NOTE

Influence of molecular orientation on mixtures of 4-*n*-pentyl-4′-cyanobiphenyl and biphenyl-dimethacrylate monomers for polymerization

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INTRODUCTION

Polymer formation in liquid crystals (LCs) is of current scientific and technological interest because of the new molecular architecture for advanced materials and practical applications, such as optical and holographic memories,[1–3] polarized emission devices[4–6] and display devices.[7–10] In particular, the polymer formation in LCs by photo-polymerization affects the scattering parameters of polymer dispersed LCs,[7,8] stability of the LC alignment[9,10] and other properties. The polymers are formed by exposing the LC mixtures and monomers to ultraviolet (UV) light.[7–11] We hypothesize that the properties of the LC mixtures and monomers are important for the polymer formation. Moreover, the addition of initiators in the LCs is unwanted since the residual initiator in the LC induces a serious deterioration of image quality in practical use.[12] A solution to this problem is using a monomer that can spontaneously generate radicals under UV light exposure. It is well known that aryl ester derivatives undergo photo-Fries rearrangement upon exposure to UV light.[13,14] A pair of radicals, which contributes to initiating the polymerization, is produced as a result of cleavage reaction of an ester bond as the reactive intermediates. Hence, in the present work, we focused on biphenyl-dimethacrylate monomers, whose mechanism of polymerization without initiators is shown in Figure 1.

We investigated the influence of the molecular structure of biphenyl-dimethacrylate monomers on the polymerization in the LC and the molecular orientation of LC molecules using Fourier transform infrared (FT-IR) spectroscopy, liquid chromatography, scanning electron microscopy (SEM), ^{1}H-NMR, polarized optical microscopy (POM) and differential scanning calorimetry (DSC) techniques. We used two monomers, 4,4′-dimethacryloyloxy-biphenyl (4,4′-DMOB) and 3,3′-dimethacryloyloxy-biphenyl (3,3′-DMOB), as shown in Figures 2a and b, respectively. These monomers have different substituent positions of the methacryloyloxy group attached to the biphenyl core. We used 4-*n*-pentyl-4′-cyanobiphenyl (5CB) as the LC material.

EXPERIMENTAL PROCEDURE

Samples

For the FT-IR measurements, two samples were prepared with the monomers 4,4′-DMOB and 3,3′-DMOB in 5CB. First, 0.5 wt% of the monomer (4,4′-DMOB or 3,3′-DMOB) was dissolved in 5CB. Each solution was sonicated to a mixture; then, 1 g of each mixture was deposited on a glass substrate. For the polymerization, two samples were exposed to UV light with the light source of FHF-32BLB (Toshiba, Japan) at 35 °C. After 10 min of UV light exposure, white precipitates were obtained. The precipitates obtained from each sample were cleaned with acetone, filtered and dried for 12 h at 35 °C before the FT-IR measurements.

For the liquid chromatography, SEM and POM evaluations, other samples were prepared as follows. First, a polyamic acid solution was spin-coated on the substrates and baked at 200 °C for 60 min to form a polyimide layer. The polymers produced from the monomers in the LC are effectively adsorbed on the surface of the polyimide layer.[15] Then, each polyimide layer was rubbed to produce an anti-parallel alignment, the substrates were assembled and each mixture of 5CB and monomer was injected. Finally, the samples were exposed to UV light at 35 °C for 2, 4, 6, 8 and 10 min. For comparison, other samples were also prepared by exposing to UV light at 50 °C for 1, 2, 3 and 4 min. After the samples decomposed, 5CB with residual monomer was dissolved in acetonitrile for the liquid chromatography measurements. Moreover, the substrates were placed in hexane for 90 min to remove 5CB. For the SEM observation, osmium was coated onto the substrates.

Measurements

FT-IR spectra. FT-IR spectra were obtained as KBr pellets on a Thermo Fisher Scientific Nicolet370 spectrophotometer (Yokohama, Japan). The KBr pellets were prepared using the monomers and the precipitates from the samples after the UV light exposure.

Liquid chromatography. To determine the residual monomer concentration in 5CB, liquid chromatography measurements were performed on an Agilent Technologies 1100 with a detector of UV220 (Tokyo, Japan) using water/acetonitrile as the eluent at 40 °C.

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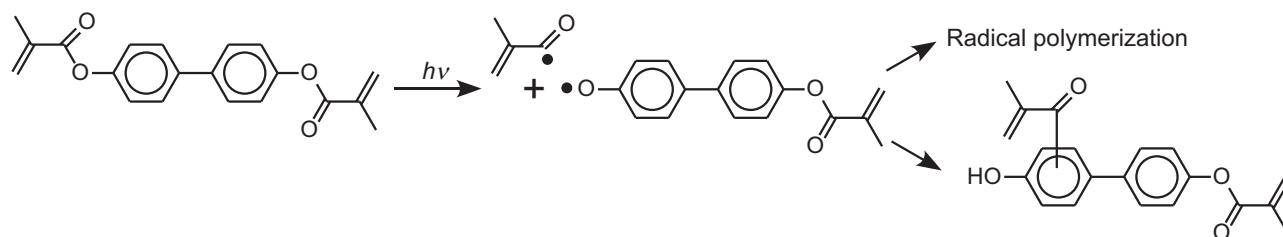E-mail: mizusaki.masanobu@sharp.co.jp or yusa@eng.u-hyogo.ac.jp

Figure 1 Mechanism of the photo-Fries rearrangement with biphenyl-dimethacrylate monomer.
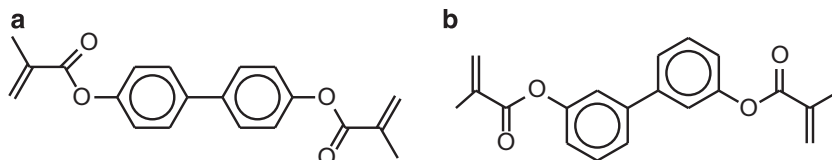

Figure 2 Chemical structures used in this study: (**a**) 4,4′-DMOB and (**b**) 3,3′-DMOB. DMOB, dimethacryloyloxy-biphenyl.
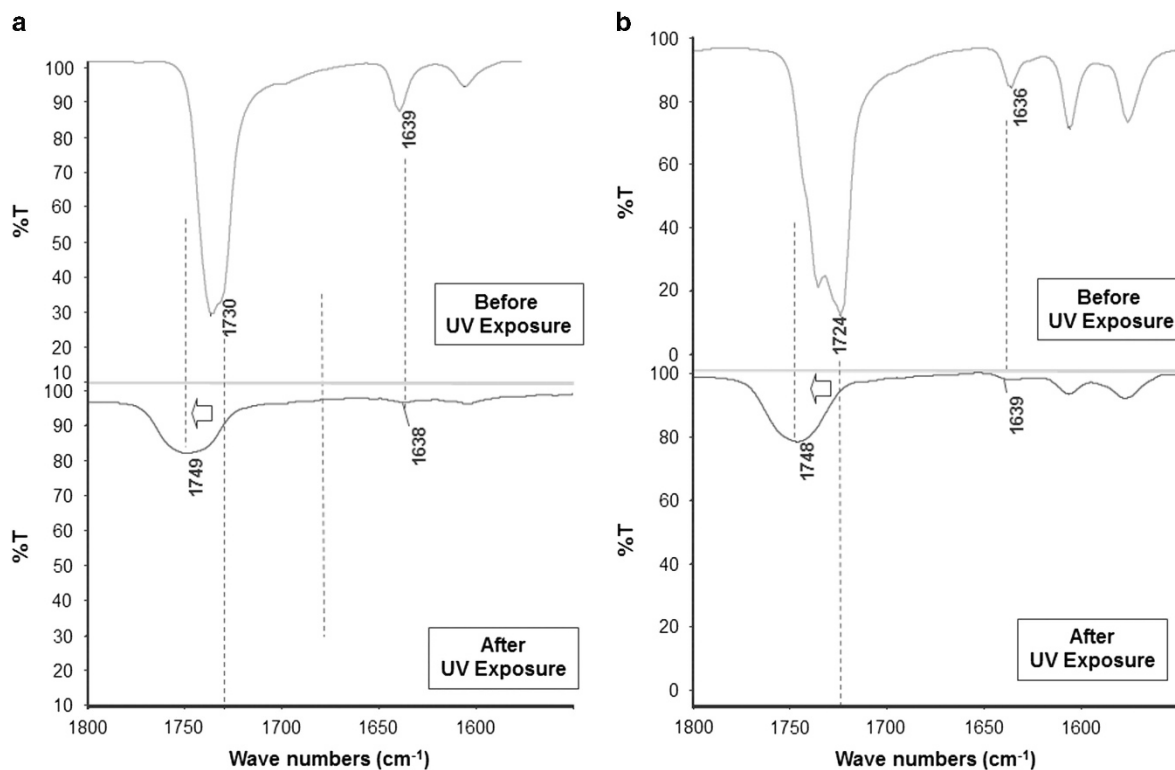

Figure 3 IR spectra of the monomers (before UV light exposure) and the polymers (after the UV light exposure) for (**a**) 4,4′-DMOB and (**b**) 3,3′-DMOB. DMOB, dimethacryloyloxy-biphenyl; IR, infrared; UV, ultraviolet. A full color version of this figure is available at *Polymer Journal* online.

SEM analysis. SEM analyses were performed on a Hitachi S-4800 microscope (Hitachi, Japan) with an accelerating voltage of 2 kV.

^{1}H-NMR spectra. The ^{1}H-NMR spectra of 5CB with and without the monomers were recorded with a Bruker DRX-500 spectrometer (Yokohama, Japan) with a deuterium lock using dimethyl sulfoxide-d_6-containing sealed tube.

POM analysis. POM observations were performed with an ECLIPSE E600 POL system developed by Nikon Corp (Tokyo, Japan). The samples were put on a hot plate and the temperature was set at 35 °C.

DSC analysis. DSC analyses of 5CB with and without the monomers were performed on a Seiko Instruments SSC/5200 (Chiba, Japan) in N_2 atmosphere. Before the measurements, calibration was conducted with 4-nitrotoluene (52.5 °C), indium (156 °C) and tin (232 °C). The measurements were performed with second heating from 20 to 100 °C. The temperature was increased at a rate of 1.0 °C min^{-1}.

RESULTS AND DISCUSSION

Figures 3a and b show the FT-IR spectra of the monomers (top: before UV light exposure) and the precipitates recovered from each sample
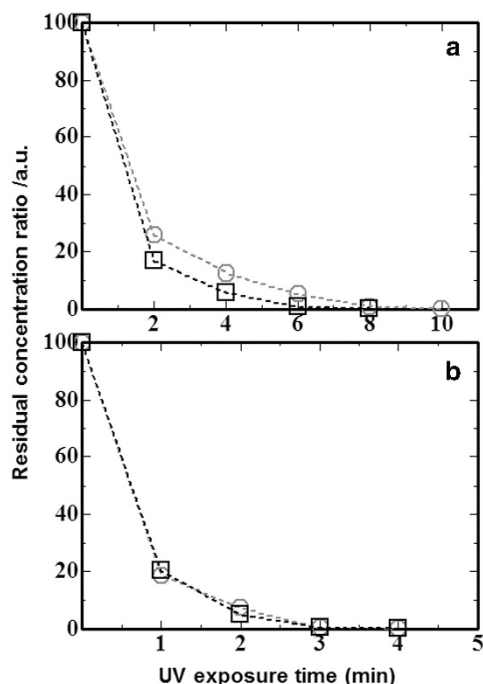
Figure 4 Residual monomer concentration of 4,4'-DMOB (○) and 3,3'-DMOB (□) as a function of the exposure time to UV light at (a) 35 and (b) 50 °C. DMOB, dimethacryloyloxy-biphenyl; UV, ultraviolet.

(bottom: after UV light exposure). The FT-IR spectra of the monomers 4,4'-DMOB and 3,3'-DMOB show peaks at 1639 and 1636 cm^{-1}, respectively, which are derived from the stretching vibration of the C=C bond. These peaks become small after the UV light exposure. Moreover, the peaks at 1724 and 1730 cm^{-1} before the UV light exposure, which are derived from the stretching vibration of the C=O bond, shift to approximately 1748 cm^{-1} after the UV light exposure. The shifts are attributable to the quenching of the conjugation of the C=O bond because the C=C bond disappears. The FT-IR spectral results confirm that the polymerization occurred in 5CB for both 4,4'-DMOB and 3,3'-DMOB without initiators.

Figures 4a and b show the residual concentration of the monomers as a function of time of UV light exposure at 35 and 50 °C, respectively. The initial monomer concentration was 0.5 wt%. According to Figure 4a, the residual concentration of 4,4'-DMOB became almost 0 wt% with 8 min of UV light at 35 °C, whereas that of 3,3'-DMOB was consumed after 5 min of UV light exposure. This result indicates that the rate constant for the polymerization of 3,3'-DMOB is larger than that of 4,4'-DMOB. In the case of UV light exposure at 50 °C, the difference in rate constant for the polymerization between 4,4'-DMOB and 3,3'-DMOB was not observed as shown in Figure 4b. Because the nematic-to-isotropic transition temperature (T_{NI}) of 5CB is 35.3 ~ 35.5 °C,[16,17] the polymerization occurs in the isotropic state, which leads to the same rate constant of polymerization for both 4,4'-DMOB and 3,3'-DMOB.
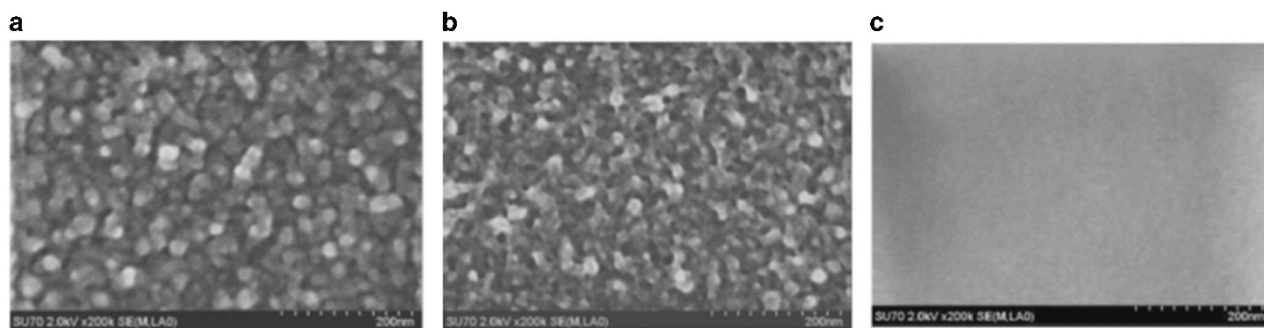

Figure 5 SEM photographs of the substrate surface after 10 min of UV light exposure for (a) the mixture of 5CB and 4,4'-DMOB, (b) mixture of 5CB and 3,3'-DMOB and (c) 5CB without the monomers. DMOB, dimethacryloyloxy-biphenyl; SEM, scanning electron microscopy; UV, ultraviolet.
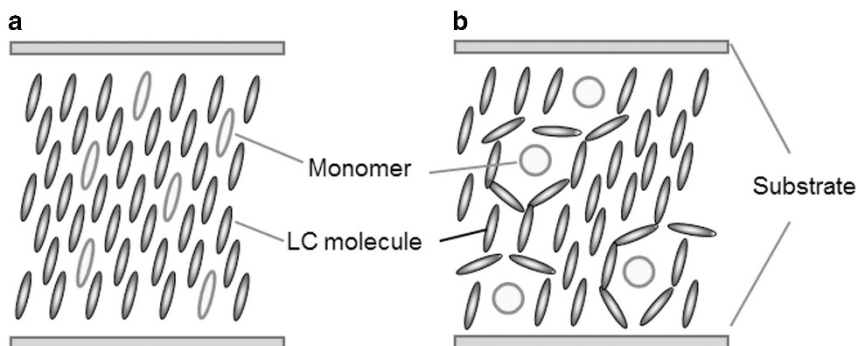

Figure 6 Schematic illustrations of the orientations of the LC and monomer molecules: (a) the monomer has a similar molecular structure to that of the LC and (b) the molecular structure of the monomer is not similar to that of the LC. LC, liquid crystal. A full color version of this figure is available at *Polymer Journal* online.
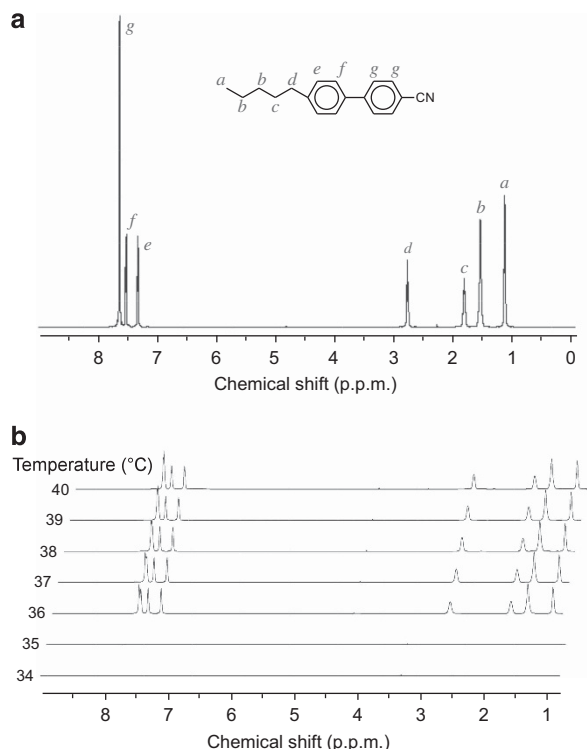
Figure 7 (**a**) ^{1}H-NMR spectrum of 5CB at 60 °C and (**b**) ^{1}H-NMR stack plot for 5CB at temperatures ranging from 34.0 to 40.0 °C. 5CB, 4-*n*-pentyl-4′-cyanobiphenyl. A full color version of this figure is available at *Polymer Journal* online.

Figure 8 ^{1}H-NMR spectra of (**a**) the mixture of 5CB and 4,4′-DMOB and (**b**) the mixture of 5CB and 3,3′-DMOB at 40 °C. 5CB, 4-*n*-pentyl-4′-cyanobiphenyl; DMOB, dimethacryloyloxy-biphenyl. A full color version of this figure is available at *Polymer Journal* online.

Figure 9 ^{1}H-NMR stack plots for (**a**) the mixture of 5CB and 4,4′-DMOB and (**b**) the mixture of 5CB and 3,3′-DMOB at temperatures ranging from 34.0 to 37.0 °C with an interval of 0.5 °C. 5CB, 4-*n*-pentyl-4′-cyanobiphenyl; DMOB, dimethacryloyloxy-biphenyl.

To examine the polymer formation in 5CB under UV light exposure at 35 °C, SEM observations were performed with the substrates obtained from the samples after 10 min of UV light exposure. The SEM photographs of the substrate surfaces are shown in Figure 5. The surfaces of the substrates obtained from the samples after the UV light exposure (Figures 5a and b) are covered by many grains, whose sizes are 10–20 nm, whereas that obtained from the sample with 5CB does not have any grains (Figure 5c). Thus, we believe that the grains are constructed from the polymers that are produced by 4,4′-DMOB and 3,3′-DMOB. Moreover, the grain size produced by 3,3′-DMOB is slightly smaller than that produced by 4,4′-DMOB, and the grains produced by 3,3′-DMOB are linked with one another. The result implies that the phase separation of the polymers of 5CB is different between 4,4′-DMOB and 3,3′-DMOB.

Here, the different rate constants of polymerization between 4,4′-DMOB and 3,3′-DMOB are important because the residual monomer in the LC induces serious problems in practical use.[12] For example, the electro-optical property of the LC is shifted when there is a residual monomer in the LC.[15,18] A hypothesis for the difference in rate constant of polymerization between 4,4′-DMOB and 3,3′-DMOB is as follows. The molecular structure of the monomer affects the molecular orientation of the LC molecules around the monomer. If the molecular structure of the monomer is close to that of the LC molecule, the molecular orientation of the LC molecules around the monomer is maintained as shown in Figure 6a, and the mixture exhibits the nematic state. In contrast, the molecular orientation of the LC molecules around the monomer is disrupted if the molecular structure of the monomer is not close to that of the LC molecule as illustrated in Figure 6b. In this case, T_{NI} is finally shifted. The molecular structure of 4,4′-DMOB is closer to that of 5CB than that of
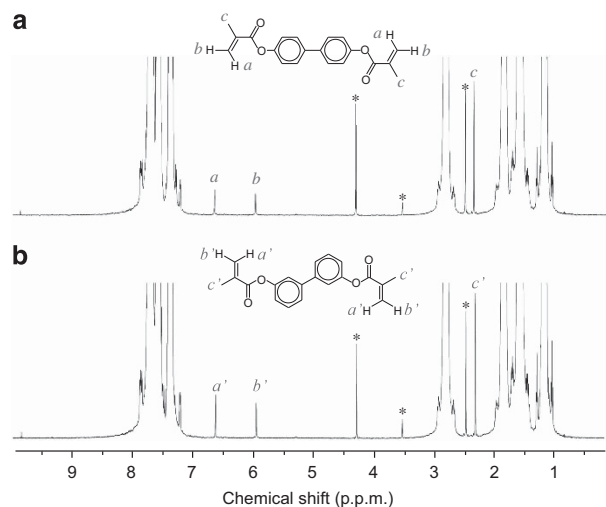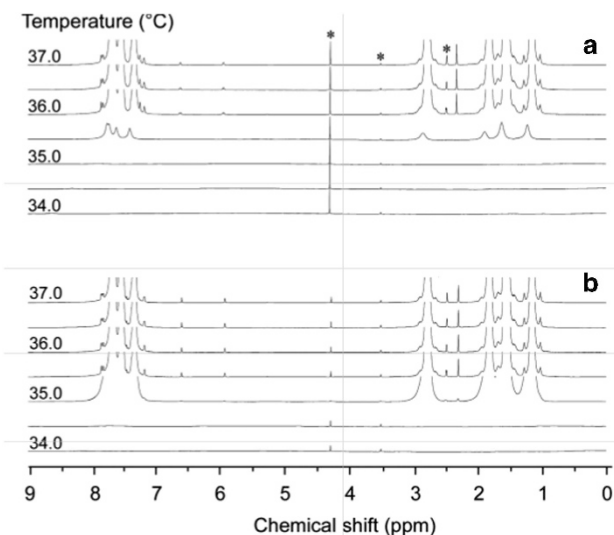
3,3′-DMOB because both 4,4′-DMOB and 5CB have substitutional groups at 4,4′-positions of biphenyl moiety.

To confirm the hypothesis, we investigated the molecular orientation for the mixture of the LC and monomer using the ^{1}H-NMR technique. The ^{1}H-NMR technique can effectively detect the motional property of the LC and monomer.[19] Figure 7a shows the ^{1}H-NMR spectrum of 5CB and the attribution of the resonance peaks. For the deuterium lock, deuterium dimethyl sulfoxide in a sealed glass tube was added to 5CB. The stack plots of the ^{1}H-NMR spectra of 5CB without the monomer in the temperature range of 34.0 to 40.0 °C with an interval of 1.0 °C are shown in Figure 7b. From these spectra, the resonance peaks are observed above 36.0 °C, which is larger than T_{NI} of 5CB.[16,17] The resonance peaks disappear below
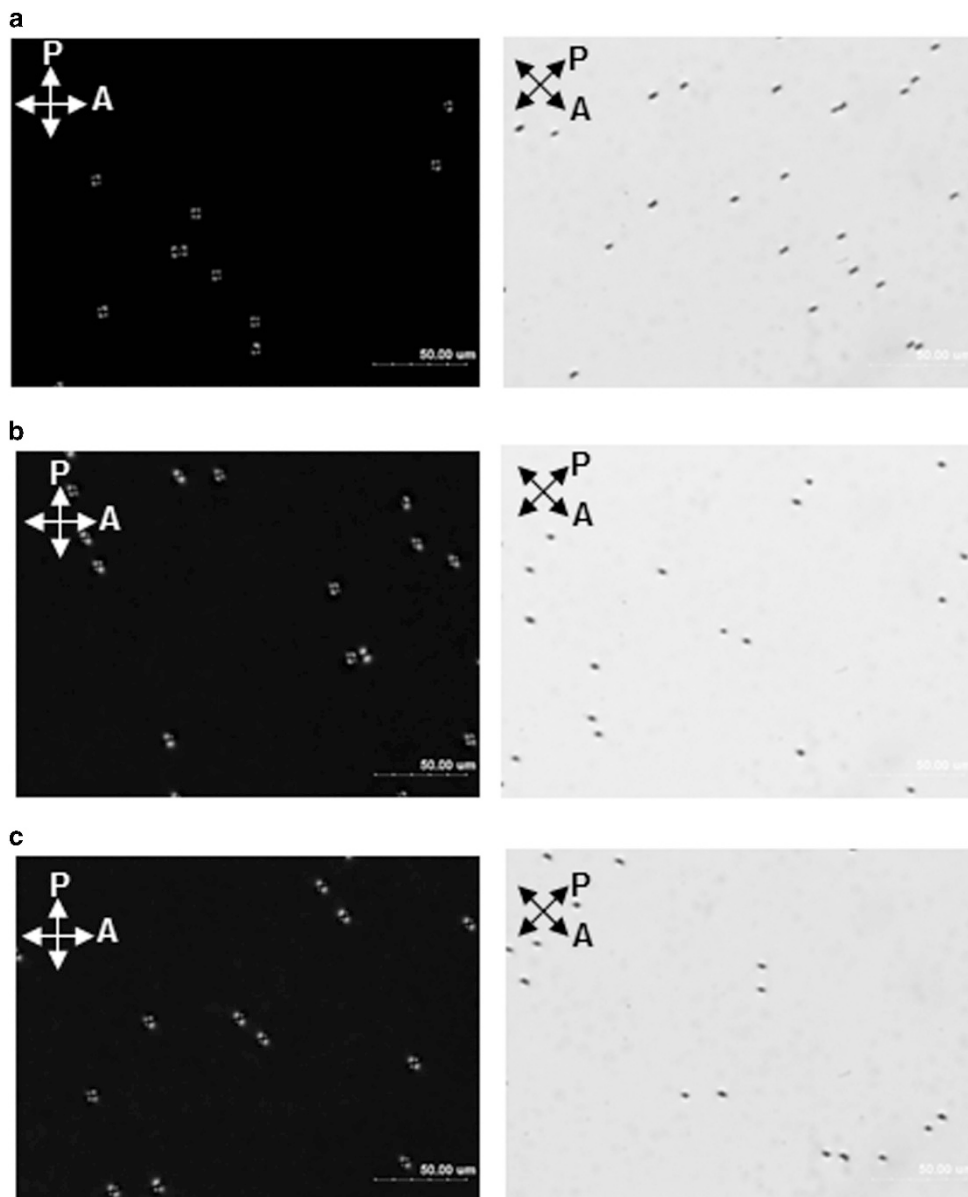
Figure 10 POM images of (**a**) 5CB, (**b**) the mixture of 5CB and 4,4′-DMOB, and (**c**) the mixture of 5CB and 3,3′-DMOB; the angles between the crossed polarizers and rubbing direction are 0 and 45°. 5CB, 4-*n*-pentyl-4′-cyanobiphenyl; DMOB, dimethacryloyloxy-biphenyl; POM, polarized optical microscopy. A full color version of this figure is available at *Polymer Journal* online.

36.0 °C because the molecular motion of 5CB is restricted in the nematic state. In contrast, the appearance of the resonance peaks above 36.0 °C implies that the motional freedom is increased in the isotropic state. To examine the molecular orientation, the mixture of 5CB and 0.5 wt% of 4,4′-DMOB or 3,3′-DMOB was used. The ^{1}H-NMR spectra of the mixtures of 5CB with 4,4′-DMOB and 3,3′-DMOB at 40 °C are shown in Figures 8a and b, respectively. In both spectra, some resonance peaks at approximately 2.4, 5.9 and 6.6 p.p.m. were observed in addition to the peaks from 5CB in Figure 7. The peaks at 5.9 and 6.6 p.p.m. are assigned to the α-methyl proton and the peak at 2.4 p.p.m. is assigned to the vinyl proton of the methacryloyloxy moiety in the monomers, respectively. The resonance peaks at approximately 2.5, 3.6 and 4.3 p.p.m., which are indicated in the spectra as asterisk signs, are derived from the deuterium dimethyl sulfoxide, water in the deuterium dimethyl sulfoxide and impurity in

5CB, respectively. Therefore, one can evaluate the shift in the molecular orientation of the mixtures using the ^{1}H-NMR technique. Figures 9a and b show the stack plots of the ^{1}H-NMR spectra of the mixtures of 5CB with 4,4′-DMOB and 3,3′-DMOB in the temperature range of 34.0 to 37.0 °C with the interval of 0.5 °C, respectively. In Figure 9a, the resonance peaks for the protons from 5CB and 4,4′-DMOB appear above 35.5 °C, which indicates that the molecular orientation for the mixture of 5CB and 4,4′-DMOB is disrupted above 35.5 °C. Because T_{NI} of 5CB without the monomer is 35.3 ∼ 35.5 °C,[16,17] one can consider that the existence of 0.5 wt% 4,4′-DMOB does not affect T_{NI} of 5CB. Moreover, for the mixture of 5CB and 3,3′-DMOB in Figure 9b, the resonance peaks of the protons from 5CB and 3,3′-DMOB appear at 35.0 °C, which is 0.5 °C lower than that for the mixture of 5CB and 4,4′-DMOB. The result indicates that the orientation for the mixture of 5CB and 3,3′-DMOB is more
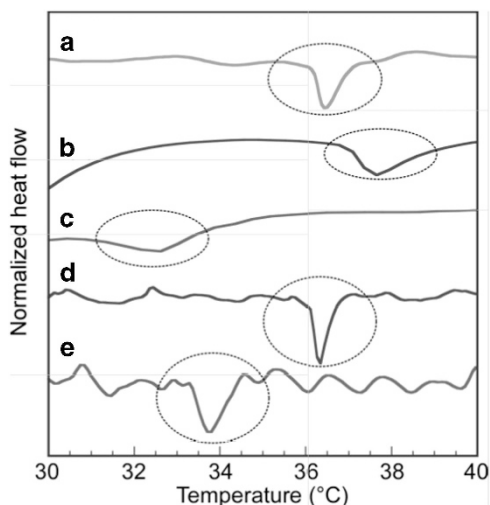
Figure 11 DSC profiles for (**a**) 5CB and the mixtures of (**b**) 5CB and 2 wt% 4,4′-DMOB, (**c**) 5CB and 2 wt% 3,3′-DMOB, (**d**) 5CB and 0.5 wt% 4,4′-DMOB, and (**e**) 5CB and 0.5 wt% 3,3′-DMOB at temperatures ranging from 30 to 40 °C. 5CB, 4-*n*-pentyl-4′-cyanobiphenyl; DMOB, dimethacryloyloxy-biphenyl; DSC, differential scanning calorimetry. A full color version of this figure is available at *Polymer Journal* online.

easily disrupted than that for the mixture of 5CB and 4,4′-DMOB because the molecular structure of 3,3′-DMOB is not close to that of 5CB. Thus, those results well support the above hypothesis. To confirm the molecular orientation of 5CB and the mixtures, the POM observation was attempted at 35.0 °C. The observations were performed under crossed polarizers, and the alignment directions of the samples were set to be 0 and 45°. The alignment direction indicates the rubbing direction. In the case of the sample produced from 5CB without the monomers, which is shown in Figure 10a, the dark state was obtained at the alignment direction of 0°, whereas the high transmittance was obtained at the alignment direction of 45°. The small dots in the images were derived from spacer beads to avoid contact of the substrates. The result indicates that homogeneous alignment was obtained for the sample. Thus, we confirm that the nematic state appeared for 5CB at 35.0 °C. Figures 10b and c show the POM images with the samples of 5CB that contained 0.5 wt% 4,4′-DMOB and 3,3′-DMOB, respectively. The results have the same tendency as the result of 5CB without the monomers (Figure 10a). Therefore, both mixtures also show the nematic states at 35.0 °C.

To more accurately evaluate the phase transition of the mixtures, the DSC measurements were performed using the mixtures of 5CB and monomers. To critically observe the endothermic peak, the monomers were dissolved at 2 wt% in 5CB, which was close to the saturation level of solubility. Figure 11a shows the DSC curve for 5CB at the temperature range of 30 to 40 °C. The endothermic point was observed at approximately 36.2 °C, which is different from the result of ^{1}H-NMR (Figure 7a).[16,20] However, we can estimate that the peak is derived from the transition from the nematic to the isotropic state of 5CB (T_{NI}) because we do not observe any peaks at approximately 35.0 ~ 35.5 °C. Figures 11b and c show the DSC curves for the mixtures of 5CB and 2 wt% 4,4′-DMOB or 3,3′-DMOB. For the mixture of 5CB and 4,4′-DMOB, the endothermic point is 37.4 °C, which is higher than that of the T_{NI} of 5CB and different from the ^{1}H-NMR result (Figure 9a). We determined the endothermic point from DSC using the intersection of the original baseline and tangent line at the inflection point. In contrast, the endothermic point for the mixture of 5CB and 2 wt% 3,3′-DMOB is 32.5 °C (Figure 11c), which is lower than T_{NI} of 5CB. The endothermic points estimated from DSC for 5CB with 0.5 wt% 4,4′-DMOB and 3,3′-DMOB were 36.4 and 33.6 °C, respectively (Figures 11d and e). These observations indicate that the molecular orientation for 5CB with 3,3′-DMOB may disrupt more easily than that with 4,4′-DMOB. However, the tendency for the shift of the endothermic point as a function of the monomer concentration was opposite between 4,4′-DMOB and 3,3′-DMOB. The endothermic point decreased with decreasing concentration of 4,4′-DMOB but increased with decreasing concentration of 3,3′-DMOB. In addition, the ^{1}H-NMR and POM analysis results show that the nematic state was obtained at 35.0 °C for the mixture of 5CB and 3,3′-DMOB, which is different from the DSC result. Here, using DSC measurements, Takanishi *et al.*[21] found that nanoscale phase separation occurred in the mixture of rod-like liquid-crystalline molecule and bent-core molecule. Hence, the peak obtained from the mixture of 5CB and 4,4′-DMOB or 3,3′-DMOB may also be derived from the nanoscale phase separation between 5CB and the monomer.

In conclusion, the FT-IR spectra reveal that the polymerization of 4,4′-DMOB and 3,3′-DMOB occurs with the generation of radicals from the monomers as reactive intermediates of photo-Fries rearrangement under UV light exposure. The rate constant of the polymerization of 3,3′-DMOB is larger than that of 4,4′-DMOB in 5CB. From the ^{1}H-NMR and POM analyses, we confirmed that the rate constant of the polymerization was affected by the molecular orientation of the mixtures of 5CB and each monomer. Moreover, we estimated that the molecular orientation of the mixtures was affected by the molecular structure of the monomer from the ^{1}H-NMR and DSC analyses.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

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