Photopolymerization Behavior of Ferroelectric Liquid-Crystalline Monomers

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Ferroelectric liquid crystals (FLCs) exhibit spontaneous polarization and show a response to change in the electric field. Switching of this field causes a reversal in the direction of polarization. Here we report in-situ photopolymerization behavior of FLC monomers and image storage using bistable switching by applying electric field. Polymerization behavior was considerably affected by the length of alkyl spacer and structure of functional groups.

Keywords: liquid crystal, ferroelectric phase, photopolymerization, packing

1. Introduction

Chiral smectic C (SmC*) phase of ferroelectric liquid crystals (FLCs) exhibits spontaneous polarization (Ps), and the FLC molecules are aligned parallel to each other to form a layer with a tilt between the direction of the long axis of the FLC molecule and the normal to the smectic layer.[1] The average direction of the molecular long axis is defined in each layer, and owing to the chiral group in the FLC molecules the director adopts a helicoidal structure with a characteristic pitch. If the FLC molecules are placed in a cell with a small gap (<2 µm), the molecular long axis in every layer is aligned in the same direction with the smectic layers oriented roughly perpendicular to the cell surface. As a result, the polarization of all layers is also aligned in one direction. In addition, when the polarity of the electric field is reversed, the polarization flips into opposite direction. These two states are stable and therefore FLCs exhibit bistability.[1]

Highly oriented polymers exhibit anisotropy of optical, electrical and thermomechanical properties. Polymerization of LC monomers has been conducted extensively to obtain polymer liquid crystals (PLCs).[2] The LC monomers can be macroscopically oriented by external forces, such as an electric or magnetic field, elongational flow and surface orientation.[3] Monomer organization may affect the polymerization kinetics, the polymer structure and the microstructure of polymers.[4] If polymerizable FLCs are used, it is assumed that the polymerizable groups adjoin and are aligned in one direction in each layer of the SmC* phase. In-situ photopolymerization, which offers an advantage in that the temperature can be chosen precisely, of FLC monomers is expected to show specific polymerization behavior. The effect of LC ordering on the rate of free-radical polymerization of mesomorphic vinyl monomers has been discussed extensively.[2] There are at least two types of polymerization behavior reported previously on polymerization of LC monomers. First, the polymerization does not involve any rate enhancement. For instance, some LC monomers possess mesogenic groups decoupled from reactive functional moieties by a methylene spacer. In this type of LC monomers, the polymerization is little affected by the LC ordering. Second, the effect of LC ordering can have marked consequence concerning the rate enhancement of polymerization. If an alkyl spacer attached to the functional group is long, the orientation of polymerizable groups between LC molecules is disordered even though the core part of mesogens is highly oriented. On the other hand, in the case of short spacer, the orientation of...
mesogens affects that of functional groups, improving molecular packing in an LC phase.[5]

In a previous paper, we reported in-situ photopolymerization behavior of FLC monomer possessing a long spacer.[6] However, the effect of length of alkyl spacer on photopolymerization behavior of FLC monomers has not yet been reported. In this study, we synthesized chiral LC vinyl monomers with methacrylate group attached to the rigid core through a short methylene spacer (carbon number of 2) and a long methylene spacer (carbon number of 11) and investigated the LC behavior of these monomers. We next explored the effect of molecular packing of the LC monomers on polymerization behavior by photoinitiation which is advantageous in that polymerization can be initiated at any temperature after complete equilibrium LC ordering of the LC monomers is attained.

2. Experimental Section

2.1. Material

2.1.1. FLC Monomers

The structure and phase transition temperature of the three PLC monomers, M11, M2, and A11, used in this study are shown in Fig. 1.[6,7] The phase transition temperature and the phase structure were determined by differential scanning calorimetry (DSC; cooling rate, 1 °C/min) and optical polarizing microscopy. The PLC monomers showed various phases with temperature: crystalline (K), SmC*, chiral smectic A (SmA*) and I phases.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Mn (g/mol)</th>
<th>Mw/Mn</th>
<th>Phase transition temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(M11)</td>
<td>64000</td>
<td>3.5</td>
<td>G 37 SmC* 150 SmA* 161 I</td>
</tr>
<tr>
<td>poly(M2)</td>
<td>63000</td>
<td>4.1</td>
<td>G 138 SmA* 220 Decomposition</td>
</tr>
<tr>
<td>poly(A11)</td>
<td>18000</td>
<td>1.6</td>
<td>G 37 SmC* 149 SmA* 162 I</td>
</tr>
</tbody>
</table>

G, glassy; SmC*, antiferroelectric chiral smectic C; SmA*, chiral smectic A; I, isotropic.

2.2. In-Situ Photopolymerization Procedure

Photopolymerization was performed in a glass cell with a gap of 2 µm without an electric field or under dc electric field of 3 V/µm. The glass cell was composed of two indium tin oxide (ITO) glass substrates with polyimide alignment layers rubbed in an antiparallel direction. Samples for photopolymerization were prepared by injecting the PLC monomer containing a photoinitiator (2 mol%) into the glass cell in the I phase using capillary action. It was confirmed that the concentration of the photoinitiator was too small to destabilize the LC phases and no spontaneous thermal polymerization occurred during injection of the PLC monomers into the glass cell. Furthermore, it was also confirmed that without the photoinitiator, the photopolymerization could not be induced even after prolonged photoirradiation at 366 nm. After the samples were prepared, they were cooled down slowly (0.5 °C/min) to a polymerization temperature. Photoirradiation was performed at 366 nm (intensity, 1 mW/cm² or 0.1 mW/cm²). In the photopolymerization under an electric field, the sample was cooled down slowly under ac electric field (1 Hz, ±3 V/µm) to a temperature for photopolymerization. After obtaining a ferroelectric monodomain structure at the temperatures for which the ferroelectric electrooptic response in the SmC* phase was fully developed, the cell was irradiated at 366 nm with the dc electric field of 3 V/µm during polymerization.

The course of the polymerization was followed by gel permeation chromatography (GPC). The
molecular weights of the polymers were determined by GPC calibrated with standard polystyrenes.

2.3. Evaluation of Alignment of Polymerized FLC

The molecular alignment of the FLCs was explored by optical polarizing microscopy after the photopolymerization of M11 was conducted in the 2-µm-gap cell at 60 °C in the surface-stabilized state.

3. Results and Discussion

3.1. In-Situ Photopolymerization Behavior

It is important to evaluate the changes in the phase transition temperature due to changes in composition of the monomer-polymer mixture.[8] Several samples were prepared in which the mixing ratio of the monomer and the polymer was altered, and the binary mixtures were subjected to DSC and microscopic observation to explore the phase behavior. The phase diagram is shown in Fig. 2. In three systems, no phase separation occurred in the range of polymerization temperature. This result indicates that in this study phase separation hardly needs to be considered to evaluate the polymerization behavior.

In the case of M11 and A11 with a relatively low polymer content, the phase transition temperature changed only slightly. This result demonstrates that the change in the phase structure could be negligible during the early stage of polymerization. The phase transition temperature of the mixtures was, however, shifted to higher temperatures as the polymer content increased, and the temperature range of the SmC* phase increased considerably. For M2 with a relatively low polymer content, the phase transition temperature changed only slightly. On the other hand, the phase structure changed considerably as the polymer content increased.

Effect of the irradiation time on the FLC monomer conversion was investigated. The samples were irradiated at 366 nm at different temperatures without or with an electric field. The conversion showed a tendency to increase with increasing the irradiation time, irrespective of the polymerization temperature. A similar trend was observed for a sample under an electric field. On the basis of the phase diagram shown in Fig. 2, it is assumed that no phase transition occurs at least on 30-s irradiation of M11 due to low content of the polymer produced. It was found that the conversions after 30-s and 60-s irradiations were proportional to irradiation time. We therefore used the conversions after 60-s irradiations as a measure to explore the in-situ photopolymerization behavior of the M11 monomer. On the other hand, for M2 which has a short spacer, the conversions after photoirradiation at 1 mW/cm² and 0.1 mW/cm² were not proportional to polymerization time. At 0.1 mW/cm², conversions after 60-s irradiation were relatively low.

For A11, it is assumed that no phase transition occurs at least on 5-s irradiation due to low content of the polymer produced. On the other hand, after 60-s irradiation the conversions reached to above 50 % irrespective of polymerization temperature. Under such condition the in-situ photopolymerization may be accompanied by changes in the phase structure of the polymerization mixture. We therefore used the conversions after 5-s irradiation as a measure to explore the in-situ photopolymerization behavior of the FLC monomer.

3.2. Polymerization Behavior in Early Stage of Polymerization

3.2.1. Polymerization Behavior of M11

The relation between conversion and temperature in photopolymerization of M11 is shown in Fig. 3. Conversions after 60-s
irradiation were plotted as a function of temperature, since after 30-s irradiation a similar profile was obtained. Conversion and Mn of the polymer produced in the SmC* phase were highest after irradiation without electric field (Fig. 3, O). The distances between polymerizable groups become small when monomer shows high orientation. Therefore, it is anticipated that polymerization is fast and Mn increases. It is expected that the polymerization rate would be enhanced significantly when the FLC monomers are highly aligned by application of the electric field. Such effects of the external electric field on the polymerization rate have been observed also for the chiral LC monomer showing SmA* phase and the polymerization rate seems to be dependent on the efficient collision between polymerizable groups.[9] The result exhibited that conversion increased and Mn of polymer produced decreased under dc electric field (Fig. 3, ●). The monomer shows high orientation (ferroelectric surface-stabilized state) under electric field in the SmC* phase and the distances between the polymerizable groups become small. Then, it is expected that Mn increase by electric field. However, the decrease of Mn by applying electric field may be due to chain transfer of propagating radicals.

3.2.2. Polymerization Behavior of M2

Polymerization of M2 monomer having a short spacer was also conducted. M2 exhibited different polymerization behavior from M11 (Fig. 4). At a light intensity of 0.1 mWcm², the formation of polymer was confirmed in M2, but not in M11 by GPC. This result suggests that density of polymerizable groups affects polymerizability. At 1 mWcm², conversion and Mn were independent of temperature and applied electric field in the polymerization of M2. This implies that phase transition to SmC₄* phase occurs during polymerization as demonstrated in Fig. 2. To investigate the effect of phase structure of monomer on polymerization behavior, photopolymerization was conducted at 0.1 mWcm². When the light intensity is low, phase transition does not occur during polymerization because of low conversion, and we can investigate the effect of phase structure of monomer on the polymerization behavior.

The relation between temperature and conversion is shown in Fig. 4. Conversion was high in the SmC* under electric field and the SmA* phases. These phases have high orientation and the distances between polymerizable groups become small, which results in fast polymerization. On the other hand, Mn was largest at SmC₄*-SmA* phase transition temperature and Mn was almost constant under electric field.

3.2.3. Polymerization Behavior of A 11

The open symbols in Fig. 5 show plots of conversion after 5-s irradiation versus temperature without an electric field. The conversion was high below 50 °C at which the FLC monomer shows SmC₄*, SmC₅*, and SmC* phases. This result suggests that the enhancement of polymerizability is due to the proximity of the polymerizable groups in highly ordered systems. It is expected that the initial polymerization rate would be enhanced significantly when the FLC monomers are highly aligned by application of the electric field. On the other hand, it has been also reported that the macroscopic alignment of the LC monomers does not affect the polymerization kinetics.[8] Unfortunately, the conversions obtained by photoirradiation after 5-s irradiation with the dc electric field were much smaller than those obtained without the electric field.

![Fig. 3. Polymerization behavior of M11 after 60-s photoirradiation at various temperatures. (A), conversion; (B), Mn; O, without an electric field; ●, with an electric field of 3 V/µm.](image1)

![Fig. 4. Polymerization behavior of M2 after 60-s photoirradiation at various temperatures. (A), conversion; (B), Mn; O, without an electric field; ●, with an electric field of 3 V/µm.](image2)

![Fig. 5. Polymerization behavior of A 11 after photoirradiation at various temperatures.](image3)
The FLCs have a helicoidal structure in the bulk. Injection of FLCs into a glass cell with a narrow gap (1-2 µm) suppresses the helix formation by surface stabilization. The FLCs become highly aligned, in principle, in a 2-µm-gap cell, however, it was difficult to align completely the FLC monomer used in this study even in the 2-µm-gap cell. Practically, even when the FLC monomer showed the surface-stabilized state in the presence of an external field, relaxation of the molecules was observed when the application of the electric field was ceased. From viewpoint of molecular alignment, therefore, the polymerization under an electric field is more favored than that without an electric field.

Although we expected that the polymerizability in the presence of an electric field was superior to that in the absence of an electric field, the result obtained was contrary to our prediction. One possible explanation is that the photopolymerization behavior depends not only on molecular alignment, but also on kinetic factors such as mobility, diffusion and molecular rearrangement of FLC monomers in the LC phase. In fact, in K phase in which the FLC molecules show no mobility, the conversion was extremely low (Fig. 5A, △). Consequently, the polymerizability of the FLC monomers in early stage of polymerization is governed by their molecular alignment as well as their mobility in the LC phase.

The relation between molecular weight of the polymer produced and polymerization temperature is shown in Fig. 5B. The values of number-average molecular weight were larger in low temperature region (SmCA* , SmCY* and SmC* phase). This is presumably due to decrease in termination rate, resulting from lower mobility of the FLC molecules in highly ordered systems. Furthermore, the molecular weight of the polymer in the K phase was low. These results indicate that the molecular mobility as well as the orientation are needed to obtain high molecular weight polymers.

3.2.4. Effect of Alkyl Spacer Attached to Functional Group

The mesogenic units are already ordered in the monomeric phase and the spacer is meant to allow the formation of polymer chains independently from the topology of the mesogens. Consequently, for polymerizable groups, the length of the alkyl spacer may have a significant influence on the polymerization behavior. M2 monomer exhibited different polymerization behavior from M11 (Fig. 3 and 4). At the light intensity of 0.1 mW/cm², the formation of polymer was confirmed in M2, but not in M11 by GPC. This result suggests that density of polymerizable groups affects polymerizability. To compare polymerization behavior between monomers which have different length of alkyl spacer (M11 and M2), we evaluated the relative conversion (the ratio of conversion under electric field to conversion without electric field) in the SmC* phase as a function of applied voltage. It was found that relative conversion of M2 is 3.1 and that of M11 is 1.1. This result demonstrates that the change of macroscopic structure is more effective in the polymerization behavior of M2 having a short spacer.

3.2.5. Effect of Functional Groups

The kinetics is affected by molecular orientation and mobility. It is known that methacrylates lead to higher viscosity than acrylates. Therefore, we evaluated polymerization behavior of two systems (M11 and A11). Conversion of M11 was much higher than that of A11 in the case of application of electric field. These results suggest that increase of conversion is based on Trommsdorff effect by higher viscosity.

3.3. Image Storage

The optical texture after photoirradiation was the same as that before photoirradiation, but the polymerized FLC showed no response to the electric field. It was confirmed that electric field to the sample results in appearance of the immobilized SmC* phase in which all mesogens of the polymerized FLC were aligned into one direction leading to the formation of a monodomain of LC phase. Such immobilization
of the SmC* phase is quite favorable from viewpoint of optical applications.

The diagram for the image storage is shown in Fig. 6. An LC cell containing a monomer and a photoinitiator was covered with a photomask and LC molecules were oriented in the SmC* phase, then photoirradiation was conducted for 60 s under dc electric field. The monomer was polymerized only in the irradiated part by this method. In this part, LC molecules showed no response to the electric field of 3 V/μm. By applying an electric field with reverse polarity which was larger than the threshold value, the polarization flipped into the opposite direction in the unpolymerized part. After removing the photomask, photoirradiation was conducted for 60 s again. We observed bright and dark views oppositely every 45° by rotating the sample with respect to the plane of polarization. Furthermore, the stored image by photopolymerization in the SmC* phase has been stable for 10 months at room temperature. These results suggest that the procedure is applicable to optical recording.

4. Conclusion
We used FLC monomers with polymerizable group attached to the rigid core through a short alkyl spacer and a long alkyl spacer, and evaluated its in-situ photopolymerization behavior on the basis of molecular alignment in the LC phase. Polymerization behavior was considerably affected by length of alkyl spacer and functional group. The change of macroscopic structure is more effective in the polymerization monomer having a short spacer. The initial rate of polymerization was affected strongly by molecular alignment, and polymerizability of the FLCs was highest in the SmC* phase in the absence of an external electric field. When the FLC monomers were highly ordered by the external electric field, the acrylate exhibited different polymerization behavior from methacrylate. These results suggest that the polymerizability of the monomeric FLCs is dependent on the viscosity in early stage of polymerization. In addition, we demonstrated image storage using bistable switching by applying electric field.

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References