In Situ Photopolymerization Behavior of a Chiral Liquid-Crystalline Monomer Showing a Ferroelectric Phase

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ABSTRACT: The in situ photopolymerization behavior of a ferroelectric liquid-crystalline (FLC) monomer possessing a chiral moiety is discussed on the basis of molecular alignment in the liquid-crystalline phase. In an early stage of polymerization, the polymerizability of the FLC monomers was highest in the ferroelectric chiral smectic C (SmC*) phase in the absence of an external electric field. The polymerization behavior was found to depend mainly on the molecular alignment in the initial state of polymerization. In contrast, in the late stage of polymerization, the polymerization behavior of the FLC monomers was governed by their diffusion rather than their alignment. This may be due to the change in the phase structure during in situ polymerization. In addition, the alignment of the photopolymerized FLC was evaluated by optical polarizing microscopy. It was found that the application of an electric field to the FLC monomer resulted in the appearance of the immobilized SmC* phase, in which all mesogens of the resulting FLC polymer were aligned in one direction, leading to the formation of a monodomain of LC phase.

I. Introduction

Currently, precision polymerization is a topical subject of study in polymer chemistry. In the preparation of functionalized synthetic polymers, it is important to control molecular weight, molecular weight distribution, polymer sequence, stereoregularity, and highly ordered structures.[1] In particular, many studies have been performed on the control of the stereoregularity of synthetic polymers by radical,[2] cationic,[3] anionic,[4] and coordination[5] polymerization techniques. Stereoregularity arises mainly from nonbonded interactions (steric hindrance) between a growing chain and an entering monomer (chain-end control)[2−4,5d,h] and between a catalyst and an entering monomer (enantiomorphic-site control).[5a−c,e−g,i] In both cases, chiral species in the vicinity of the growing chain end including the catalyst act as an active site to control the stereoregularity of the polymers produced.[6] Alternatively, it may be possible that the stereoregularity can be controlled by molecular alignment in liquid-crystalline systems. Liquid crystals (LCs) spontaneously form organized molecular systems, and their alignment can be controlled readily by the application of an external field.[7] So it is expected that polymerization in a highly aligned state such as an LC phase can produce polymers with special properties. Such control by molecular alignment in whole polymerization processes could be promising as a novel approach to control of the stereoregularity.

Ferroelectric LCs (FLCs) have been studied for photonic and nonlinear optical materials.[8] The advantages of FLCs in electrooptical applications are their rapid response and their high intrinsic molecular hyperpolarizability.[9] FLCs, which contain a chiral group in a molecule, are characterized by the existence of spontaneous polarization and specific phase structure [chiral smectic C (SmC*) phase], particularly when thinly sandwiched between two glass substrates.[10] This phase is called the surface-stabilized ferroelectric liquid crystal state, in which FLC molecules are organized to give a state with C_2 symmetry. 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 to be within the LC temperature range, of FLC monomers is expected to show specific polymerization behavior. Many studies have been performed so far on the polymerization behavior of LC monomers in nematic (N), smectic (S), and cholesteric (N*) phases,[11] but the photopolymerization behavior of the FLC monomer showing the SmC* phase has not yet been reported except for the study on its application to optoelectric materials.[12] In the present study, we used an FLC monomer, which had an acrylate polymerizable unit and a chiral group in terminal aliphatic chain, and evaluated the photopolymerization behavior as well as the molecular alignment before and after photoirradiation.

II. Experimental Section

II.1. Materials. II.1.1. FLC Monomer. The structure and phase transition temperature of the FLC monomer {(*R*)-1-methylheptyl4′-[(4-((ω-(acryloyloxy)undecyl)oxy)benzoyl)oxy]-biphenyl-4-carboxylate} used in this study are shown in Figure 1. The FLC monomer was prepared according to the synthetic method reported previously.[13] The compound was characterized by means of ^{1}H NMR (Bruker AC200, 200 MHz), IR

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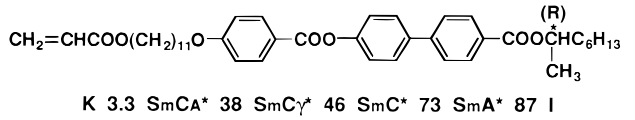

Figure 1. Chemical structure and phase transition temperature of the ferroelectric liquid-crystalline monomer used in this study.

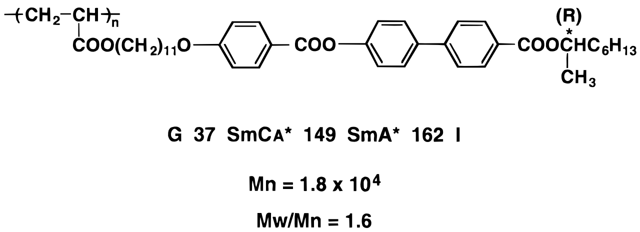

Figure 2. Structure and characteristic of the polymer obtained by solution polymerization of the ferroelectric liquid-crystalline monomer.

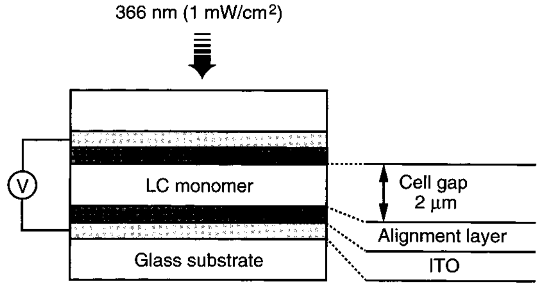

Figure 3. Ferroelectric liquid-crystal cell used in the evaluation of in situ photopolymerization behavior.

(Hitachi 260-10), and elemental analysis. The phase transition temperature and the phase structure were determined by differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C; cooling rate, 1 °C/min) and optical polarizing microscopy (Olympus Model BH-2; Mettler FP82HT hot stage and Mettler FP90 central processor). As described in Figure 1, the FLC monomer showed various phases with temperature: crystalline (K), antiferroelectric ($\mathrm{SmC_A}$*), ferrielectric (SmCγ*), ferroelectric (SmC*), smectic A* (SmA*), and isotropic liquid (I) phases.

II.1.2. Preparation of Phase Diagram. Before evaluation of the in situ photopolymerization behavior of the monomeric FLCs, we evaluated the phase transition behavior during polymerization because it is assumed that, during photoirradiation, accumulation of the polymer produced in the LC phase is accompanied by changes in the phase transition temperatures due to change in the composition of the monomer–polymer mixture. To prepare the phase diagram in the binary mixture of the polymer and the monomer, the FLC polymer was synthesized by the conventional solution polymerization (Figure 2). Radical polymerization of the monomer (0.3 g) with 1 mol % of azobis(isobutyronitrile) (AIBN) in dry dimethylformamide (3 mL) was carried out in a tube under vacuum for 48 h at 60 °C. The polymer produced was precipitated into a large excess of methanol. To purify the polymer, it was dissolved in chloroform and precipitated into methanol. The purification was repeated until no monomer was detected by gel permeation chromatography (GPC). The polymer was dried in vacuo at room temperature. The phase transition temperature and the phase structure were determined by DSC (10 °C/min) and optical polarizing microscopy. The polymer exhibited glassy (G), $\mathrm{SmC_A}$*, SmA*, and I phases.

II.2. In Situ Photopolymerization Procedure. Photopolymerization was performed in a glass cell with a gap of 2 μm without an electric field or under a 3 V/μm dc electric field. The glass cell was composed of two indium tin oxide (ITO) glass substrates with rubbed polyimide alignment layers (Figure 3). Samples for photopolymerization were prepared by injecting the FLC monomer, containing benzoin as a photoinitiator (2 mol %), into the glass cell in the I phase at 90 °C using capillary action. Here we confirmed that the concentration of the photoinitiator was small enough not to destabilize the LC phases, and no spontaneous thermal polymerization occurred during injection of the FLC 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 slowly (0.5 °C/min) to a temperature at which photopolymerization was attempted. Photoirradiation was performed at 366 nm (intensity, 1 mW/cm^2), isolated with glass filters from a 500-W high-pressure mercury lamp. In the photopolymerization under an electric field, the samples were cooled slowly under an ac electric field (1 Hz, 3 $\mathrm{V_{pp}}/\mu$m) 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 a dc electric field of 3 V/μm during polymerization.

The course of the polymerization was followed by gel permeation chromatography (GPC, JASCO DG-980-50; column, Shodex GPC K802 + K803 + K804 + K805; eluent, chloroform). The conversion was estimated from eq 1

$$\text{conversion (\%)} = P/(P + M) \times 100 \qquad (1)$$

where P is the peak area in the GPC chart corresponding to the polymers produced and M is that corresponding to the unchanged monomers. The molecular weights of the polymers were determined by GPC calibrated with standard polystyrenes. Each GPC measurement was repeated three times, and we confirmed that the reproducibility of the conversion and the molecular weight was invariably good. This fact was verified by the interval estimation of each data point, which was the mean for triplicate runs. The statistics showed that the 95% confidence limits analyzed from the sample mean and the sample standard deviation on the repeated runs were within ±3% and ±5600 for conversion and molecular weight, respectively. These results indicate clearly that the GPC method is reproducible and that the resulting experimental data are reliable.

II.3. Evaluation of Alignment of Polymerized FLC. The degree of alignment of the polymerized FLC after photoirradiation with and without an electric field in the 2-μm-gap cell was explored by means of optical polarizing microscopy. The molecular alignment was evaluated from the angular dependence of the transmittance of linearly polarized light through the sample cell.

As described in the previous section, FLCs have a spontaneous polarization in the surface-stabilized state due to the alignment of dipoles into one direction, and they exhibit bistable states via inversion in the direction of the spontaneous polarization. When an electric field with reverse polarity is applied across the cell, the polarization flips into the opposite direction and simultaneously the aligning direction of the long axis of each FLC molecule changes. In the polymerized FLC, we examined if the polarization flipped by changing the polarity of the applied electric field and evaluated the difference in electric response between the irradiated and the unirradiated sites in a sample cell.

III. Results and Discussion

III.1. In Situ Photopolymerization Behavior. It is important to investigate the changes in the phase transition temperature due to changes in composition of the monomer–polymer mixture.[14] Several samples were prepared in which the mixing ratio of the monomeric and the polymeric FLCs was altered, and the binary mixtures were subjected to DSC and microscopic observation to explore the phase transition. The phase

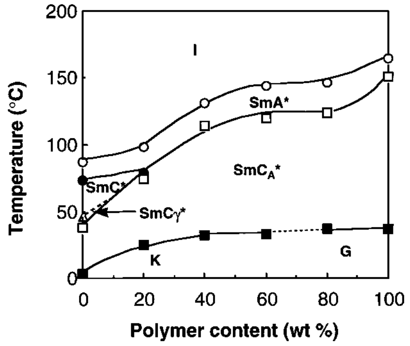

Figure 4. Phase diagram for mixtures of monomer and polymer.

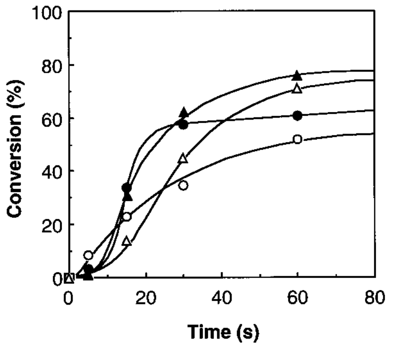

Figure 5. Time–conversion curves for photopolymerization at various temperatures in a glass cell with a gap of 2 μm: (○ and ●) 40 °C; (△ and ▲) 80 °C; (○ and △) without an electric field; (● and ▲) with an electric field of 3 V/μm.

diagram is shown in Figure 4. In the region with a low polymer content (less than 10 wt %), the phase transition temperature changed only slightly. This result demonstrates that the change in the phase structure could be negligible during the early stages 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$_A$* phase increased considerably.

The 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 time–conversion curve obtained by photoirradiation at the light intensity 1 mW/cm^2 is shown in Figure 5. The conversion showed a tendency to increase with increasing irradiation time, irrespective of the polymerization temperature. The time course of the photopolymerization was similar to that of the general thermal polymerization in solution.[15] A similar trend was observed for a sample under an electric field. On the basis of the phase diagram shown in Figure 4, it is assumed that no phase transition occurs at least on 5-s irradiation due to the low content of the polymer produced. On the other hand, after a 60-s irradiation the conversions reached above 50% irrespective of polymerization temperature. Under such conditions 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 and 60-s irradiations as a measure to explore the in situ photopolymerization behavior of the FLC monomer.

III.1.1. Polymerization Behavior in Early Stage of Polymerization. The open symbols in Figure 6 show plots of conversion after a 5-s irradiation versus

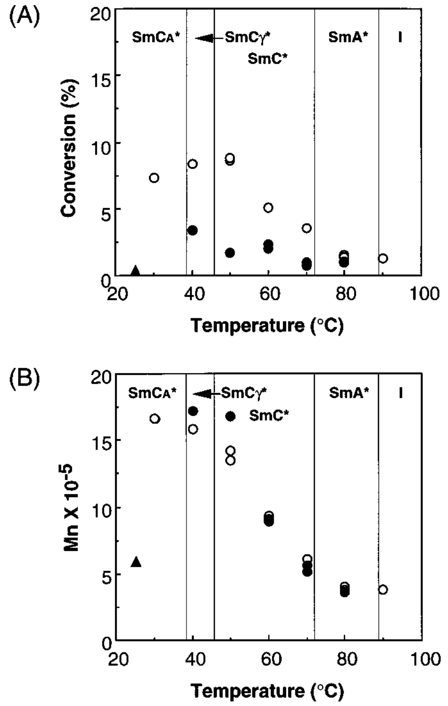

Figure 6. Polymerization behavior after a 5-s photoirradiation at various temperatures in a glass cell: (A) conversion; (B) number-average molecular weight; (○) without an electric field; (●) with an electric field of 3 V/μm; (▲) K phase at 25 °C for 24 h after cooling.

temperature without an electric field. The conversion was high below 50 °C, at which the FLC monomer shows SmC$_A$*, SmCγ*, 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. Such effects of the external electric field on the polymerization rate have been investigated also for the chiral LC monomer showing the SmA phase, and the polymerization rate seems to be dependent on the efficient collision between polymerizable groups.[16] Therefore, the enhancement of polymerizability may be due to the proximity of the polymerizable groups in the surface-stabilized state, in which the distance between the polymerizable groups is very small in each layer of the SmC* phase. It has also been reported that the macroscopic alignment of the LC monomers does not effect the polymerization kinetics.[11j] Unfortunately, the conversions obtained by photoirradiation after a 5-s irradiation with the dc electric field were much smaller than those obtained without the electric field (closed symbols in Figure 6A).

The FLCs have a helicoidal structure in the bulk. This helical structure arises from two kinds of molecular interactions: one is a spontaneous bend which is a result of the polar symmetry.[17] 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 the

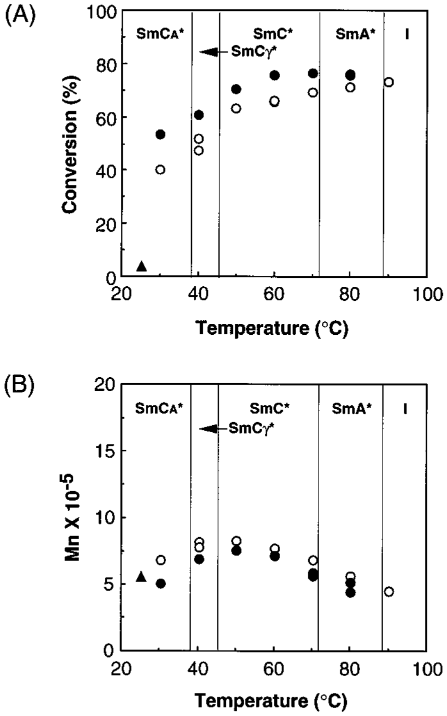

Figure 7. Polymerization behavior after a 60-s photoirradiation at various temperatures in a glass cell: (A) conversion; (B) number-average molecular weight; (○) without an electric field; (●) with an electric field of 3 V/μm; (▲) K phase at 25 °C for 24 h after cooling.

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 the K phase, in which the FLC molecules show no mobility, the conversion was only 0.13% and their polymerizability was extremely low (triangular symbol in Figure 6A). Consequently, the polymerizability of the FLC monomers in an early stage of polymerization is governed by their molecular alignment as well as their mobility in the LC phase.

The relation between the molecular weight of the polymer produced and polymerization temperature is shown in Figure 6B. The values of the number-average molecular weight were larger in the low-temperature region (SmC$_A$*, SmCγ*, and SmC* phases). This is presumably due to a decrease in the 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 is needed to obtain high-molecular-weight polymers.

III.1.2. Polymerization Behavior in Late Stage of Polymerization. The polymerization behavior on a 60-s irradiation was different from that on a 5-s irradiation. As shown in Figure 7A, the conversion increased monotonically with the temperature. This result demonstrates that the polymerization behavior in the late stage of polymerization was not affected by the initial molecular alignment of the FLC monomer. On the basis of the phase diagram and the time−conversion curve shown in Figures 4 and 5, respectively, during a 60-s irradiation the initial phase structure is assumed to change to SmC$_A$* in the wide temperature region. Thus, the observed polymerization behavior may be ascribed to the change in the phase structure during photoirradiation. This is also evident from the fact that the molecular weights are almost the same irrespective of the initial phase structure (Figure 7B). A similar phase transition during photoirradiation has been reported by Hoyle et al. The photopolymerization behavior has been affected by phase changes during polymerization.[11h,i,14] In addition, by applying the electric field during polymerization, the conversion increased slightly at any temperature (closed symbols in Figure 7A). These results suggest that, in the late stage of polymerization, the polymerization behavior of the FLC monomers is governed by molecular diffusion, as described above, rather than their alignment.

III.2. Stereoregularity of FLC Polymer. The stereoregularity of the FLC polymer produced was evaluated by ^{13}C NMR spectroscopy (JEOL EX400, 400 MHz).[18] The chemical shift of the carbonyl near the polymer backbone of the photopolymerized FLC was found to be 176−178 ppm, which was similar to that of an atactic FLC polymer obtained by solution polymerization. Unfortunately, the stereoregularity could not be controlled by the molecular alignment in the LC phase. The FLC monomer used in this study possesses a long alkyl spacer between the polymerizable group and the aromatic rigid core. The terminal polymerizable groups attached to the rigid cores through the long chain are not aligned fully even in the ferroelectric surface-stabilized state due to the flexibility of the alkyl chain, resulting in the nonappearance of the stereoregularity. This may be solved by reduction of the spacer length between the polymerizable group and the core.

III.3. Alignment of Photopolymerized FLC. The molecular alignment of the FLCs was explored by optical polarizing microscopy after the photopolymerization was conducted in the 2-μm-gap cell at 60 °C in the SmC* phase. Figure 8 shows the optical textures of the FLC after photoirradiation in the absence of the electric field, where the left and the right halves of each micrograph show the irradiated and the unirradiated sites, respectively. In the unirradiated site, when the alternating electric field of ±3 V/μm was applied across the cell, the dark and the bright views of birefringent texture were observed alternatively according to the polarity of the electric field (Figure 8A and B). This result implies that the polarization flipped from one direction to the opposite direction. In contrast, in the irradiated site, such a change in the texture was not observed. Furthermore, when the sample was heated to 90 °C, which was higher than the SmA*−I phase transition temperature of the monomeric FLC, the optical texture disappeared only in the unirradiated site, irrespective of the polarity of the electric field (Figure 8C). Therefore, in the unirradiated site the polymerization was not initiated, while in the irradiated site the initial aligned state was stabilized by the photopolymerization even in the absence of the electric field.

Figure 9 shows the polarized optical micrographs of the sample before and after photopolymerization in the presence of a 3 V/μm dc voltage. Before photoirradiation, the polarization flip was confirmed at first to occur

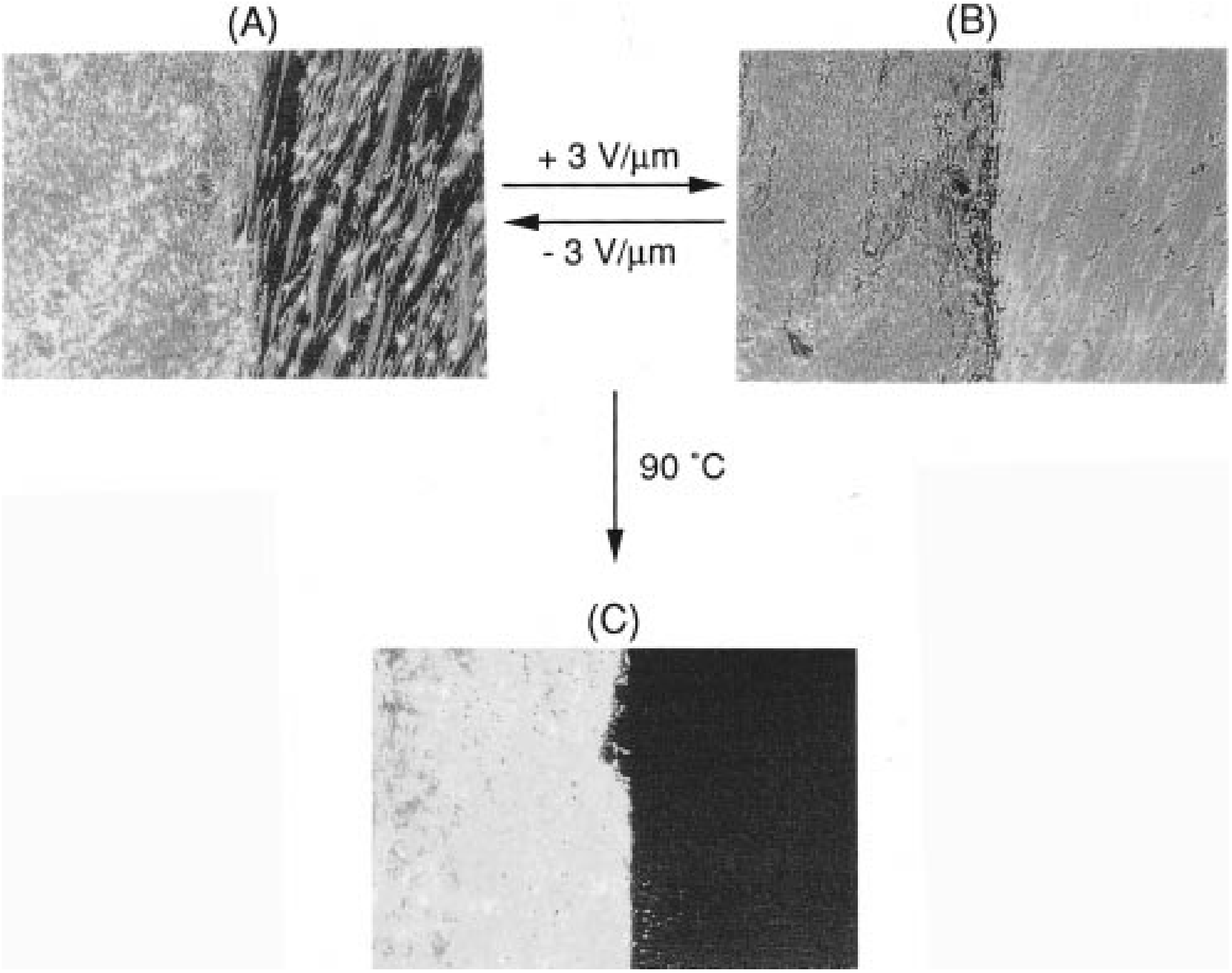

Figure 8. Polarized optical micrographs of the texture observed in the 2-μm-gap cell after a 60-s photoirradiation of the FLC monomer without an electric field at 60 °C in the SmC* phase. The left and the right halves of the figures correspond to the irradiated and the unirradiated sites, respectively: (A) texture obtained on application of an electric field of -3 V/μm; (B) texture observed on application of an opposite electric field (3 V/μm); (C) texture obtained after heating to 90 °C, at which the FLC monomer shows an I phase.

by application of the alternating electric field (Figure 9A and B). The optical texture after photoirradiation was the same as that before photoirradiation (Figure 9C), but the polymerized FLC showed no response to the electric field (0.1 Hz to 1 kHz, 10 V_{pp}). This immobilization of molecular alignment could be attributed to low mobility of mesogens of the polymerized FLC. It is known that the general vinyl monomers are accompanied by volume shrinkage on polymerization, and the degree of the volume shrinkage is approximately 15−35%.[19] The shrinkage during the polymerization, practically, was observed for the LC monomer showing S and N phases.[11j] Since the mobility of LC molecules could be affected significantly by a change in environmental conditions, the mobility of the FLC molecules linked to a polymer backbone may decrease in comparison with that of free FLC molecules. It is reasonable that the decrease of the mobility of mesogens by the polymerization results in no change in the molecular alignment even in the presence of the external field.

The effect of electric field on the alignment of mesogens of the polymerized FLCs was investigated in more detail. The optical textures observed at the ITO electrode−glass substrate interface in the LC cell are shown in Figure 10. The left side of each figure shows the texture of the polymerized FLC obtained by the polymerization with the electric field, and the right side shows that obtained without the electric field. The angular dependence of the transmittance of linearly polarized light through the FLC cell was significantly different between the left and right sides. As shown in Figure 10, the position of the sample cell between the crossed polarizers was adjusted at first so as to transmit thoroughly the linearly polarized light. When the sample cell was rotated with respect to the polarizers, only the left side became dark. The contrast between the dark and the bright views on the left side was found to be highest at every 45° interval. This is because the tilt angle of the FLC monomer at 60 °C is 23°. On the other hand, on the right side the brightness of the optical texture was almost independent of the rotation of the cell. These results clearly indicate that the application of the external electric field to the sample results in the appearance of the immobilized SmC* phase, in which all mesogens of the polymerized FLC are aligned into one direction to form a monodomain of the LC phase. Such immobilization of the SmC* phase is quite favorable from the viewpoint of optical applications.

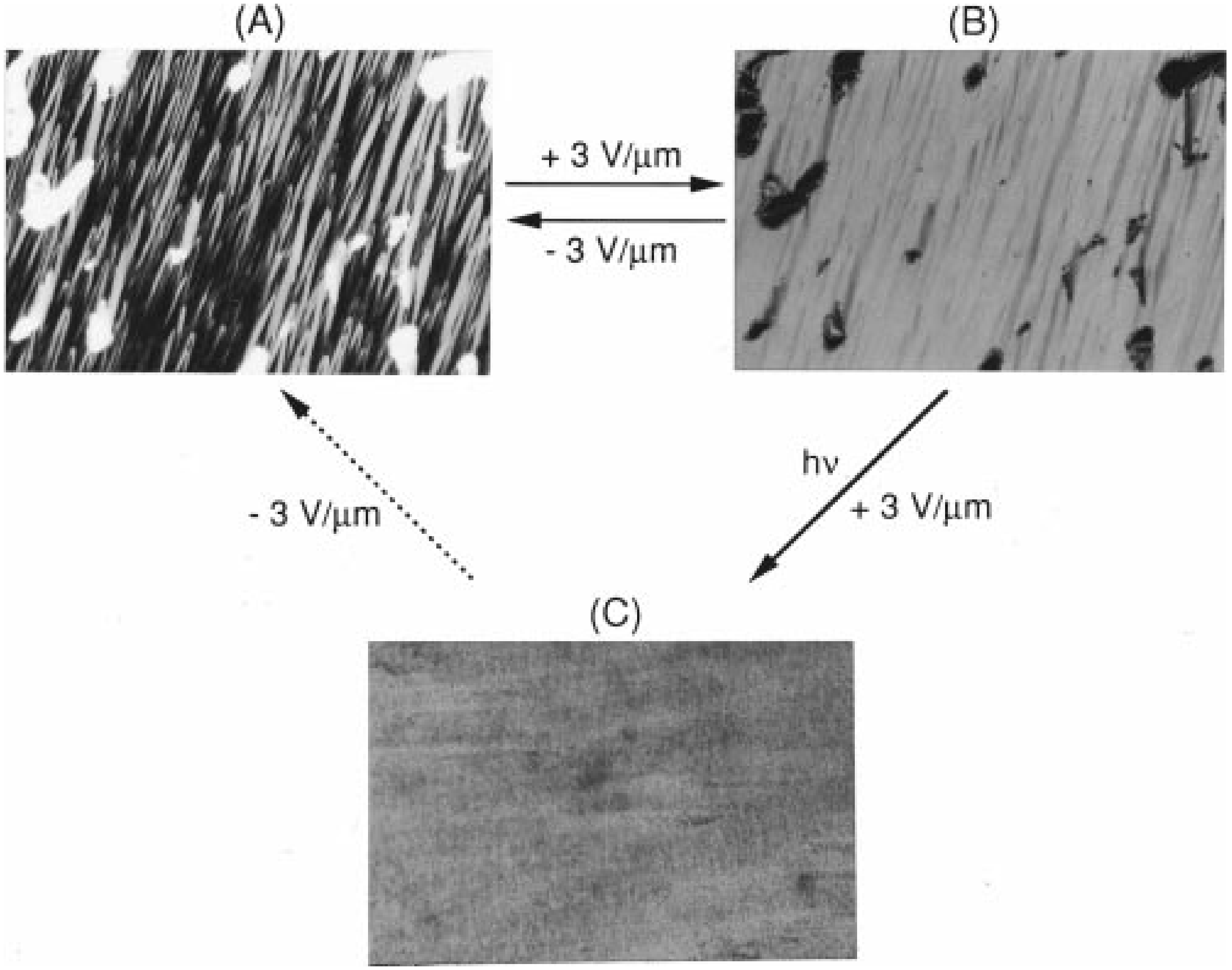

Figure 9. Optical textures observed in the 2-μm-gap cell before and after photopolymerization of the FLC monomer under the constant electric field of 3 V/μm. Photoirradiation was carried out at 60 °C for 60 s: (A) dark view with an electric field of -3 V/μm before polymerization; (B) bright view on application of an opposite electric field (3 V/μm); (C) texture obtained after polymerization.

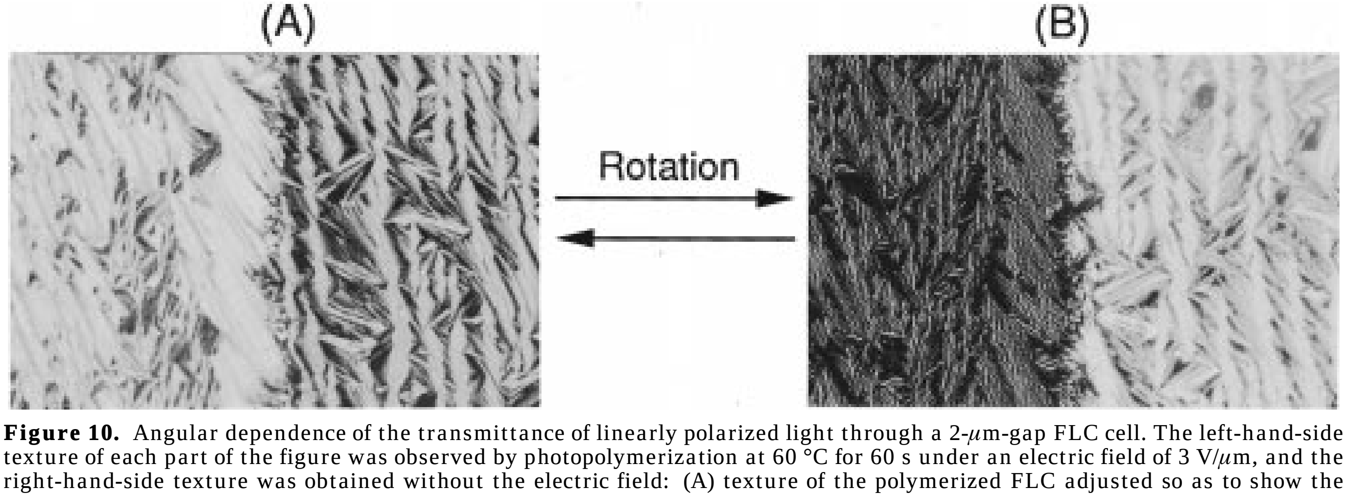

Figure 10. Angular dependence of the transmittance of linearly polarized light through a 2-μm-gap FLC cell. The left-hand-side texture of each part of the figure was observed by photopolymerization at 60 °C for 60 s under an electric field of 3 V/μm, and the right-hand-side texture was obtained without the electric field: (A) texture of the polymerized FLC adjusted so as to show the maximum brightness; (B) texture observed when the FLC cell was rotated 45° with respect to the initial position.

IV. Conclusion

We used a chiral liquid-crystalline monomer showing a ferroelectric phase and evaluated its in situ photopolymerization behavior on the basis of the molecular alignment in the LC phase. The initial polymerization rate was affected strongly by molecular alignment, and the 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, however, the conversions obtained were much smaller than those obtained without the electric field irrespective of polymerization temperature (i.e., phase structure). These results suggest that in the early stage of polymerization the polymerizability of the monomeric FLCs is dependent on both the molecular alignment and the molecular diffusion. Conversely, in the late stage of polymerization, the polymerization behavior of the FLC monomers was governed by their diffusion rather than their alignment. The conversion monotonically increased with the temperature. This may be ascribed to the change in the phase structure during in situ polymerization. In addition, the alignment of the photopolymerized FLC was evaluated by optical polarizing microscopy. It was found that the FLCs polymerized under the electric field formed the immobilized SmC* phase retaining the monodomain of the LC phase before photopolymerization. The stereoregularity of the polymerized FLC was evaluated by ^{13}C NMR spectroscopy. Unfortunately, the stereoregularity could not be controlled by the molecular alignment in the LC phase. In the near future, this may be solved by improvement of molecular design.

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