

Fast charged carrier mobility of a triphenylene-based polymer film possessing nematic order

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A polymer film was prepared by the photopolymerization in a discotic nematic (N_D) mesophase of a mixture of the polymerizable triphenylene mesogen isomers. It was found that the film shows a relatively fast mobility of charged carrier ($10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), which is probably faster than that of the monomeric N_D mesophase. The microscopic domains in the film were found to keep the liquid crystalline order even after the polymerization evidenced by the IR spectra showing the small decrease in the local order parameter and by the X-ray diffraction (XRD) patterns comparable to those before the polymerization. It was indicated that in the photopolymerization, the long range order of molecules can be almost remained, the short range one is variant and, thus, such an in-situ liquid crystalline polymerization could lead to the enhancement of charge transport efficiency. Furthermore, the polymerized film was applied to a simple electroluminescent device to reveal that it certainly works as a hole transport layer because the luminescence is clearly induced under bias.

Keywords: liquid crystalline semiconductor, discotic nematic phase, photopolymerization, charged carrier mobility, triphenylene, electroluminescent device.

1. Introduction

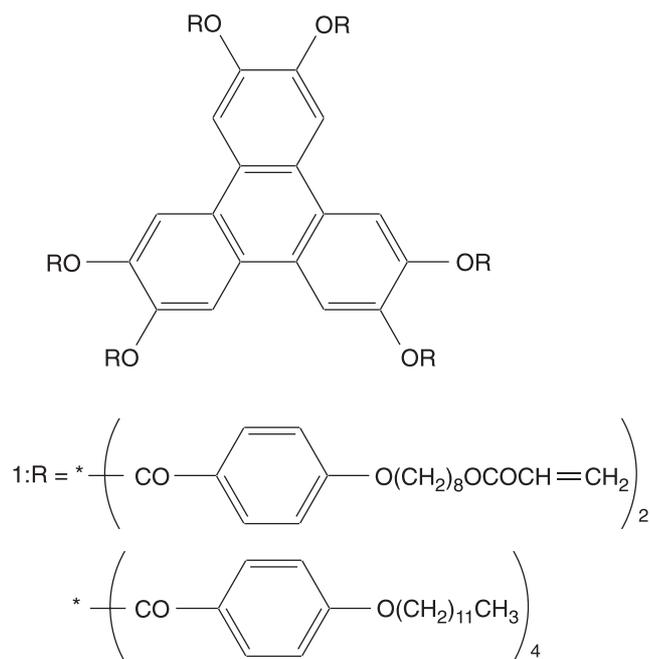
Studies on organic electronic devices have been extensively carried out in recent years and in particular, some of the promising devices such as electroluminescence (EL), field effect transistor (FET), thin film transistor (TFT), etc., have drawn some attention to provide lots of evidences that one could realize flexible electronic devices using polymer substrates [1–5]. Furthermore, a variety of methodologies for organic semiconductors to deposit on substrates and to fabricate functionalized domains have been reported so far and very attractive techniques such as inkjet printing [6] have been developed in which the device fabrication process could be attained by the wet process using soluble organic semiconductors into conventional organic solvents [7]. Therefore, except for amorphous materials the alignment control of molecules is strongly required for such highly anisotropic systems in order to realize the highest performance of devices owned by the ordered molecular materials because of the highly anisotropic nature of the electronic properties.

From these points of view, liquid crystalline semiconductors are one of the most interesting categories of or-

ganic semiconductors which are applicable to those electronic devices, considering their high solubility into organic solvent and relatively good controllability of the alignment on/between substrates, as the mobility of the charged carriers in mesophase is nowadays reached in the order of $10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [8–10] and this is slower than those of the crystalline semiconductors of organics, but almost comparable to those of amorphous silicon. Some of these liquid crystalline semiconductors have been provided for the application to an organic electronic devices and a successful result was attained to give a certain performance to the devices by use of a room-temperature mesophase semiconductor [11].

However, a temperature-independent nature of the charge transport property of liquid crystalline materials is involved in the tough issues to be resolved in the applications to such devices as the practical point of view, meaning no phase transitions changing the molecular order of orientation takes place in the wider range of temperature around room temperature. The temperature range of mesophase is essentially important and the wider range sometimes very difficult to get for the practical usage, while not so much temperature-independent property of the mobility in mesophase was reported [12]. In order to avoid the substantial

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Scheme 1. Chemical structure of mesogen.

disturbance for the device performance caused by the phase transitions of the material, one can easily imagine that the polymer film containing an appropriate order of molecules which is suitable for the charge hopping should be expected as one of the interesting candidates as a novel material showing semiconducting properties for practical use.

Here in this article, the interesting results of charged carrier mobility observed for the polymer film prepared by photopolymerization in N_D mesophase are reported as to a photopolymerizable triphenylene mesogen **1**.

2. Experimental

2.1. Compound

The synthesis of **1** was carried out according to the literature with a slight modification [13]. The details of synthetic procedure were described elsewhere [14]. The purification was carried out by column chromatography using silica-gel with a benzene-hexane mixture as eluent. The residual product obtained by the solvent evaporation was recrystallized from ethanol to give white powder. The sample crystal showed a low electric conductivity in the order of $10^{-12} \sim 10^{-11}$ S/cm at room temperature, which is almost in the insulating range.

2.2. Mesomorphism characterization

The liquid crystalline properties of **1** were studied using DSC (TA Instruments, DSC2500), XRD (Rigaku Geigerflex, Cu-K α) as well as optical texture observation by polarizing microscope (Olympus BH-2) equipped with a temperature-controllable hot-stage (Mettler FP82HT and FP90).

2.3. Photopolymerization

Photopolymerization was executed using a Xe lamp system for irradiation (Ushio, panaflex with an optical cut filter for 365 nm) with 0.2 mWcm^{-2} of the light power. Irgacure 651 (Chiba Specialty Chemicals Ltd.) was used as the initiator, which was mixed in CH_2Cl_2 solution of the monomer compound quantitatively. The polymerization was initiated by the irradiation of photon flux which leads to a sandwich-type cell consisting of two ITO-coated BaF_2 plates with glass beads of $2\text{-}\mu\text{m}$ diameter as spacer. The cell was set into the hot-stage (Mettler FP52) to be heated up to the temperature of the liquid crystalline state. The light beam was guided by the optical fiber to the cell as shown in Fig. 1.

2.4. Mobility measurements

The mobility μ measurements were carried out by time-of-flight (TOF) technique using the equation below

$$\mu = d/t_\tau E$$

where t_τ is the transient current determined by the inflection point in the double logarithmic plots of the photocurrent against time, d is the sample thickness, and E is the applied electric field.

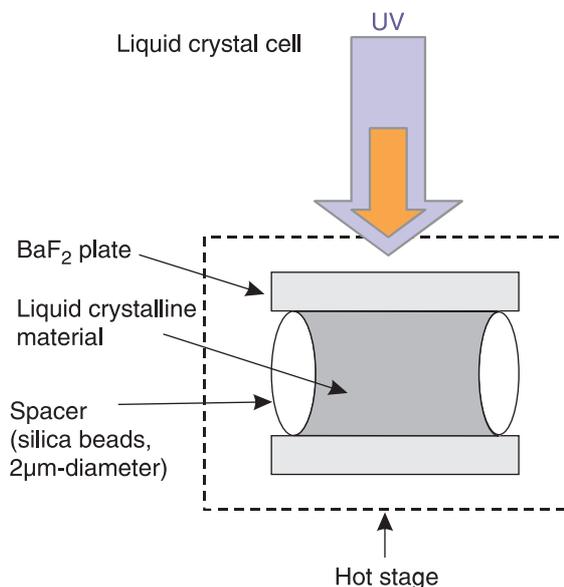


Fig. 1. A schematic representation of the set-up for photopolymerization of monomer triphenylene liquid crystal.

3. Results and discussion

3.1. Phase transition behaviour

The compound **1** is actually a mixture of the four isomers and shows a rectangular columnar Col_r and a discotic nematic N_D mesophases between 67°C and 130°C , and 130°C and 177°C , respectively. No detection of the thermal poly-

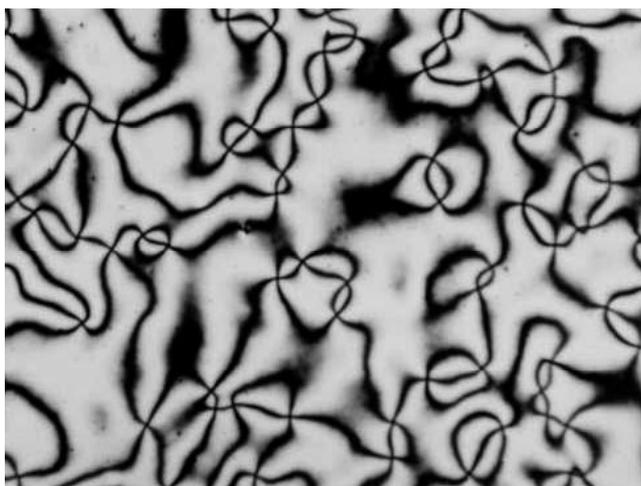


Fig. 2. An optical texture of N_D mesophase of **1** at 120°C.

merization was observed up to 160°C. A typical Schlieren texture was observed with POM as shown in Fig. 2. It is quite reasonable to think this mesomorphism is similar to those of a series of long-chain hexabenzoyl-oxytriphenylenes because of the structural similarity of mesogen [13].

3.2. Photopolymerization

This mixture was easily photopolymerized in two mesophases. The correlation of polymerization progress and the local order parameters which were evaluated by infrared dichroic method proposed by Vij *et al.*, [15,16] was already reported elsewhere [17,18]. The order parameters are decreased to some extent as the polymerization proceeds, but not so large decrease was observed to be about 30% against the initial value as shown in Fig. 3. In a macroscopic point of view for the optical texture, there never been observed a change during the photopolymerization in these conditions. This strongly indicates that the photopolymerization does not give any significant change to their domain states, but a small change of the local order parameters, in particular the

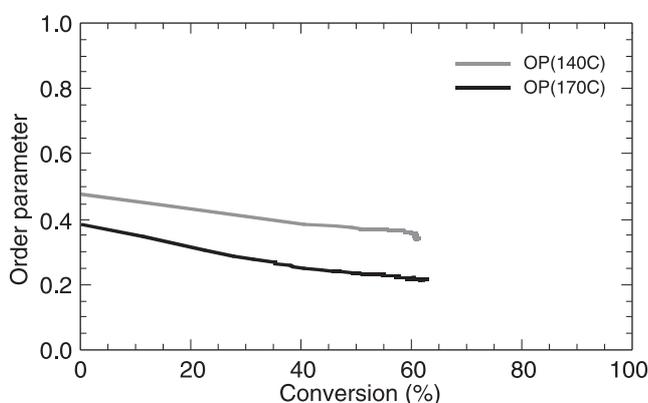


Fig. 3. Order parameter change under the photopolymerization at 140°C and 170°C. The order parameter values were obtained with monitoring the aromatic C–C stretching band of triphenylene core according to Vij's method.

central core moiety of triphenylene, are caused during the polymerization as the averaged view of the static order of molecular orientation. The charge transport mechanism for liquid crystalline semiconductors is thought to be “hopping” of charged carriers among the molecules. Thus, the probability of charge hopping would be sometimes so sensitive even for a small degree of the order parameter change. The films obtained by photopolymerization do not show any phase transitions both on heating and cooling between room temperature and 200°C, where the monomeric mixture **1** shows the melting and isotropization.

3.3. Charged carrier mobility

Figure 4 shows a typical transient decay curve detected in TOF measurements for the polymerized film sandwiched by two ITO-coated BaF₂ plates. The alignment of molecules in this cell was almost homeotropic, which was attained with a strong tendency of spontaneous formation of homeotropic alignment for the N_D phase between the ITO-coated BaF₂ substrates. The homeotropic texture (dark view observed through a polarized microscope under crossed polarization condition) was found to be maintained during the photopolymerization and this is a similar behaviour to that previously reported [17].

The decay curves show only one inflection point for the double logarithmic plot in the time scale of our measurements. Considering that SmA (Smectic A)-like “lamello-columnar” mesophase shows two inflection points on the transient decay curves and the faster one which has the carrier mobility in the order of $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, whilst the slower one is in the order of $10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, being specu-

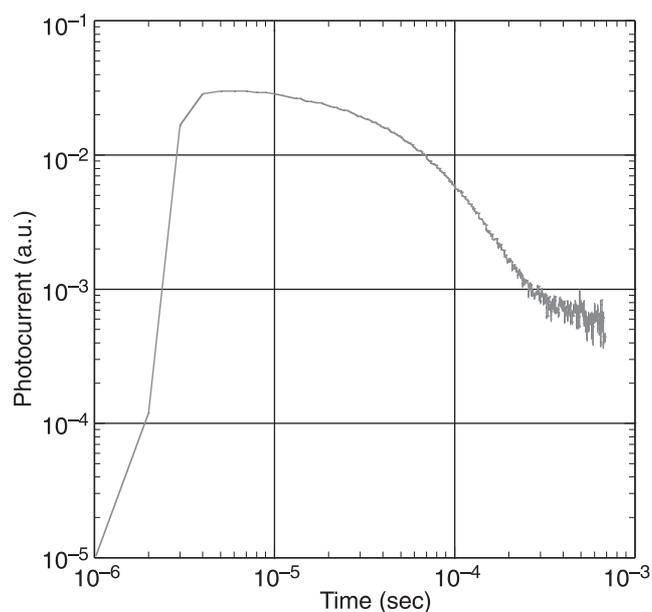


Fig. 4. A typical transient decay curve for the polymerized film sandwiched by two ITO-coated BaF₂ plates, detected in the TOF measurements at room temperature. Applied bias: 30000 Vm⁻¹, cell thickness: 30 μm, photopolymerized at 140°C.

lated that the former is originated from an electronic process and the latter from an ionic process for the charge transport, respectively [19]. Therefore, the resulting decay curve indicates this polymer has a solid-like matrix for the ionic impurities containing in the system, considering the mobility estimated from the transit time and the temperature dependence of the dark and photocurrent for this film [20]. In fact, no detection was attained in the slower regime of transit time for this polymer.

The resulting TOF decay curves gave the relatively higher mobility, $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and this order of the charged carrier mobility is quite comparable to that of hexagonal columnar (Col_h) mesophase shown by hexapentyloxytriphenylene [21]. This value is clearly too large for the charged carrier mobility for ionic process of the transport considering the mobility reported in nematic and SmA phases of conventional calamitic liquid crystals (10^{-6} and $10^{-4} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively) [22,23]. In this work, it was not successful to observe the clear transient decay curve in the TOF measurements for the monomeric N_D mesophase due to the high degree of the dark current.

Figure 5 shows the temperature dependence of the hole mobility for the photopolymerized film and surprisingly observed was the almost temperature independent nature in the wider range of temperature involving the melting and clearing points, which surely suitable for the application of this film to organic electronic devices such as electroluminescent (EL) one. In fact, it was successfully demonstrated that a simply structured EL device using this film as a hole transport layer shows a certain level of luminescent under the bias as shown in Fig. 6.

Figure 7 shows the XRD results of the N_D mesophase (a) and the photopolymerized film (b). It is so clear that the time-averaged order of molecules was not changed so much by the photopolymerization. In the latter case, one can recognize the two broad reflection peaks in the wider

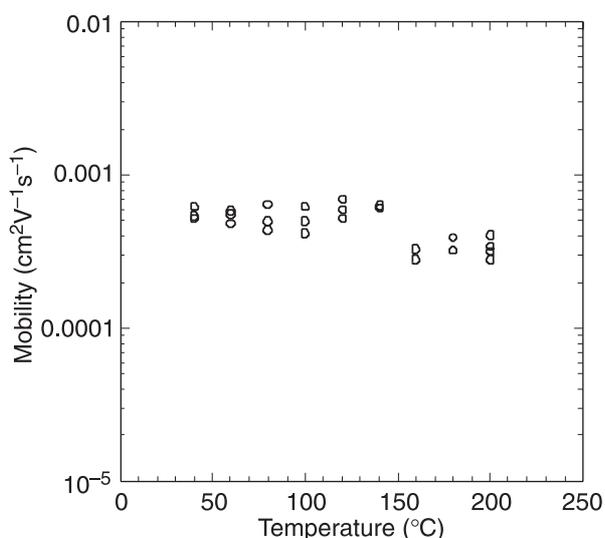


Fig. 5. Temperature dependence of the hole mobility for the photopolymerised film. Applied bias: 30000 Vm^{-1} , cell thickness: $30 \mu\text{m}$, photopolymerized at 140°C .

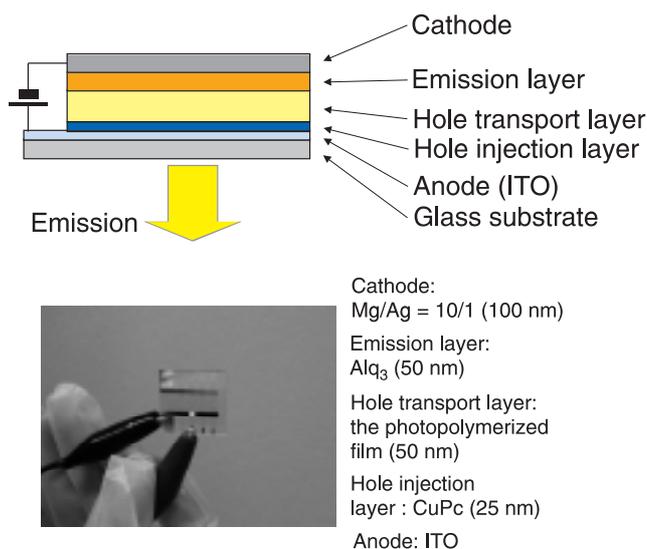


Fig. 6. A simply structured EL device using this film as a hole transport layer showing clear luminescent under the bias.

angle region and the one at the wider angle is not seen for the monomeric N_D mesophase which corresponds to 3.7 \AA . This reflection can be seen even for the film photopolymerized in the isotropic liquid (Iso) phase. This value is close to that of the intracolumnar order of Col_h mesophase. Also the broad halo of 4.8 \AA is observed, but the width of this reflection was clearly decreased after the photopolymerization. These strongly indicate that the photopolymerization gives rise to the solidification of N_D mesophase to generate a level of columnar structure within the nematic order of molecules. However, it might be possible to form a more long-range order of molecularly stacked columnar structure in a polymerization condition and it could contribute to the increase in mobility.

These results strongly indicate that the photopolymerization in mesophase is surely expected to give a polymer film possessing a temperature independent mobility of charged carriers in the wider temperature range than that of the monomeric mesogen showing the melting and clearing points. Generally, it is not unreasonable to think the phase transitions involving the change of mesophase structure and dynamics of molecules causes a drastic change of the physical properties. In particular, charge migration by electronic hopping process is subjected to the change of relative order and dynamics of molecules in mesophase, considering the molecular order as the time-averaged view surely affect the mobility [24] and the time scale of molecular fluctuations in a Col_h mesophase is reported to be in the order of pico second [25]. Therefore, photopolymerization might provide a promising technique to obtain a practical charge transport materials using liquid crystalline semiconductors and some reports are already seen for EL devices [26]. However, it will be probably necessary to get some technique for fine control of the molecular order in the progress of the polymerization.

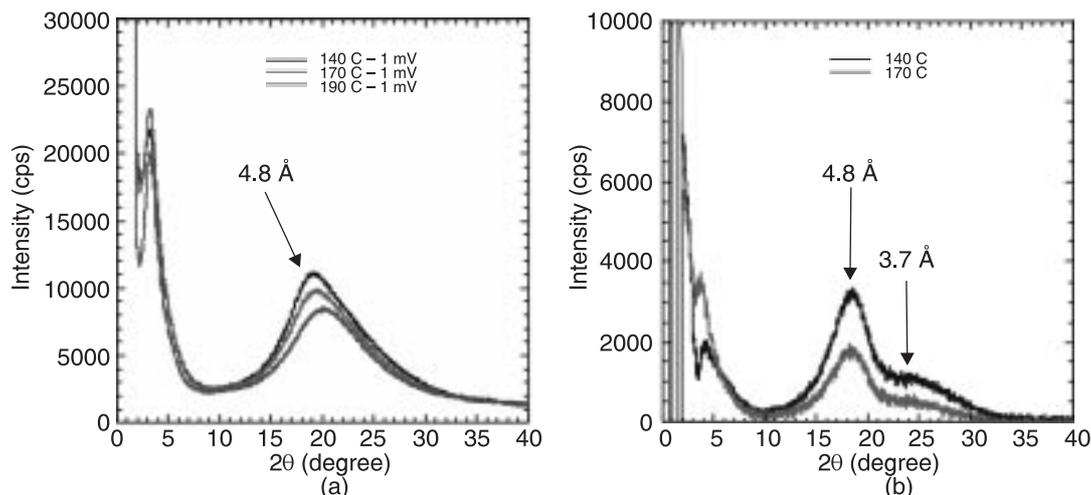


Fig. 7. XRD patterns of (a) the N_D (140°C and 170°C) and Iso phases (190°C) and (b) the photopolymerized film (25°C, photopolymerization temperatures are 140°C and 170°C).

4. Conclusions

In this work, a mesomorphic mixture of triphenylene mesogens with polymerizable acryl groups at the end of the peripheral chains which shows a N_D mesophase, was examined for the photopolymerization in the mesophase to give a polymer film with nematic order of molecules. A sandwich-type cell containing this film was found to show relatively fast mobility of hole carriers ($10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). It was demonstrated that the polymerization in the mesophase could be a promising technique to give a semiconducting film of polymers with a liquid crystalline order.

Acknowledgments

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