT-O4 nor any significant change in phase-transition temperatures, as confirmed by texture observation under a polarized optical microscope. In dilution experiments, we can clearly distinguish electronic conduction from ionic conduction:[21,22] when charge-carrier transport is governed by electronic conduction, the mobility in the diluted samples decreases because the average distance between 8O-PBT-O4 molecules for the carriers to hop is increased by dilution; in contrast, when it is governed by ionic conduction, the mobility increases because the viscosity of the diluted 8O-PBT-O4 decreases, as indicated by Walden's rule.[23] In fact, as the concentration of *n*-tetradecane increased, we found that the fast transit time shifted to a longer time range in the nematic phase of diluted 8O-PBT-O4, as shown in Fig. 6: for instance, the transit time of 8O-PBT-O4 diluted with 10 mol % *n*-tetradecane was about 1.2 times of that of undiluted 8O-PBT-O4. On the other hand, when the concentration of *n*-tetradecane increased, the slow transit slightly shifted to a shorter time range, as shown in Fig. 6. This small change in the transit time probably occurs because the viscosity of 8O-PBT-O4 is quite similar to that of *n*-tetradecane. The fast and slow mobilities for diluted and nondiluted samples are plotted as a function of temperature in Fig. 7. From the results of the dilution experiments, the fast and slow transits in the nematic phase are attributed to electronic and ionic conductions, respectively.

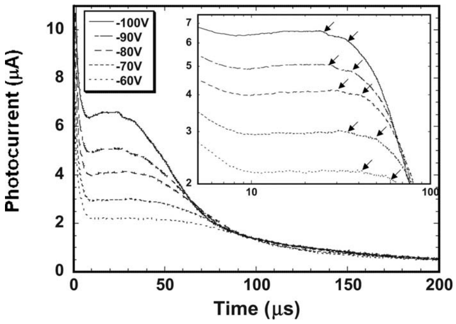


FIG. 5. Negative transient photocurrents in nematic phase measured at various applied voltages. The cell thickness was 4.8 μm. The arrows in the figure indicate transit times for fast and slow carriers.

We do not think that ionic species are responsible for the slow transit that results from the dissociation of ionic impurities; however, we attribute them to ionized nonionic impu-

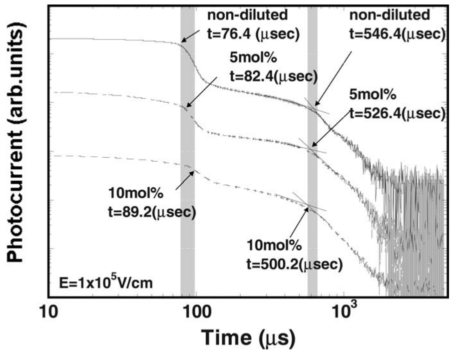


FIG. 6. Transient photocurrents for positive carriers in nondiluted and diluted 8O-PBT-O4 (moderately purified) containing 5 and 10 mol % *n*-tetradecane as a function of time in the nematic phase. The cell thickness was 10 μm.

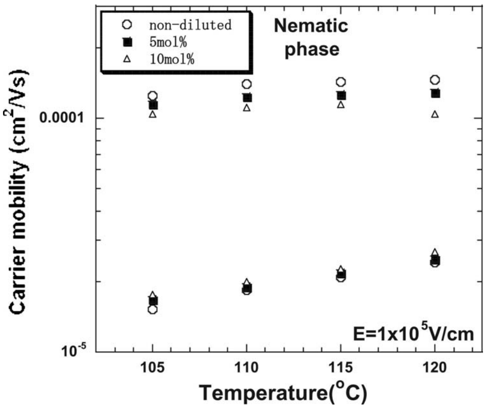


FIG. 7. Mobilities for positive carriers in nondiluted and diluted 8O-PBT-O4 containing 5 and 10 mol % *n*-tetradecane as a function temperature in the nematic phase. The cell thickness was 10 μm.

rities that contaminate 8O-PBT-O4 during its synthesis. In fact, the nonionic impurities that have highest occupied molecular orbital (HOMO) and/or lowest unoccupied molecular orbital (LUMO) levels in the energy gap of the host liquid crystal are ionized easily through energy transfer from excitons and trapping of photogenerated carriers in the host liquid crystal, in addition to direct photoionization. According to our detailed studies on the effects of impurities on charge-carrier transport in liquid-crystalline materials,[16,17] we can estimate the concentration of electrically active impurities that induce ionic photoconductivity to be less than tens of ppm at the most although their chemical structures are not identified.

In order to validate the present results on the nematic phase of 8O-PBT-O4, we investigated the carrier transport properties of 5O-PBT-12. We observed similar behavior of fast and slow transits in the nematic phase after dilution with *n*-tetradecane although its temperature range for the nematic phase was quite limited. The mobilities of positive carriers for the fast and slow transits were determined to be 7.8×10^{-5} and 7.9×10^{-6} cm^2/V s, respectively. These are consistent with the values of the carrier mobilities in the nematic phase of 8O-PBT-O4. Therefore, we conclude that intrinsic charge-carrier transport in the nematic phase of 2-phenylbenzothiazole derivatives is basically electronic and ambipolar, and its mobility for electrons and holes is around 10^{-4} cm^2/V s.

The present results prove that electronic conduction in the nematic phase is determined not by the size of the π-conjugate system of the core moiety but by the purity of the material. The occurrence of electronic conduction in the nematic phase of phenylbenzothiazoles indicates that charge-carrier transport in the mesophase is intrinsically electronic, irrespective of molecular size.

Electronic conduction in the discotic liquid crystals occurred in various discotic columnar phases; however, no result on the disconematic phase has been reported, except for the disconematic phase of polymeric liquid crystal having a triphenylene core moiety.[24] According to our present conclusion, it is highly plausible that the intrinsic nature of charge-carrier transport in the disconematic phase of small molecules is electronic and ambipolar because their viscosity is higher than that of the nematic phase of rodlike liquid crystals.

Our findings come to the final answer to the historical quest for electronic conduction in liquid crystals over several decades and are the key to clarifying the mechanism of electronic conduction in liquid crystals. In addition, they pose a new question: what is the mechanism of intrinsic charge-carrier transport in fluidic materials?

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