Charge Carrier Transport in Polymeric Smectic Liquid Crystals

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Abstract

Recently the liquid crystals are being recognized to be a quality organic semiconductor, since the fast charge carrier transport was discovered in some types of liquid crystals including *discotic* (disk-like) and *calamitic* (rod-like) liquid crystals. In the present study, we have synthesized a polymeric liquid crystal exhibiting smectic (Sm) mesophases, i.e., polyacrylates having 2-phenylnaphthalene moiety as mesogenic group (PNP-acrylate) and investigated its charge carrier transport properties by time-of-flight experiments. We found that the smectic A phase of the polymer exhibited a high hole mobility of 10^{-4} cm^2/Vs, which was comparable to that in the smectic A phase of small molecule, 2-phenylnaphthalene derivatives. Furthermore, the fast hole transport was also observed in Sm glassy phase at ambient temperatures, when a small amount of 2-phenynaphthalene derivative was added to the polyacrylate. These facts indicate that the Sm mesophases in polymeric liquid crystals exhibit fast charge carrier transport comparable to the small molecular weight Sm liquid crystals basically.

Introduction

After the discovery of fast electronic conduction in some types of liquid crystals, i.e., a discotic liquid crystal of hexapentyloxytriphenylene in 1993[1] and a smectic (Sm) liquid crystal of 2-(4'-heptyloxypheny)-6-dodecyl thiobenzothiazole in 1995,[2] it has been revealed that various liquid crystals exhibit the fast electronic conduction characterized by a high mobility over 10^{-3}cm^2/Vs[3-8] Now, the liquid crystal is being recognized as a quality organic semiconductor exhibiting self-organization.

This fast conduction in liquid crystals is originated from an enhanced hopping transport of charges among self-organized closely packed molecules in columns or layers, which are called mesophases, i.e., discotic columnar phase and smectic phase, as shown in Fig. 1. The charge carrier transport in these mesophases is quite different from those in conventional organic amorphous semiconductors such as molecularly doped polymers with small organic semiconductors and their vacuum evaporated thin films as shown in Fig. 2.

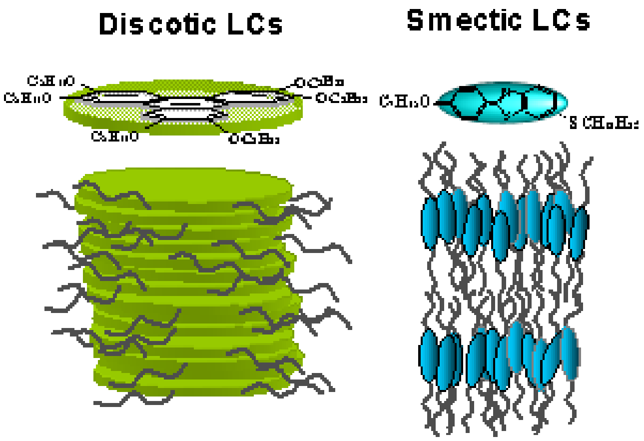

Figure 1. Self-organized molecular aggregates exhibiting fast electronic conduction: discotic columnar phase of hexapentyloxy-triphenylene (left) and smectic phase of 2-phenylbenzothiazole derivative (right)

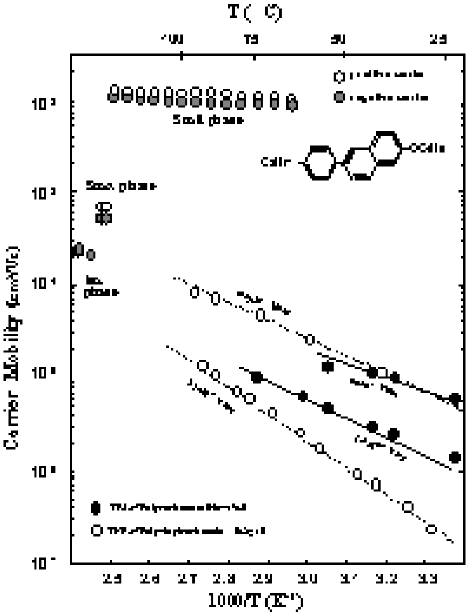

Figure 2. Arrhenius plots of charge carrier mobility in a typical Sm liquid crystal of 8-PNP- and two conventional organic amorphous semiconductors of TPA-polycarbonate and PVK-TNF.

The charge carrier transport in liquid crystalline semiconductors are characterized by following unique properties:[2,3,5,7]

(1) Anisotropic carrier transport.
(2) Low-dimensional hopping transport, e.g., one-dimensional in discotics and two-dimensional in smectics.
(3) Very fast carrier mobility ranges up to 10^{-2} cm^2/Vs.
(4) Bipolar carrier transport.
(5) Electric field-independent mobility.
(6) Temperature-independent mobility.

Above all, the field-and temperature-independent carrier transport, which gives us a great advantage in device applications, is a clear contrast to that governed by Poole-Frenckel type of behavior in disordered organic solids.

Here is an interesting question: *Does the polymeric Sm mesophase exhibit the fast charge carrier transport as the small molecular smectic mesophase does?,* while it was reported recently that a nematic phase of polyfluorenes, which is a main chain π-conjugated polymer, exhibits the fast hole transport characterized by a high mobility of 9×10^{-3} cm^2/Vs. Thus, we have synthesized a model Sm polymer and investigated its charge carrier transport properties by time-of-flight experiments.

Experimental

Materials

We selected a side chain polymer of the acrylate polymer with a liquid crystalline mesogenic moiety of 2-phenynaphthalene with reference to a well-characterized Sm liquid crystal of 2-(4'-octylphenyl)-6-dodectloxy naphthalene (8-PNPO12) and synthesized it as usual as shown in Fig. 2.

The PNP-acrylate monomer was polymerized with an initiator of azobisisobutyronitrile (AIBN, 3mol%) and the resulting polymer was purified by reprecipitation from methanol.

Liquid crystal cells were prepared by capillary-filling the polymerized PNP-acrylate slowly at high temperatures into the cells made of two ITO (In_2O_3) coated glass plates.

Measurement of Electrical Properties

The liquid crystal cell was mounted on the hot stage controlled at a given temperature by PID thermo-controller within an accuracy of 0.1 K. The carrier transport properties were evaluated by measuring transient photocurrents induced by a short pulse of N_2 laser (337nm, 600ps). The transient photo-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:

$$\mu = d^2/V \tau_T \qquad (1)$$

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

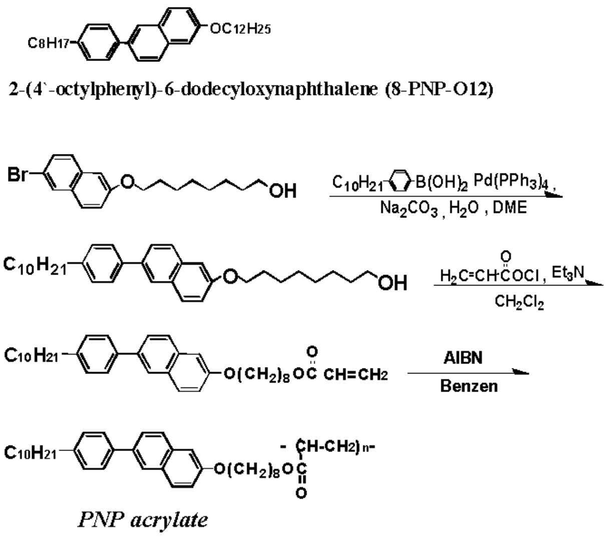

Figure 3. Chemical structure of 8-PNP-O12 and a PNP- acrylate and its synthetic route

Results and Discussion

1. PNP-Acrylate

The PNP-acrylate showed SmA phase at a temperature range between 120°C and 165°C as shown in Fig. 3 and kept the texture when rapidly cooled, indicating a stable Sm glassy phase.

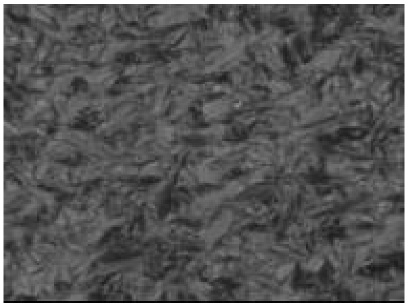

Figure 4. SmA texture in PNP-acrylate at 140°C.

In SmA phase, the transient hole photocurrent was dispersive, but we could determined a transit time as an inflection point in double logarithmic plots of photocurrent and time as shown in Fig. 5 (top). The hole mobility was determined to be 2×10^{-4} cm^2/Vs, which is the same as that in SmA phase of 8-PNP-O12, which is a small molecular weight liquid crystal of having the same core moiety of phenylnaphthalene as shown in Fig.2.

This result suggests that the molecular alignment in SmA plays a dominant role for charge carrier transport irrespective of molecular difference in PNP-acrylate and 8^PNP-O12.

The transient photocurrents in Sm glassy phase, however, exhibited no inflection point in double logarithmic plot of time and photocurrent, as shown in Fig. 5 (bottom).

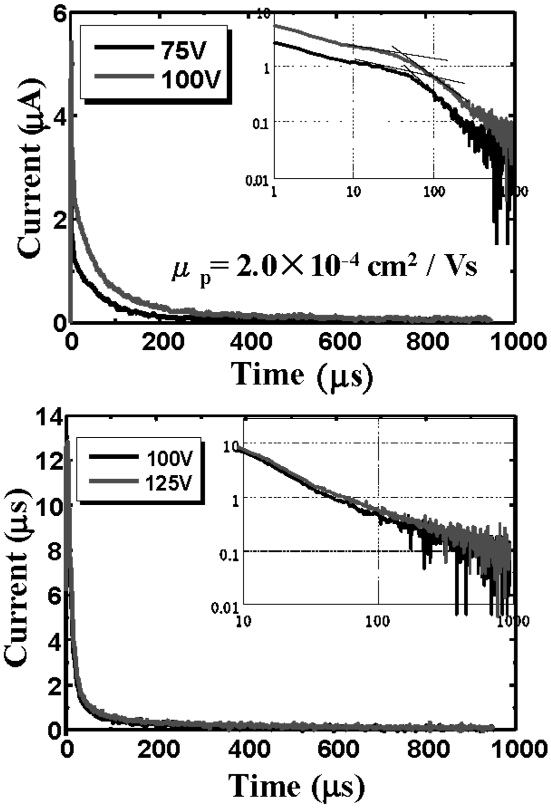

Figure 5. Transient photocurrent in SmA (top) at 140°C and Sm glassy phase at 25°C (bottm) of mA (top) and Sm glassy phase (bottm) of PNP-acrylate. The cell thickness is 9μm.

This clear difference in the transient photocurrents of SmA and Sm glassy phases dose not indicate that the molecular motion of liquid crystalline molecules is associated with the charge transport because the hopping frequency in such a fast charge transport characterized by a mobility over 10^{-3}cm^2/Vs is much higher than those in the molecular motions such as translational one. Therefore, this photocurrent decay in the Sm glassy phase is probably attributed to charge trapping at the localized states related to heavily disordered molecular alignment including domain boundaries, which can be caused by limited self-organization due to bound mesogenic groups to the main-chain of the polymer.

2. PNP-Acrylate Mixed with 8-PNP-O12

According to the discussion about results in previous section, it is plausible that the molecular alignment in the glassy phase are so heavily disordered, especially at the domain boundaries that the charge carrier cannot transport. Therefore, it is expected that the addition of small amount of the non-polymeric Sm liquid crystal such as 8-PNP-O12, which may act as a plasticizer, should improve the charge carrier transport in the glassy phase. Thus, we investigated the carrier transport in PNP-acrylate mixed with 8-PNP-O12.

Figure 6 shows the DSC curve for 16.7wt% 8-PNP-O12 doped PNP-acrylate, which has SmA, SmB, a highly ordered and unidentified Sm phase (SmX), and LC glassy phases at indicated temperature ranges.

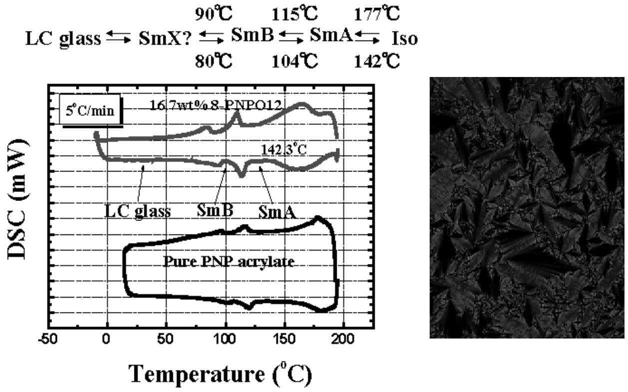

Figure 6. DSC curves for PNP- acrylate doped with 8-PNP-O12 of 16.7wt%. (left) and a typical texture of LC glassy phase prepared by rapid cooling from SmA pahse (right)

The transient photocurrents in SmA and Sm glassy phases of mixed PNP-acrylate are shown in Fig. 7. The photocurrent in SmA was dispersive and very similar to that in pure PNP-acrylate: the hole mobility was determined to be 2×10^{-4}cm^2/Vs, which was the same as that in pure PNP-acrylate. In its Sm glassy phase, the photocurrents depended on how the glassy phase were prepared: the glassy phase exhibited dipersive hole transport when prepared by rapid cooling from SmA phase and allowed us to determine the mobility as shown in Fig. 7; the hole mobility was 1×10^{-3}cm^2/Vs, which is one order of magnitude higher than that in SmA phase at elevated temperatures over 115°C.

On the other hand, the photocurrents show no clear transit when prepared by slow cooling. In addition, we often observed the space charge effect caused by charge trapping in the deep states, suggesting formation of localized states in glassy phase. These are probably due to the defective domain boundaries, while no such the effect was observed in the small molecular weight Sm liquid crystals.[9]

We looked at the charge carrier transport in the glassy phase of the mixed PNP-acrylate and found that the charge carrier transport hardly depend on temperature and electric field as shown in Fig. 8, while the temperature range measured was very limited. This behavior is very similar to those in small molecular Sm liquid crystals as reported.

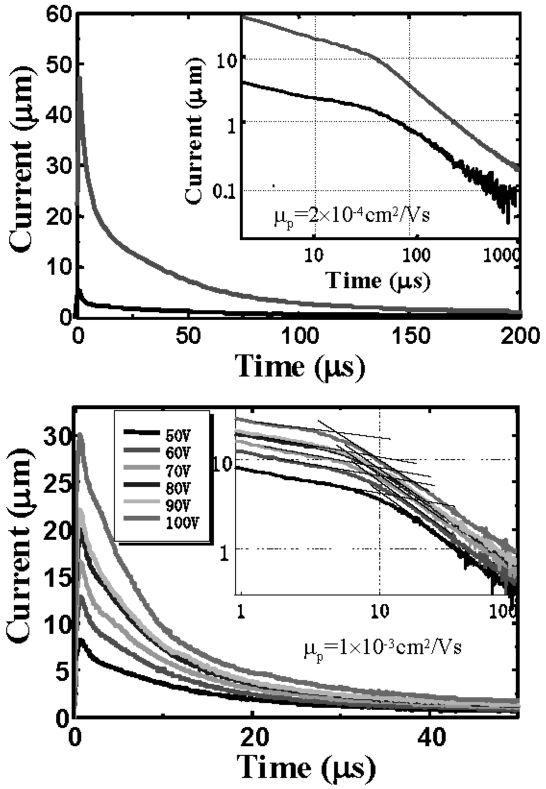

Figure 7. Transient photocurrent in SmA (top) at 140°C and Sm glassy phase at 35°C (bottm) of mA (top) and Sm glassy phase (bottm) of PNP-acrylate. The cell thickness is 9μm.

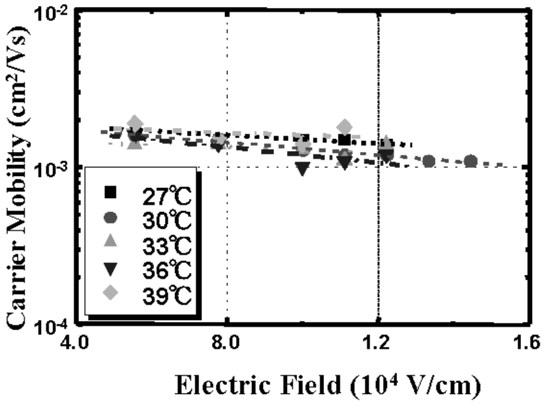

Figure 8. Hole mobility in Sm glassy phase of PNP-acrylate mixed with 8-PNP-O12as a function of temperature and electric field.

Conclusion

We synthesized a side-chain polymeric Sm liquid crystal with phenylnaphthalene moiety as a mesogenic group, PNP-acrylate, and investigated its charge carrier transport properties in Sm and Sm glassy phases. According to the present experimental results, the charge carrier transport in the side-chain polymeric Sm liquid crystals exhibits the fast charge carrier transport comparable to those in the Sm mesophase of small weight liquid crystals basically. The fact that a small amount of 8-PNP-O12 improves the charge carrier transport in Sm glassy field suggests that the mesogenic group in PNP-acrylate does not align as well as 8-PNP-O12 and that some molecular design is necessary for a quality *polymeric self-organizing molecular semiconductor.*

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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 Doctor degree in Imaging Science and Engineering from the same Institute in 1982. He joined the present laboratory as a research associate in Tokyo Institute of Technology in 1977 and promoted to professor of Faculty of Engineering in 1993. He has studied new imaging materials and their application to the imaging systems. His recent interests are in large-area electronic materials including low-temperature CVD poly-Si thin films and liquid crystalline semiconductors for imaging devices. hanna@isl.titech.ac.jp