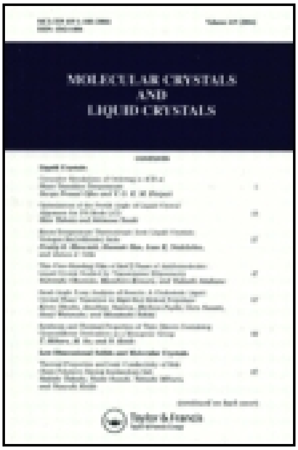

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Effect of Domain Boundary on Carrier Transport of Calamitic Liquid Crystalline Photoconductive Materials

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Smectic mesophases in the calamitic liquid crystalline materials such as 2-phenylnaphthalene derivatives exhibit fast ambipolar carrier transport, whose mobility is up to 10^{-2} cm^2/Vs. For these mesophases, we have investigated the effect of defects in the bulk and at the domain boundary on these carrier transport by measuring transient photocurrents in thick cells up to 120 μm in thickness and in the cells of different domain sizes of 10~100s μm. It was found that non-dispersive carrier transports was observed for all the cells and the carrier transport was affected neither by cell thickness nor by domain sizes. Thus, it was concluded that there are few deep defects in the bulk and that the domain boundary is electrically inactive in these mesophases, demonstrating their high potential for practical application to large-area electronic devices.

Keywords: calamitic mesophase; photoconductivity; carrier transport; poly domain; Smectic B; Smectic E

INTRODUCTION

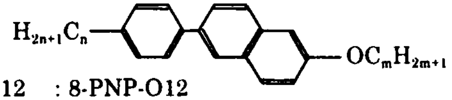
Organic photoconductors have been utilized in photoreceptors for xerographic copiers and laser printers [1], and more recently in active components of electroluminescent devices [2]. These applications require large-area uniformity in thin layer, so that the materials practically used are amorphous and prepared either by polymerization, vacuum evaporation, or molecule doping into polymer films, of photoconductive small molecules. However, the electrical properties of resulting amorphous films are degraded significantly compared with their own molecular crystals: the carrier mobilities are decreased down to $10^{-6} \sim 10^{-5}$ cm^2/Vs and depend on both electric field and temperature. In addition, carrier traps play serious role for determining the response time, which are caused by impurities and carrier-dipole interactions in the disordered photoconductors. These limit their practical applications. The considerable improvement of mobility has been achieved up to $10^{-3}cm^2/Vs$ by utilizing less polar polymer matrices for the moleculary doped polymers in order to reduce the carrier-dipole interaction [3]. However, there still remains a serious problem of the field and temperature dependence.

In order to relax the present limitation of the organic photoconductors in device application, a new material exhibiting a high mobility independent of electric field and temperature and few deep defect density has to be realized. From this viewpoint, we had paid our attention to the liquid crystalline materials exhibiting fluidity and at the same time give a high potential of realizing the enhanced carrier transport due to their self-organized molecular alignment. We found that the calamitic, i.e., rod-like liquid crystals exhibit the fast electronic carrier transport [4,5,6,7] comparable to the discotic ones[8], whose electrical conduction had been thought to be ionic due to ionic impurities and/or their own ionized species since the first report of Heilmeier[9]. 2-phenylnaphthalene derivatives are typical examples, whose smectic mesophases exhibit unique features in carrier transport, i.e., a fast hole or electron mobility up to 10^{-2} cm^2/Vs and its independence of temperature and electric field. Interestingly, the carrier transport vanishes when the mesophases transforms into crystalline phase irrespective of any smectic phases. This is probably attributed to the carrier trapping in the deep defects created at the grain boundary, where impurities piles up and defective molecular alignment. Thus, we have been interested in how the defects in the bulk and at the domain boundary affect the carrier transport in mesophases.

In this report, we have investigated the effect by measuring transient photocurrents in the cells with different thickness and domain sizes.

EXPERIMENTAL

We used two materials, 2-(4'-octylphenyl)-6-dodecyloxy-naphthalene (8-PNP-O12; K 79°C SmB 101°C SmA 128°C Iso) and 2-(4'-octylphenyl)-6-butyloxynaphthalene (8-PNP-O4; K 50°C SmE 123 °C SmA 128°C Iso), resulting in comparison between SmB and SmE phases. These materials were synthesized as described elsewhere [5], and purified with recrystalization from n-hexane. The purified samples were capillary filled into the cells which consisted of two ITO electrodes spaced by silica particles for thin cells (up to 25 μm) or polyimide film spacer for thick cells (up to 120 μm). We did not use any alignment technique for preparing liquid crystal cells so as to enhance the defect formation in the bulk and at the boundary, in order to exclude experimental ambiguity. By changing the cooling rate from isotropic phase to mesophases, we controlled the domain size of smectic texture in a range of 10 ~100s μm.



n=8, m=12 : 8-PNP-O12
n=8, m=4 : 8-PNP-O4

Figure 1. Chemical structure of phenylnaphthalene derivatives

For characterization of carrier transport properties, the time-of-flight (TOF) measurement [11] was used. In the TOF measurement, the liquid crystal cell was fixed on a hot stage within accuracy of 0.1 degree. Photoexcitation in main absorption band of these compounds was carried out with beam expanded N_2 pulse laser (λ = 337nm, pulse width = 600ps, illuminated area = 10mm square). Transient photocurrent under applying a constant DC voltage to the sample was recorded by a digital storage oscilloscope. Applied electric fields to the cells were fixed at 10^5 V/cm in order to simplify the discussion. Such the strength of field did not make any change of the molecular alignment while applying across the liquid crystal layer. The transit time of carriers, t_T was determined by a inflection point in a double logarithmic plot of the obtained transient photocurrent curves as a function of time. In this measurement, one carrier condition was well established because of a sufficiently short penetration depth of the illuminated light in the sample cell compared with the cell thickness.

RESULTS AND DISCUSSIONS

Controlled domain size

Obtained textures at the different cooling rates for 100 µm thick cell are shown in Fig.2 and Fig. 3. The thicker the cell thickness over 50 µm was the easier the domain size of the resulting mesophases was controlled.

It is plausible that the multi-domains are formed in the bulk liquid crystalline layer when the liquid crystal cells over several tens µm are cooled from isotropic phase for SmA at a rate high enough to result in polydomains with small domain sizes compared with the cell thickness. Therefore, measuring transient photo-currents in such a cell gives good information about how the domain boundary affects the carrier transport, because the photo-generated carriers have to step over the domain boundaries without fail before reaching the counter electrode.

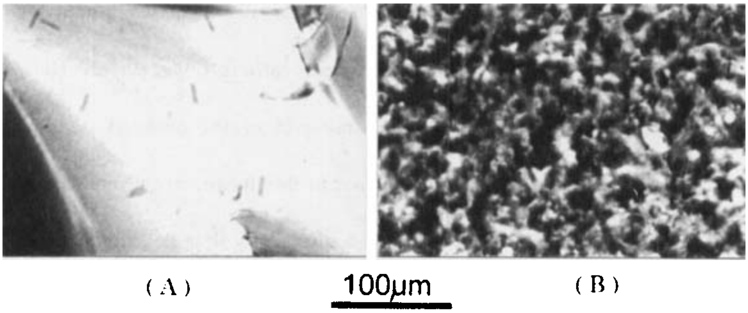


Figure 2. Optical polarized micrographs of 8-PNP-O12 (crossed nicol, 90°C, SmB phase, the thickness of sample is 100 μm) : cooling down from Isotropic for SmA phase at a rate of (A) 1°C/min. domain size is much larger than the cell gap, (B) at the rate over 10°C/min. the domain size was smaller than cell gap.

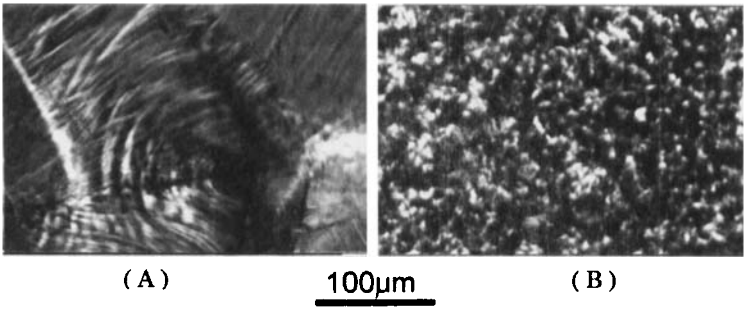


Figure 3. Optical polarized micrographs of 8-PNP-O4 (crossed nicol, 90°C, SmE phase, the thickness of sample is 100 μm) : cooling down from Isotropic for SmA phase at a rate of (A) 1°C/min. the domain size is much larger than the cell gap, (B) at a rate over 10°C/min. the domain size is smaller than the cell gap.

Effect of domain boundaries in carrier transport

Fig.4 and Fig.5 show transient photo-currents from the liquid crystal cells (50 μm and 100 μm) with large and small domain sizes in SmB and SmE phases, respectively. Even if the thickness of the liquid crystal layer exceeded 100 μm, these materials exhibited non-dispersive transport as is clearly seen in the figures irrespective of domain sizes, giving fast mobilities of $10^{-3}cm^2/Vs$ in SmB and of $10^{-2}cm^2/Vs$ in SmE, respectively. The carrier mobility was independent of not only the thickness of liquid crystal layer but also the domain size. Moreover, the photo-current decay after the transit times were almost same in the cells with different domain sizes at a given cell thickness. These mobility and their temperature independence coincide with our recent works [4,5,6,7]. Therefore we can say that the type of carrier transporting in the liquid crystal is hole for positive bias and is electron for negative bias.

These results indicated that the density of deep traps is very small, judging from no significant change in the shape of transient photo-currents and the calculated mobilities, which is affected substantially by space charges in the bulk attributed to carier trapping at the deep defect states. In addition, no difference in the carrier mobility indicates no additional increase of the shallow traps when the domain size was reduced, in other words, the domain boundary was increased. Thus, we come to a conclusion that the domain boundary of liquid crystals is electrically inactive and does not degrade the carrier transport.

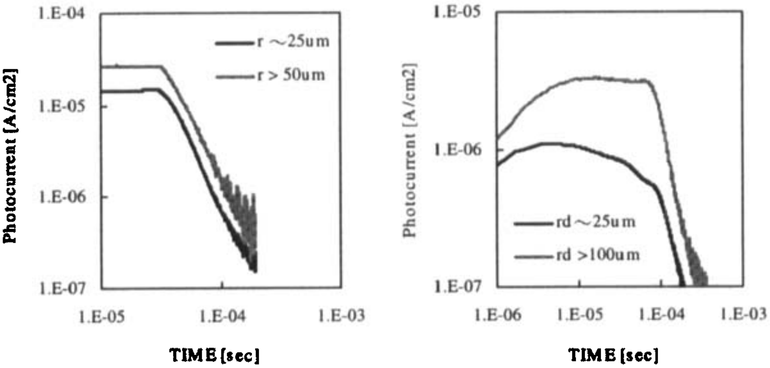


Figure. 4 Transient photocurrents in different domain size of 8-PNP-O12 (SmB, 90°C, positive carrier) (a) cell gap =50um (b) cell gap ≈100um. transit time and inclination of attenuation does not change.

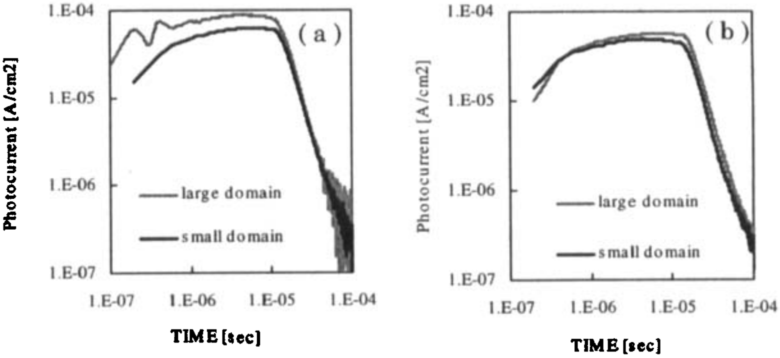


Figure. 5 Transient photocurrents in different domain size of 8-PNP-O4 (SmE, 90°C, positive carrier) (a) cell gap =50um (b) cell gap =100um. transit time and inclination of attenuation does not change.

This was experimentally re-confirmed by another TOF measurements in the thick liquid crystal cells with graded domain sizes across the liquid crystal layer. Fig.6. shows the transient photo-currents in the cells cooled heterogeneously by contacting a surface of the cell with a metal block. In fact, we could see small domains of ~10 μm in the rapid cooling side and large ones of >100 μm in the slow cooling side, but there were no difference in the shape of transient photo-currents when illuminated either on the small domain side or on the large domain side, except for the photo-current intensity determined by the mean photo-absorption for incident light.

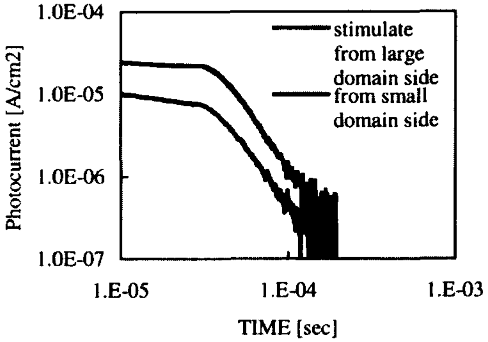


Figure.6 Transient photocurrents in a cell which have distribution of domain size formed in direction of the thickness of the sample. (8-PNP-O12, SmB, 90°C, positive carrier)

CONCLUSION

For polycrystalline materials, because of deep traps generated by abrupt change in molecular alignment and probable accumulation of impurities at the grain boundaries, the photocurrent is subject to the lifetime limited regime, resulting in no carrier transit in the transient photocurrent measured by the TOF technique. In cotrast, for liquid crystalline materials, because of neither deep nor shallow traps at the domain boundaries, the carrier transport is not degraded even in polydomain. It is likely that these superior carrier transport properties are attributed to no discontinuity of molecular alignment in a short range order originated from the fluid nature of liquid crystals. .

Judging from the present and established facts, i.e., the excellent single-domain-like carrier transport in polydomain and fast mobility up to 10^{-2} cm^2/Vs independent of electric field and temperature, it is concluded that the liquid crystalline photoconductors have a high potential to relax the present limitation of the conventional organic photoconductors in device application.

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