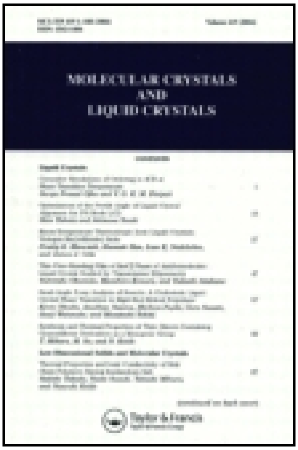

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Fast Electron Transport in Discotic Columnar Phase of Triphenylene Derivative, Hexabutyloxytriphenylene

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We have re-investigated the charge carrier transport in a discotic columnar phase of triphenylene derivative, hexabutyloxytriphenylene (H4T) by time-of-flight experiments. We observed two transits for negative charge carriers in a different time range that corresponded to a fast mobility of $10^{-2}\,cm^2/Vs$ and a slow mobility of $10^{-5}\,cm^2/Vs$ in the discotic hexagonal plastic phase of H4T, while a high mobility on the order of $10^{-2}\,cm^2/Vs$ as reported previously. These were attributed to the electronic conduction caused by fast electron transport along with the discotic columns and slow ionic conduction caused by drift of ionized impurity molecules that accepted photo-generated electrons, respectively.

Keywords: carrier transport; charge carrier mobility; discotic liquid crystal; electronic transport; ionic transport; triphenylene derivative

INTRODUCTION

Since the electronic conduction in the liquid crystal was established in discotic columnar phase of a triphenylene derivative, hexapentyloxytriphenylene (H5T) [1] and the smectic phase of 2-phenylbenzothiazole derivative, (4′-heptyloxyphenyl)-2-(6-dodexylthiobenzothiazole) (7O-PBT-S12) [4], it has been revealed that various types of liquid crystals

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exhibit the fast electronic conduction characterized by a high mobility over $10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$ up to $0.1\,\mathrm{cm}^2/\mathrm{Vs}$ [1–3].

In the original paper, it was reported that in the discotic hexagonal columnar phase of hexaphentyloxytriphenylene(H5T), the hole mobility is on the order of $10^{-3}\,\mathrm{cm}^2/\mathrm{Vs}$ [1], which does not depend on temperature and electric field, but the mobility for negative charge carriers was two orders of magnitudes smaller than that for hole, which depended on temperature.

On the other hand, in smectic phases of calamitic liquid crystals, fast ambipolar carrier transport has been observed in various type of liquid crystalline compounds: the negative charge carrier mobility is as high as hole mobility [5]. As the basic properties of charge carrier transport in liquid crystals has been clarified, it becomes recognized that the electronic and ionic charge carrier transports take place simultaneously in the smectic mesophases, and that electronic conduction disappears easily when the liquid crystal is contaminated with a trace amount of chemical impurities responsible for the deep trap states, resulting in the ionic conduction [6].

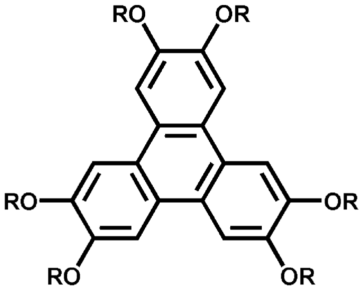
Therefore, the slow negative charge carrier transport in triphenylene derivative originally reported is suspected to be ionic and probably results from the contamination of chemical impurities in its synthesis.

Thus, in this report, we have re-investigated negative charge carrier transport in a discotic liquid crystal of hexabutyloxytriphenylene (H4T) for electronic conduction.

EXPERIMENTAL

The hexabutyloxytriphenylene (H4T), whose chemical structure is shown in Figure 1, was synthesized. As-synthesized H4T by oxidative coupling of o-dibutyloxybenzene with $MoCl_5$ [7] usually includes imperfectly butylated compounds as an impurity and turns pink in color when stored ambient atmosphere. Therefore, as-synthesized H4T was re-butylated again in the presence of butylbromide and sodium hydroxyde in ethanol. The re-butylated product was purified with flush chromatography and recrystallized from ethanol and n-hexane several times.

H4T exhibits discotic hexagonal plastic phase ($\mathrm{Col_{hp}}$) between 88°C and 146°C. The purified H4T was capillary-filled into the liquid crystal cells, which was consisting of two semitransparent aluminum or ITO coated glass plates spaced by silica particle. The cell thickness was from 7 μm to 16 μm, which was estimated from the interference



H4T ($R{=}C_4H_9$)

FIGURE 1 Chemical structure of 2,3,6,7,10,11-hexabutyloxytriphenylene (H4T).

patterns in an uv-visible spectrum. In the liquid crystal cell, H4T can be easily oriented homeotropically to yield large domains by cooling from isotropic phase into $\mathrm{Col_{hp}}$ phase very slowly.

The cell was set on the 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 ($\lambda = 337\,\mathrm{nm}$, pulse duration $= 600\,\mathrm{ps}$) 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 one carrier condition was well established due to short penetration depth of 0.7 µm for 337 nm excitation light. The transit time of carriers, τ_T, was determined from a kink point of the transient photocurrent measured.

RESULT AND DISCUSSION

Figure 2 shows the transient photocurrents of H4T at a temperature of 100°C in an 8 µm thickness cell for positive carrier. The well-defined non-dispersive transient photocurrents were observed for positive carriers, even though an initial slow rise of photocurrent was obvious. The mobility is estimated $1.6 \times 10^{-2}(\mathrm{cm^2/Vs})$, which can be attributed to hole transport and shows a good agreement with the previous result. The inset in Figure 2 shows the transient photocurrent in a double logarithm plot. The photocurrents after transit times decay steeply and monotonously in a few orders of magnitude, indicating the intrinsic nature of charge carrier transport in H4T.

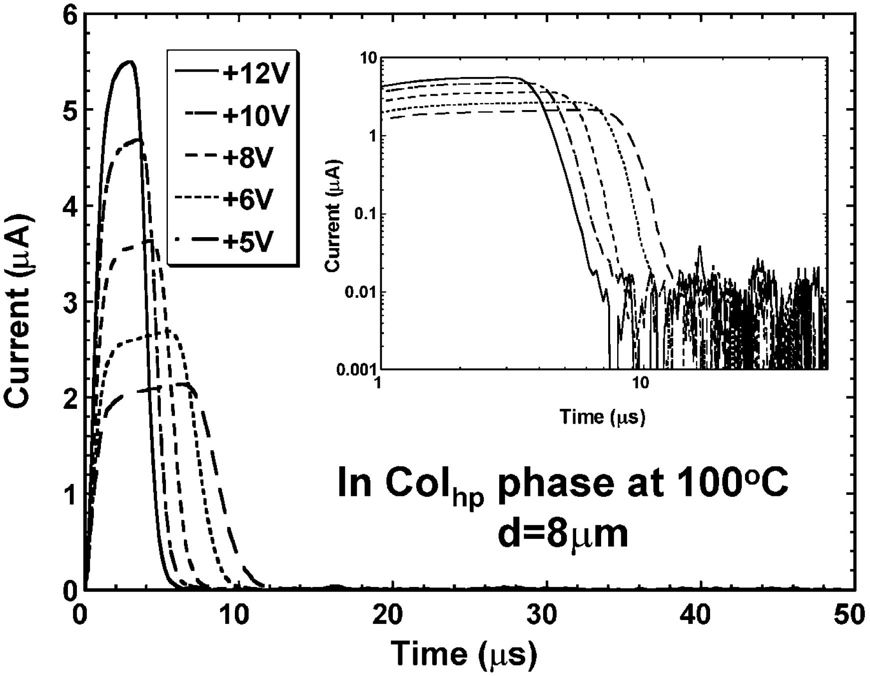


FIGURE 2 Linear plot of typical transient photocurrents for positive charge carrier as a function of time in $\mathrm{Col_{hp}}$ phase of H4T at 100°C. The inset shows the logarithm plots of the same transient photocurrents. The sample thickness was 8 μm. The electrodes were ITO.

On the other hand, for negative charge carriers, the transient photocurrents exhibited two kinks at different time range of μ sec and msec in $\mathrm{Col_{hp}}$ phase at 100°C as shown in Figure 3. We estimated the mobility to be $1.9 \times 10^{-2}(\mathrm{cm^2/Vs})$ and $8 \times 10^{-5}(\mathrm{cm^2/Vs})$ for the fast and slow transits, respectively.

We measured the charge carrier mobility in the $\mathrm{Col_{hp}}$ phase of H4T as a function of temperature as shown in Figure 4. The mobility obtained from the transit for the positive and the fast transit for negative charge carrier did not depend on either the electric field or the temperature. The mobility obtained from the slow transit for negative bias exhibited Arrhenius type temperature-dependence, although it did not depend on the electric field. This behavior is very similar to that in the negative charge carrier transport in the smectic mesophases of 2-phenylnaphthalene derivatives. In the 2-phneylnaphthalene derivative, the fast transit characterized by a high

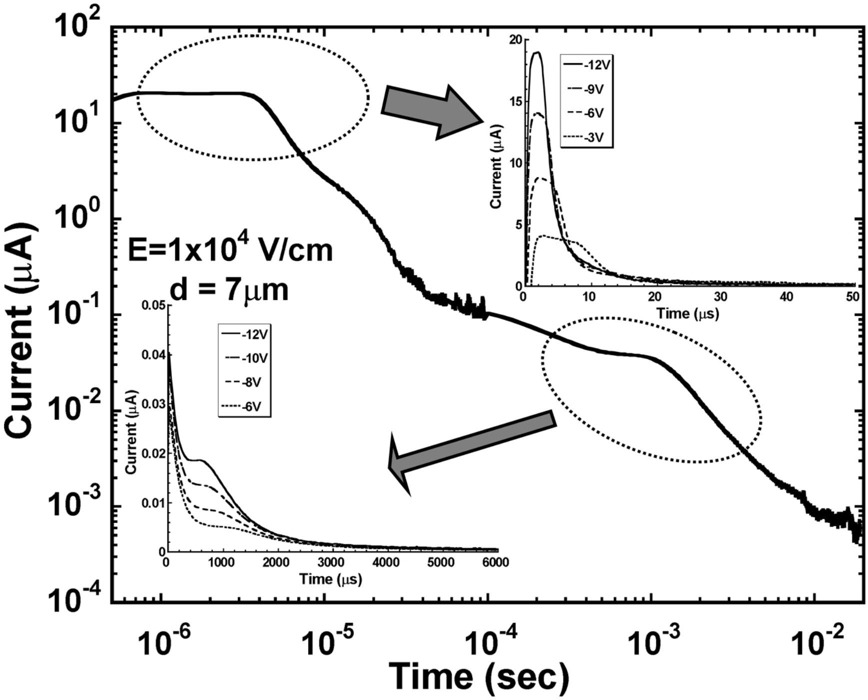


FIGURE 3 Logarithm plots of typical transient photocurrents for negative charge carriers as a function of time in $\mathrm{Col_{hp}}$ phase of H4T at 100°C. The insets show linear plots of the transient photocurrents in each time range indicated with dotted circles. The sample thickness was 7 μm. The electrodes were semi transparence aluminum.

value over $10^{-3}\,\mathrm{cm^2/Vs}$ is proven to be electron transport experimentally, which is intrinsic charge carrier transport in this material. On the other hand, the slow transit is decided to be ionic experimentally, which is extrinsic charge transport due to the drift of ionic species.

Thus, the fast and slow transits in H4T can be attributed to the electronic transport of electron and the ionic transport of anions, respectively. In fact, the activation energy of the slow mobility, 0.36 eV, is a typical value for that of viscosity in hydrocarbons with a small molecular weight.

In order to clarify the origin of the ionic transport in H4T, we investigated the negative charge carrier transport in $\mathrm{Col_{hp}}$ phase at a temperature of 100°C as a function of cell thickness, from 8 μm to 16 μm. The mobilities for the first transit did not depend upon sample thickness at all, and so the second transit as shown in Figure 5, in

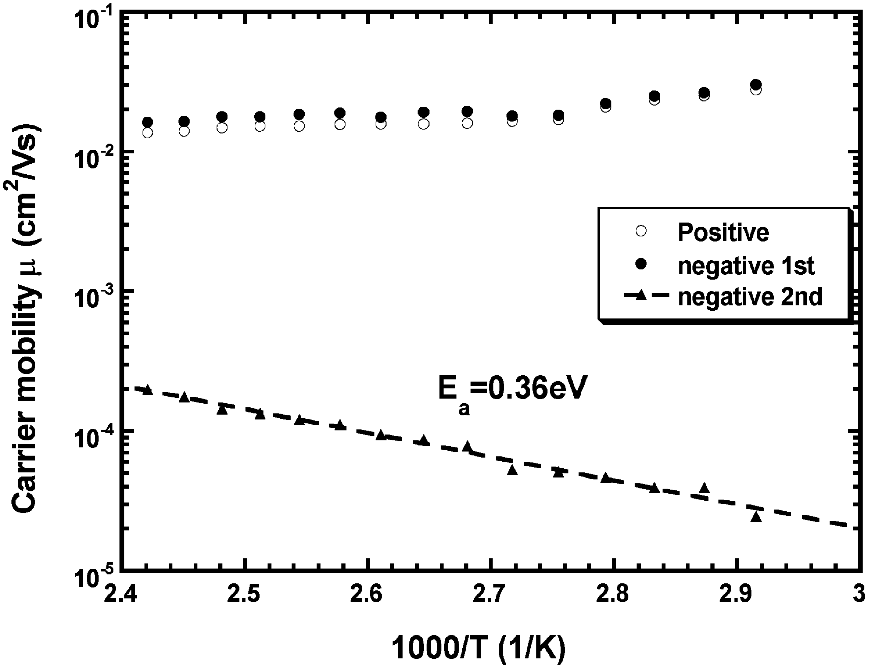


FIGURE 4 Arrhenius plots of the charge carrier mobility for positive charge carrier and for the fast and slow negative charge carriers corresponding the first and second transits in Col_{hp} phase of H4T. The sample thickness was 7 μm. The electrodes were semi transparence aluminum.

which the transient photocurrent is plotted in double logarithm as a function of time normalized by first transit time in each sample with various thickness. These results are a good sign indicating that all these transient photocurrents are determined by the charge carrier transport properties in the bulk of H4T.

Furthermore, we investigated the fractional contribution of the electronic current to the total current flowed, by integrating the transient photocurrent as a function of time and found that it depended on sample thickness. For example, in a thin sample of 8 μm, the current plateau of the fast transport is about 10^3 times larger than that of the slow one. On the other hand, in a thick sample of 16 μm, the current plateau is on the same order of that of the slow one. This result indicates that the contribution of ionic currents is determined by bulk effects and supports an idea that the photo-generated electrons are trapped at the deep states in the column during transit to the counter electrode, which are originated from contaminated chemical

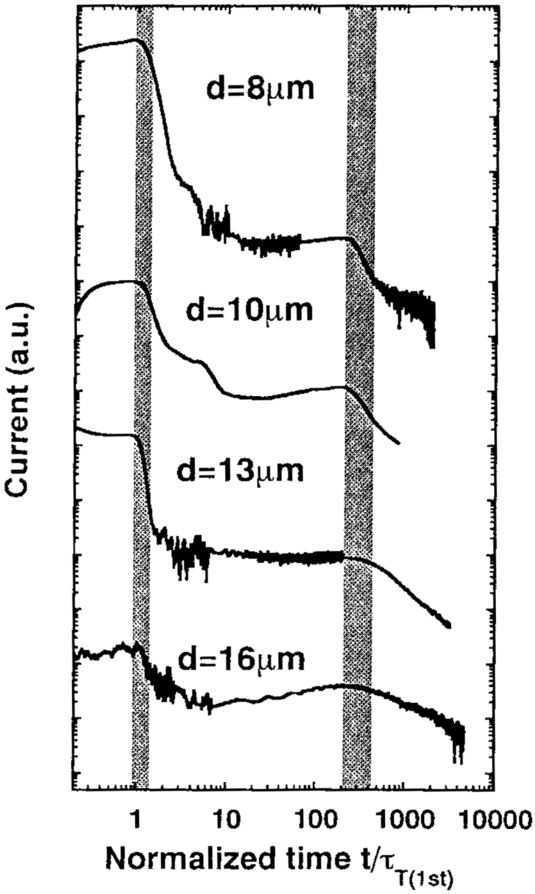


FIGURE 5 Logarithm plots of transient photocurrents for negative charge carriers as a function of time normalized by the first transit time in each transient photocurrent of various sample thickness, i.e., 8 μm, 10 μm, 13 μm and 16 μm. The dark areas are the guides to the eye. The electrodes were ITO.

impurities and cannot stay in the column as the space charge, and the resulting ionized impurity molecules start to move as mobile ions, thanks to the fluidity in the discotic columnar mesophase. Thus, the longer the transport distance of the charge carriers, the more is the contribution of ionic conduction. As for the ionic transport, it is likely that that the ions move in the micro separated hydrocarbon region among the columns with reference to the experimental results on the same behaviors for the negative charge carrier transport in a smectic liquid crystal of a 2-phenynaphethalene derivative [6].

In the previous report, the transient photocurrents were measured with a thicker cell, e.g., 30 μm typically [3]. Therefore, it is plausible that most of photo-generated electrons were trapped during the transit in the bulk, and consequently the first kink corresponding to the electron transport did not appear and resulted in single kink at a slow time range attributed to ionic conduction. In this study, with thinner cells and purified materials, we could observe the fast electron transport, in which most of photo-generated electrons could arrive at the counter electrode before they encountered and were captured by impurity molecules.

CONCLUSION

We re-investigated charge carrier transport in a discotic columnar phase of hexabutyloxytriphenylene, H4T, by time-of-flight experiments. For positive carriers, we confirmed that the fast transport took place in its hexagonal plastic phase, which was attributed to be hole transport, and determined the mobility to be $1 \times 10^{-2}\,\mathrm{cm^2/Vs}$ as previously reported. For negative carriers, we found that two carrier transports took place in a different time range simultaneously: the fast transport characterized by a high mobility comparable to hole mobility was attributed to electron transport along the columns; the slow transport previously reported was attributed to the ionic conduction induced by ionized impurity molecules captured photo-generated electrons.

In conclusion, the charge carrier transport in purified H4T is bipolar, and hole and electron mobilities are comparable, and are $10^{-2}\,\mathrm{cm^2/Vs}$ independent of electric field and temperature.

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