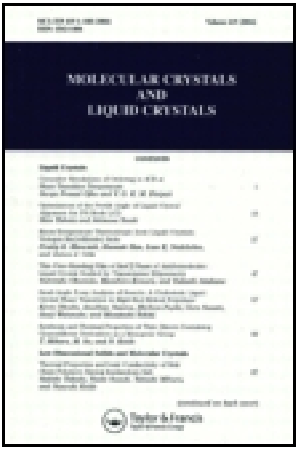

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Masaaki Inoue [a] , Masakatsu Ukon [a] , Hirosato Monobe [b] , Takushi Sugino [b] & Yo Shimizu [b]

[a] Japan Chemical Innovation Institute, Osaka Laboratory, Osaka National Research Institute, AIST-MITI 1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan

[b] Advanced Liquid Crystal Group, Department of Organic Materials, Osaka National Research Institute, AIST-MITI 1-8-31 Midorigaoka, Ikeda, Osaka, 563-8577, Japan

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Effect of Photopolymerization on Photoconductive Behavior in Triphenylene Discotic Liquid Crystals

MASAAKI INOUE[a], MASAKATSU UKON[a], HIROSATO MONOBE[b], TAKUSHI SUGINO[b] and YO SHIMIZU[b]

[a]*Japan Chemical Innovation Institute, Osaka Laboratory and* [b]*Advanced Liquid Crystal Group, Department of Organic Materials, Osaka National Research Institute, AIST-MITI 1–8–31 Midorigaoka, Ikeda, Osaka 563–8577, Japan*

Photoconductivity of the polymerized triphenylene film and monomer liquid crystal were evaluated for the nematic order. For the polymerized triphenylene film with a cross-linked network, which was derived from the monomers with six acrylate groups, the observed photocurrent was undetectable ($<10^{-10}$A, 50kV·cm^{-1}) though the monomer film before polymerization showed it in the detectable level. On the other hand, the photocurrent of the polymer film from the monomer with two acrylate groups was sufficiently detectable ($>10^{-9}$A, 30kV·cm^{-1}). Furthermore, the temperature range where the photocurrent is obtained was extended up to 200°C for the polymer film.

Keywords: discotic liquid crystal; photopolymerization; photoconductivity; triphenylene

INTRODUCTION

The liquid crystalline state is characterized by the good controllability of molecular alignment for the film preparation. It has been expected to provide a new technology for the novel highly-functionalized polymer possessing the well-defined molecular alignment. In fact, the negative optical anisotropy, which is one of unique properties of discotic nematic liquid crystal, was applied to enlarge the view angle of LCD on an industrial level [1].

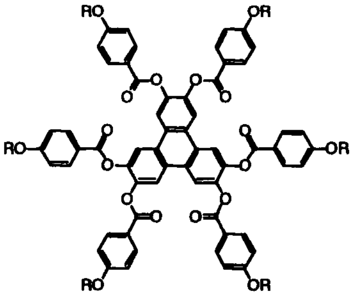
On the other hand, a fast hole-mobility was recently found in a plastic columnar mesophase [2], which has been paid some attention to as a potential candidate for novel photonic/opto-electronic devices [3].

On the advantage of ultra fast reaction for the preparation of polymer network, the photoinduced polymerization has been investigated in these years as a method to stabilize the molecular alignment of liquid crystals in the film. However, the effect of photopolymerization for photoconductivity has not been studied yet. In this work, the preliminary results of the molecular order of polymer films and the photocurrent are reported.

EXPERIMENTAL

Synthesis

A polymerizable discotic liquid crystal, 2,3,6,7,10,11-hexakis(4-(8-(acryloyloxy)octyloxy)benzoyloxy)triphenylene (abbreviated as 6ABTP), was synthesized. In order to prevent thermal polymerization, the long alkyl spacer was designed to reduce the clearing temperature. 6ABTP was synthesized from 2,3,6,7,10,11-hexamethoxytriphenylene as a starting material according to the literature [4]. Another polymerizable discotic liquid crystal 2A/4CBTP, which has two acrylic residues and four alkyl chains, was also synthesized. This is a mixture



6ABTP : $R = -(CH_2)_8OCOCH{=}CH_2$

2A/4CBTP : $R = -(CH_2)_8OCOCH{=}CH_2$
or $-(CH_2)_{11}CH_3$

of their four isomers. 2A/4CBTP was designed to reduce the density of polymer network.

Characterizations

DSC measurements were carried out using TA Instruments 2920 MDSC. The texture observations were performed by a polarizing microscope (Olympus BH12) equipped with a hot stage (Mettler FP82 HT).

Order Parameter

The order parameter was evaluated using an infrared dichroic method by Vij *et al.* [5]. The order parameter S is defined as

$$S=1-3(\sin^2\Theta)/2$$

Θ is the angle between the director of the aromatic core and the direction of an IR beam. The dichroic ratio (Ri) is the ratio of the integrated absorbance of a vibrational band for the mesophase (I_D) to that for the isotropic phase (I_I).

$$Ri=I_D/I_I$$

If the transition dipole moment is directed orthogonal to the director of the aromatic plane, the equation for the order parameter can be expressed as

$$S=2(Ri-1).$$

Thus, the order parameters obtained in this study are a local order parameter of the chemical bond.

Photopolymerization

Photopolymerization was carried out with the addition of 1wt% of photoinitiator (2,2-dimethoxy-2-phenylacetophenone) to both monomers. The sample cell was placed on a temperature controllable hot stage (Mettler HT82/90), and the polymerization process was monitored with the detection of a vibration band using a FT-IR spectrophotometer (Bio-Rad FTS6000) that mounts a hot stage and a UV lamp unit (Ushio SP-III) for photo irradiation. The IR beam passes through 2mm-diameter window. During the exposure of UV light (365nm, 1mW/cm^2) on the sample cell, IR spectra were collected every 12 seconds at 4cm^{-1} resolution. The conversions of acrylate were calculated using a band at 810cm^{-1} C-H out of plane vibration in monomer and the order parameters of triphenylene core were calculated using in plane C-C stretching band at 1610cm^{-1}.

Photocurrent measurements

The dark- and photo-currents were measured for a sandwich-type cell consisting of two ITO-coated glasses. The gap of two electrodes was adjusted in 25μm to 31μm by polyimide spacer. The discotic liquid crystals were filled by capillarity on heating up to the isotropic phase. A light from a Xenon lamp (Ushio WUXL-500D-O) was lead to a monochromator (JASCO CT-25N) and irradiated the cell set in a temperature-controllable cryostat. All current were performed in Ar atmosphere. The steady-state currents were detected by a digital electrometer (Advantest Ultra High Resistance meter R8340) as closed circuit current under bias.

RESULTS AND DISCUSSION

Mesophase behavior of 6ABTP and 2A/4CBTP

6ABTP showed a mesophase in a wide temperature range from 91°C to 163°C. The mesophase was characterized as N_D phase from schlieren texture under the polarized microscope. 2A/4CBTP showed D_r and N_D phases (C 67°C D_r 130°C N_D 177°C Iso).

Photocurrent behavior and polymerization

The photocurrent of 6ABTP was measured for a 25μm-gap cell. When UV light (340nm) was irradiated, 4.7nA photocurrent was detected under 1000V/cm bias. While UV light was irradiating, both of the photo- and dark-currents decrease due to the process of polymerization. This made the evaluation of photocurrent behavior more difficult for the monomeric 6ABTP.

6ABTP containing 1wt% of the photoinitiator was filled into sandwich type cell at 120°C and exposed under UV light (365nm, 1000mJ/cm^2). For this cell, photocurrent could not be detected.

The conversion rate of acrylate was obtained to give saturation at *ca.* 80% (Fig.1). This indicates that 5 of 6 acrylate parts in 6ABTP

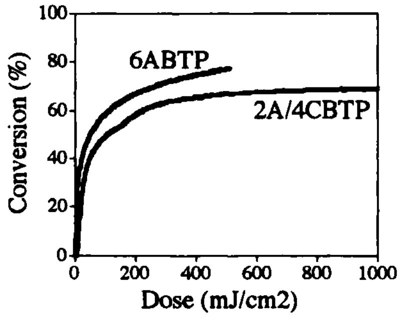


FIGURE 1 The conversion rate of acrylate residues against the irradiation power for 6ABTP and 2A/4CBTP.

were concerned with cross-linking. However, the textures before and after the photopolymerization were not changed [6].

On the assumption that a high polymer network with a nematic order depresses the photocurrent, the less density of cross-linking network should lead to increase of photocurrent. A 2A/4CBTP cell was prepared by the same method as for 6ABTP polymer at 160°C (ND phase). The acrylate conversion of 2A/4CBTP reached to 70%. The photocurrent of photopolymerized 2A/4CBTP was obviously detectable. Moreover, the photocurrent was obtained at the higher temperature than the clearing point of monomeric 2A/4CBTP as shown in Fig.2, while the monomer shows a undetectable photocurrent in the isotropic phase.

The viscosity of the system is increased with the degree of polymerization in the beginning of polymerization. Considering a fast increase of the viscosity by photopolymerization, it is difficult for the residual acrylate groups to move to react each other. In DSC

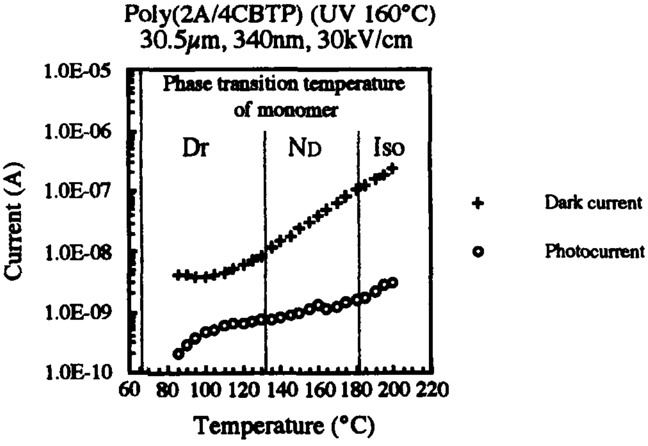


FIGURE 2 Temperature dependence of the dark- and photo-currents for 2A/4CBTP

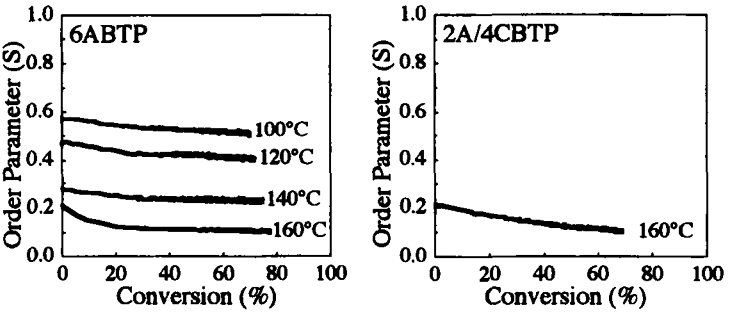


FIGURE 3 Relationship between the order parameter and acrylic conversion.

measurement, there are no significant phase change for both poly(6ABTP) and poly(2A/4CBTP).

In both materials, the order parameter of aromatic core gradually decreases, as the photopolymerization proceeds (Fig.3). The polymerized 6ABTP could not give the detectable photocurrent though it has higher order parameter than 2A/4CBTP. It may indicate that the high order parameter of aromatic core is not always a good factor for photoconductivity.

CONCLUSION

For both monomers, the order parameter of aromatic core gradually decreases to 90~50% during the photopolymerization, 20~30% of the acrylic residues leave unreacted. While the order parameter decreased during photopolymerization, the poly(2A/4CBTP) retains the photoconductive property shown in the monomeric discotic liquid crystal.

Highly cross-linked poly(6ABTP) did not give a detectable photocurrent even it had a higher order parameter than poly(2A/4CBTP). These indicate that the molecular order is important for photoconductivity, but the higher order parameter of the aromatic core may not always lead to the better photoconductivity.

Acknowledgement

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