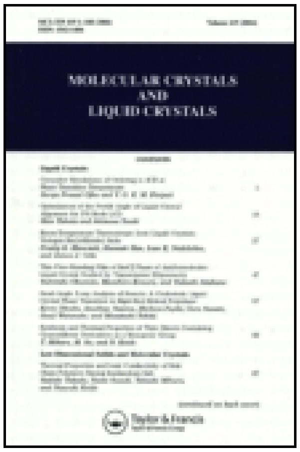

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First Electronic Conduction with High Hole Mobility in Smectic a Phase of a Calamitic Liquld Crystal

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FIRST ELECTRONIC CONDUCTION WITH HIGH HOLE MOBILITY IN SMECTIC A PHASE OF A CALAMITIC LIQUID CRYSTAL

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Abstract Liquid crystalline photoconductor 2-(4'-heptyloxyphenyl)-6-dodecylthiobenzothiazole was designed and its carrier transport characteristics was measured with Time-of-Flight (TOF) technique. In crystal state, only transient current decay originating from a capturing process of photo-generated carriers by deep traps formed at grain boundaries was observed. In smectic A (SmA) phase, non-dispersive transient photocurrent based on fast hole transport was observed, in which hole mobility was $5X10^{-3}$ cm/Vs, independent of electric field. In isotropic phase, ambipolar transport proceeded and the mobilities of both positive charge and negative charge carriers were on the order of 10^{-5} cm^2/Vs.

Introduction

The organic carrier transport materials such as molecularly-doped polymers have been applied to photoreceptors of xerographic copiers and laser printers. However, these materials are characterized by low carrier mobilities on the order of 10^{-6} cm^2/Vs and slow response, based on hopping conduction governed by the positional and energetical disorders of hopping sites and deep traps, resulting in their strong dependence on temperature and field strength. This is attributed to small intermolecular overlaps between π-orbitals among carrier transport molecules randomly doped into the matrix polymer.[1] On the other hand, band-like conduction with a high carrier mobility and a fast response can be realized in single crystals of these materials because of large overlaps between π-orbitals of the molecules ordering in the lattice and few deep traps.[2]

In order to sophisticate the carrier transport in organic materials, the molecular alignment in mesophase would be effective, in which larger electronic correlation among molecules and smaller disorder than the doped polymers can be realized. Furthermore, it is expected that the structural deep traps in polycrystalline phase should be reduced in mesophase.

In calamitic system, especially in nematic phase, only ionic conduction has been reported due to ionic impurities or photo-ionized material molecules.[3, 4, 5, 6] This is a clear contrast to the discotic mesophases, in which fast hole transport based on band-like conduction was observed.[7, 8] We are interested in a study of the carrier transport in the more liquid-like calamitic mesophase with larger thermal fluctuation than the discotic one.

We started our research focusing on smectic phase which has stronger intermolecular interaction compared with the nematic phase. We have already reported the design and photoconductive behavior of a calamitic liquid crystal, 2-(4'-heptyloxyphenyl)-6-dodecylthiobenzothiazole (7O-PBT-S12), exhibiting smectic A (SmA) phase shown in Fig. 1.[9] In this paper, we will report the carrier mobility in different phases of 7O-PBT-S12 with Time-of-Flight (TOF) method, including the first establishment of electronic conduction in calamitic mesophase.

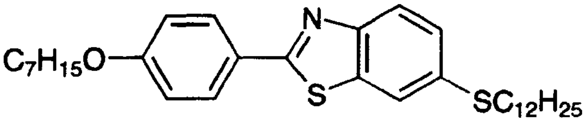

FIGURE 1 Molecular structure of 7O-PBT-S12

Experimental and Results

7O-PBT-S12 (λmax = 330 nm, ε = ca 10^7 cm^2/mol, K 90 °C SmA 100 °C Iso) was synthesized as reported elsewhere[9] and purified by flush column chromatography and recrystallization. The purified sample just before use was capillary-filled into the cell which is composed of two ITO-coated glass electrodes separated by polymer film spacer.

In TOF measurement, the cell was mounted on heater block of cryostat, whose temperature was controlled by a PID thermocontroller within the accuracy of 1 ^{0}C. The photoexcitation in the main absorption band of this material was carried out with N_2 laser (λ = 337 nm, pulse width = 600 ps, illuminated area = 0.16 cm^2, the penetration depth for the material < 1μm). The transient photocurrent was amplified by a pre-amplifier and recorded with digital oscilloscope. The transit time of the carriers was determined by an inflection point of the obtained transient photocurrent in a double logarithmic plot.[10] 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 $\mu = d^2/t_TV$, where d is cell thickness, V an applied voltage, and t_T a transit time.[10]

In polycrystalline phase, exponential decays of the photocurrents based on the extinction process of photo-generated carriers were observed for both of positive and negative carrier. This is probably because the carriers were trapped at deep levels derived from accumulated impurities and/or structural defects of polycrystalline phase at grain boundaries.

In contrast to the deep trap-dominated behavior in polycrystalline state, non-dispersive transient photocurrents based on a fast carrier transport were observed for positive charge as shown in Fig. 2(a); the collected charge (an integral of the transient photocurrent) was less than 10 % of accumulated charges estimated from capacitance of the cell. The positive carrier mobility was determined from the slope as described above as shown in Fig. 2(b), which was 5×10^{-3} cm^2/Vs independent of the electric field, implying band-like conduction, like discotic mesophase. For negative carrier, only a small current decay was obtained in SmA phase, which is compatible with the result of steady-state photocurrent measurement under the illumination of UV light.[9] This is attributed to electronic properties of the molecule favorable for hole transport. This unipolar transport is a clear contrast to the result in D_h phase of the triphenylene derivative.[7]

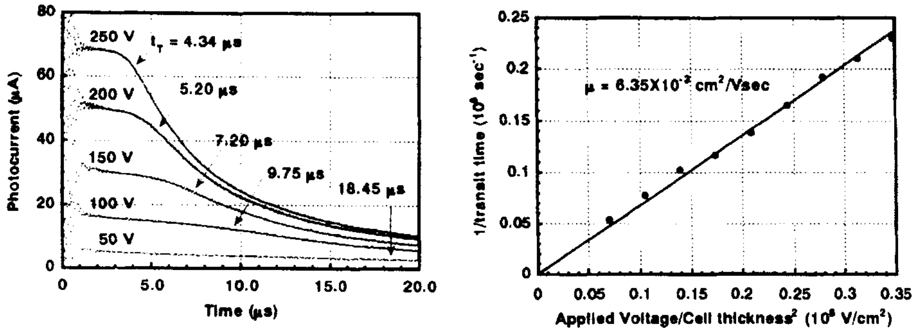

FIGURE 2 (a) Transient photocurrents for hole at various voltages in SmA phase (95 ^{0}C). (b) A plot of reciprocal transit time as a function of field strength devided by sample thickness. The sample thickness was 27 μm and effective illuminated area was 0.27 cm^2.

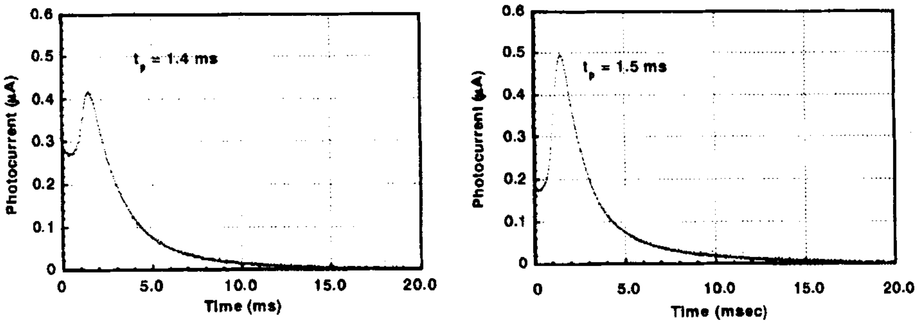

FIGURE 3 Transient photocurrents at 200 V in isotropic phase (110 ^{0}C). The sample thickness was 27 μm and effective illuminated area was 0.27 cm^2. (a) for positive carrier (b) for negative one

In isotropic phase, in spite of the same excitation condition as in the case of SmA phase, transient photocurrents with a peak were obtained regardless of directions for the applied electric field, as shown in curves (a) and (b) of Fig. 3. The shape of both transient photocurrents indicated a carrier transport limited by space charges, which are excessively photogenerated carriers because of the enhancement of effective light absorption accompanied with reduction of light scattering. Mobility was determined by the relation in the space charge limited regime: $\mu = 0.79 \cdot d^2/V t_p$, where t_p is a peak time of the transient photocurrent.[11] The estimated mobilities at 10^5 V/cm were 5×10^{-5} cm^2/Vs for both positive and negative charge carriers.

Discussions

The measured hole mobility in SmA phase was 1000 times larger than those of amorphous organic carrier transport materials as mentioned above and even 5 times larger than D_h phase of hexaalkoxy-triphenylene.[7] This fast non-dispersive carrier transport could be attributed to large intermolecular electronic correlation and less energetic and positional distribution of hopping sites due to its ordered structure. The abrupt mobility change by 2 orders of magnitude from $5\text{X}10^{-3}$ cm^2/Vs in SmA phase to $5\text{X}10^{-5}$ cm^2/Vs in isotropic phase can be referred to the disappearance of molecular alignment accompanied with the phase transition, indicating the importance of molecular alignment in mesophase. The slight negative temperature-dependence in SmA phase corresponds to the increase of thermal fluctuation of molecular ordering unlike discotic system, in which hole mobility in D_h phase is constant over the range of 50 K.[7]

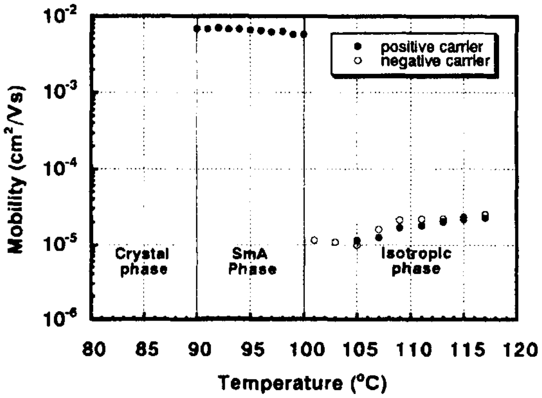

FIGURE 4 Temperature-dependence of positively charged carrier mobility. The electric field was 10^5 V/cm in isotropic phase.

The ionic conduction can be excluded in SmA phase because we could observe a clear rectification of carrier transport as expected in 7O-PBT-S12 and a slight negative temperature dependence on the mobility: a reduction of viscosity even in SmA phase should result in an increase of viscosity-influenced ionic mobility with an increase in temperature, if the ionic conduction is dominant. This is also supported by estimation of viscosity in SmA phase from Walden's rule which is valid for the ionic transport, $\mu\eta = e/6\pi r$, where η is a viscosity of mesophase, r a radius of ions. Assuming an ionic radius of 7O-PBT-S12 to be 1 nm, μ of $5X10^{-3}$ cm^2/Vs yields $1.6X10^{-5}$ Ns/m^2 for unreasonable viscosity which is one order of magnitude smaller than that of water at 20 °C. This is the first electronic conduction in calamitic mesophase. In contrast to viscous SmA phase, ionic transport is plausible in isotropic phase which promotes the ionic transport because of the smaller viscosity. In particular, negative charge transport could be caused perhaps by some anionic species other than negatively ionized liquid crystalline molecules themselve, although there still remains ambiguity in conduction mechanism for positive charge transport in isotropic phase.

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