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Polymerization of liquid-crystalline monomers having a Schiff-base structure

Sayuri Ogiri, Masanori Ikeda, Akihiko Kanazawa, Takeshi Shiono, Tomiki Ikeda*

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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Abstract

Vinyl monomers having a Schiff-base structure were synthesized and their thermal and photopolymerization behavior was explored for different phases of the monomers. It was found that conversion of the monomers increased with temperature in the nematic phase, while it decreased in the isotropic phase. This result suggests that the polymerization behavior may be affected by the molecular alignment. Arrhenius plots for the initial rates of photopolymerization showed a straight line, while those of thermal polymerization changed in slope at the nematic–isotropic phase transition temperature. For MBEA, the number-average molecular weight of the polymer produced by thermal polymerization in the nematic phase was higher than that in the isotropic phase. For ABBA, it was observed that birefringence partially remained in the polymer produced in the nematic phase, although polymer produced by solution polymerization showed no liquid-crystalline phase. In addition, the orientation of the crosslinked polymer obtained by photopolymerization was better than that of the polymer produced by thermal polymerization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Schiff-base; Liquid crystal; Orientation

1. Introduction

Highly oriented polymers exhibit anisotropy in their optical, electrical and thermomechanical properties [1–4]. Many studies have recently been reported on polymer films with an anisotropic molecular alignment obtained by the bulk polymerization of liquid-crystalline (LC) monomers such as acrylate [5–11], methacrylate [12–16], vinyl ether [17,18], epoxide [19,20] and styrene [21,22] derivatives. The LC monomers, especially nematic (N) LC monomers which exhibit a lower viscosity than smectic (S) LC monomers, can be macroscopically oriented by external forces such as an electric and a magnetic field, elongational flow and surface orientation (e.g. by a rubbed polyimide layer). The monomer organization may affect the polymerization kinetics, the polymer structure and the microstructure of the macromolecules [9–14,17,18]. The effect of LC ordering on the polymerization behavior of mesomorphic vinyl monomers has been investigated extensively. However, there is little agreement concerning the influence of the two basic properties of LC materials on the polymerization behavior: orientation and mobility, and these two competing factors make it difficult to formulate a general statement on the effect of LC ordering on the polymerization behavior and hence explain the variance in results. Paleos and Labes reported the synthesis and polymerization of acrylic and methacrylic Schiff-base molecules which formed LC phases [23]. The polymerization behavior was not affected by the phase structures and external forces. On the other hand, Perplies et al. demonstrated that the polymerization behavior of Schiff-base molecules was affected by the phase structure and external forces such as a magnetic field; the rate increased suddenly when the phase became isotropic (I) or an LC phase under an electric field [24–26]. Therefore, the polymerization of each mesomorphic monomer that has a Schiff-base structure has to be studied in more detail. The aims of the present work are to elucidate the effect of the structure of the N and I phases, on the polymerization behavior of monomers which have a Schiff-base structure, and to explore the orientation of polymers obtained by thermal polymerization and photopolymerization in detail. To eliminate the effect of the molecular structure on the polymerization behavior, methacrylate monomers having the same structures except the end-group but with different phase behaviors were examined; the monomer having an

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* Corresponding author. Tel: +81-45-924-5240; Fax: +81-45-924-5275; E-mail: tikeda@res.titech.ac.jp

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ethyl end-group shows no LC phase, while the other having an ethoxyl end-group exhibits an N phase.

2. Experimental

2.1. Materials

Three monomers: (4-methacryloyloxybenzylidene)-4-ethylaniline (ME), (4-methacryloyloxybenzylidene)-4-ethoxyaniline (MBEA) and (4-acryloyloxybenzylidene)-4-butoxyaniline (ABBA), were used in this study and the structures and transition temperatures are shown in Fig. 1. The monomers were synthesized as reported previously [26–28]. All compounds were purified by column chromatography on silica gel (eluent, chloroform–ethyl acetate (30:1)) and were recrystallized from hexane. The compounds were characterized by ^{1}H NMR spectroscopy (Brucker AC200; 200 MHz), IR spectrophotometry (Hitachi 260-10) and elemental analysis. The phase transition temperatures and the phase structures were determined by differential scanning calorimetry (DSC; Seiko I and E SSC-5200 and DSC220C; heating and cooling rate, 5°C min^{-1}) and optical polarizing microscopy (Olympus model BH-2; Mettler FP82HT hot stage; Mettler FP90 central processor).

The reference polymer of ABBA was prepared by solution polymerization with use of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator. ABBA (0.5 g) with 2 mol% of AIBN was dissolved in benzene (5 ml) and the solution was placed in a tube, which was then evacuated under vacuum and sealed. Polymerization was conducted at 60°C for 44 h. The polymer was purified by dissolution in chloroform and precipitation into methanol. The purification was repeated until no monomer was detected by gel permeation chromatography (GPC). The polymer was dried under vacuum at room temperature. Poly(ABBA) exhibited no LC phase and thermal decomposition occurred above 200°C.

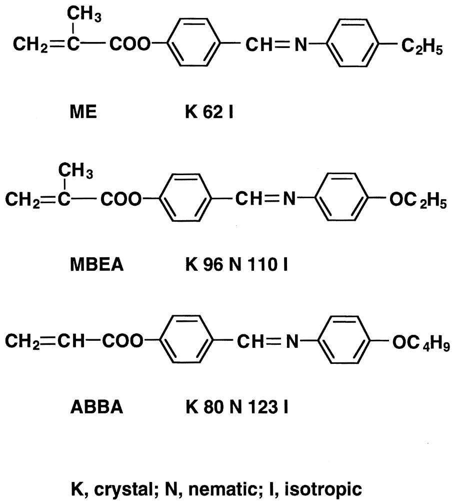

Fig. 1. Structures and phase transition temperatures of monomers used in this study.

2.2. Polymerization procedure

We confirmed that spontaneous thermal polymerization had occurred during the injection of ME or MBEA into the glass cell, so ME and MBEA were thermally polymerized without an initiator. However, no thermal polymerization occurred spontaneously during the injection of ABBA into the glass cell. Therefore, a mixture of ABBA and initiator (2 mol%) was prepared by dissolving each component in dichloromethane and subsequently evaporating the solvent under vacuum. Benzil was added as a photoinitiator and AIBN was used as a thermal initiator.

Thermal polymerization of the monomers was carried out isothermally at various temperatures within the range from 65 to 150°C. Monomer samples (5–8 mg) containing AIBN (2 mol%) were placed in indented DSC pans and the parts were sealed, and they were maintained in the I phase for 10 min in the calorimeter. For ME and MBEA, AIBN was not included in the sample. The samples were then slowly cooled down to the polymerization temperature. The conversion was determined by calculating the enthalpies from the area under the DSC curve [29,30]. The initial rate of polymerization was calculated from the initial slope of the time–conversion curve.

Photopolymerization was performed in a glass cell with a gap of 20 μm. Samples for photopolymerization were prepared by injecting ABBA containing benzil as photoinitiator (2 mol%) into the glass cell in the I phase. After the samples had been prepared, they were slowly cooled down to the polymerization temperature. Photoirradiation was performed at more than 430 nm (intensity at 436 nm, 90 mW cm^{-2}) employing glass filters and a 500 W high-pressure mercury lamp as source. The course of the polymerization was followed by GPC (Toyo Soda HLC-802; column, GMH6 $\times$ 2 + G4000H8; eluent, chloroform). The conversion was estimated from Eq. (1).

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

where P is the peak area on the GPC chart corresponding to the polymers produced and M is that corresponding to the unreacted monomers. The number-average molecular weight (M_n) of the polymers was determined by GPC calibrated with standard polystyrenes.

The gel was extracted with chloroform in the Soxhlet extractor for 15 h. The extract was concentrated and soluble polymer was recovered by precipitation of the solution into a large excess of methanol. The gel fraction was estimated by Eq. (2)

$$\text{Gel fraction}\ (\%) = G/(S + G) \times 100 \tag{2}$$

where S is the yield of soluble polymer and G is the yield of the insoluble part.

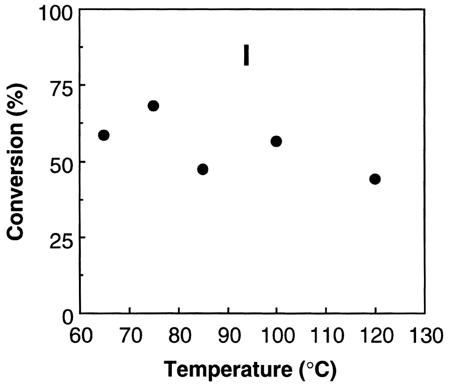

Fig. 2. Final conversion in the thermal polymerization of ME at various temperatures. Initiator was not used in the polymerization.

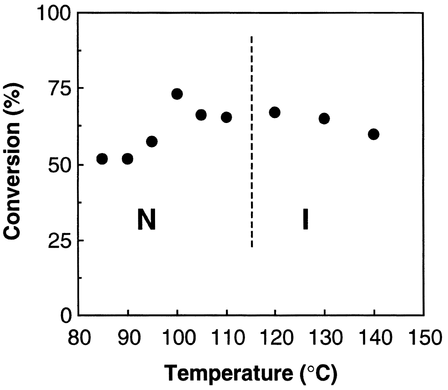

Fig. 4. Final conversion in the thermal polymerization of ABBA with AIBN (2 mol%) at various temperatures.

3. Results and discussion

3.1. Polymerization behavior

Polymerization was performed in three distinct temperature regions: (a) in the crystalline (K) phase; (b) in the N phase; and (c) in the I phase. The results are shown in Figs 2–4, where the final conversions are plotted as a function of the polymerization temperature. No polymerization occurred in the K phase of the monomers used in this study. The final conversion decreased as the temperature increased in the I phase in every monomer (Figs 2–4). However, the conversion increased with temperature in the N phase. These results are in fair agreement with those of Perplies et al. [24–26]. They suggested that the orientation of the monomers affects the polymerization behavior. Furthermore, the viscosity decreases as the temperature increases; the addition of monomers to the propagating polymer radicals then becomes favored due to enhanced diffusion of each species, which may result in a higher conversion with temperature in the N phase. For ME and MBEA, the T_g values of the polymers were 216°C and 210°C, respectively. Maximum conversions were below 75% for the three monomers in this study. It is assumed that the maximum conversions are affected by both equilibrium polymerization and diffusion-controlled termination. Since the M_n decreased with temperature for MBEA at higher temperatures (above 120°C), it is expected that equilibrium polymerization mainly affects the kinetics. For ABBA, it is expected that the half-life of the initiator decreases because of the high polymerization temperature. It can therefore be presumed that dead-end polymerization occurs in this system.

Fig. 5 shows initial rates of the thermal polymerization of ABBA with AIBN (2 mol%) at various temperatures. The initial rate of polymerization increased monotonically with temperature. Similar results were obtained for the other monomers used in this study. The rate of thermal polymerization (R_p) is expressed by Eq. (3) [31]

$$R_p = (k_p/k_t^{1/2}) \times k_i^{1/2} \times [M]^2 \qquad (3)$$

where k_p, k_t and k_i are the rate constants of propagation, termination and initiation, respectively, and [M] is the concentration of the monomer. It might be expected that the increase of k_p with temperature is larger than that of k_t in the present Schiff-base monomers. The terms $(k_p/k_t^{1/2})$ and $k_i^{1/2}$ then increase with temperature and R_p increases with temperature.

Fig. 6 shows Arrhenius plots for the initial rates of the thermal and photopolymerization of ABBA. It was observed

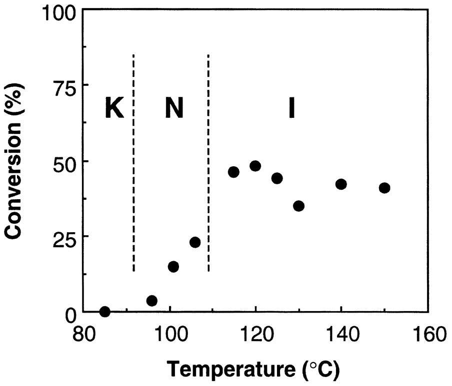

Fig. 3. Final conversion in the thermal polymerization of MBEA at various temperatures. Initiator was not used in the polymerization.

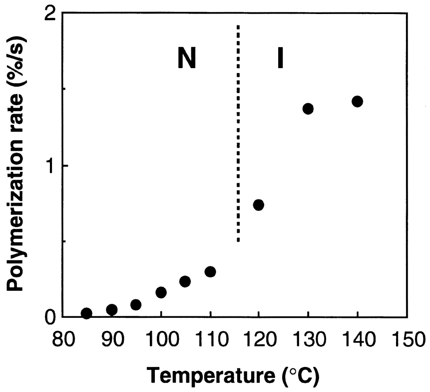

Fig. 5. Initial rates of the thermal polymerization of ABBA with AIBN (2 mol%) at various temperatures.

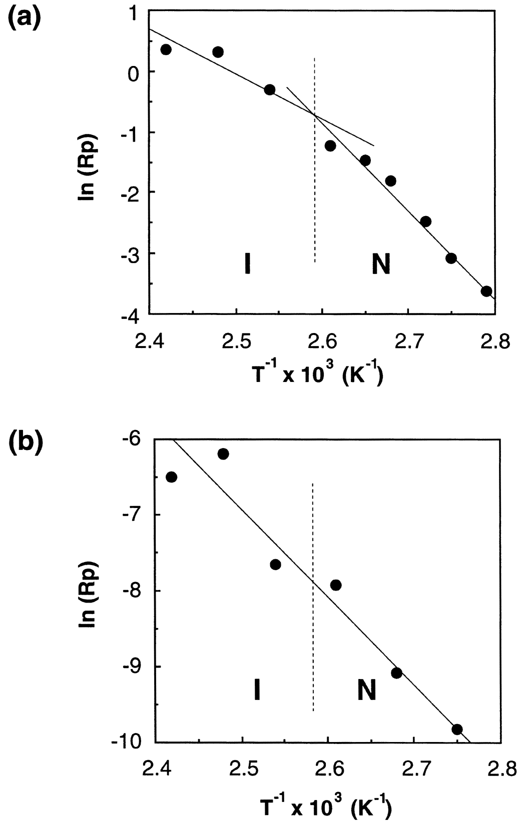

Fig. 6. Arrhenius plots for the initial rates of polymerization of ABBA. (a) Thermal polymerization with 2 mol% AIBN. (b) Photopolymerization with 2 mol% benzil.

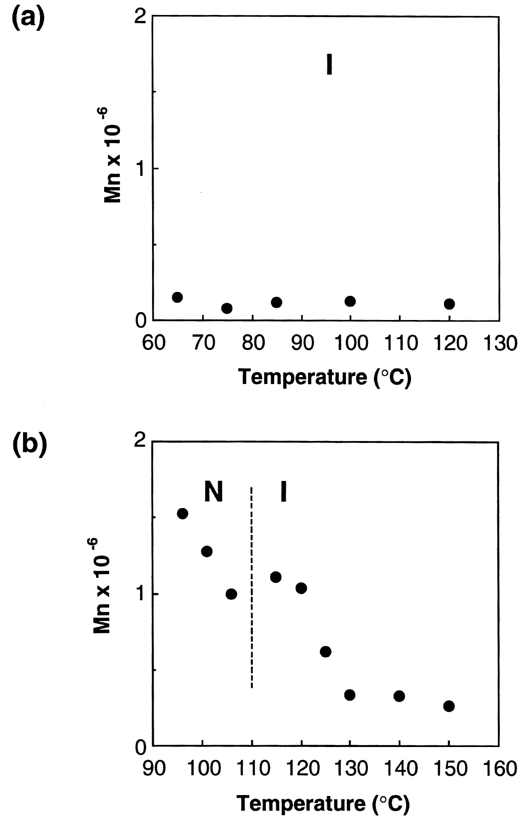

Fig. 7. The M_n of polymers obtained by thermal polymerization at various temperatures. Initiator was not used in the polymerization. (a) ME; (b), MBEA.

that for the thermal polymerization the activation energy was larger in the N phase than in the I phase. The thermal polymerization in the N phase occurs simultaneously with alignment of the monomers, so polymerization competes with the alignment process. It is expected that the alignment process of the monomers interferes with the propagation process in the polymerization. It is reasonable, therefore, that the activation energy of thermal polymerization in the N phase is larger than that in the I phase. On the other hand, the activation energy of photopolymerization was constant regardless of the phase structure of the monomer. This is presumably because photopolymerization can be carried out after the monomer is completely in equilibrium with its intrinsic phase structure.

Fig. 7 shows the relationship between the M_n of the polymer obtained and the polymerization temperature. It must be mentioned here that the M_n of the polymer produced by the thermal polymerization of ME, which showed only the I phase, was constant regardless of the polymerization temperature in Fig. 7a. On the other hand, the M_n of the polymer produced by the thermal polymerization of MBEA depended on the temperature; as is shown in Fig. 7b, the M_n of the polymer obtained in the N phase was higher than that obtained in the I phase, and the M_n increased discontinuously at a slightly higher temperature than the N–I phase transition temperature. At the latter temperature, the orientation of the monomer is absent macroscopically, but it is still present microscopically; this microscopic orientation of the monomers might then be advantageous for the reaction between propagating radicals and the monomers. At lower temperature in the I phase of the monomers, a phase transition occurs from the I to the glassy (G) phase during the polymerization of ME, although a phase transition occurs from the I to the G phase through the S phase during the polymerization of MBEA. Based on Figs 2 and 3 and Fig. 7, it is anticipated that the polymerization behavior was affected by diffusion-controlled termination for ME and by equilibrium polymerization for MBEA. This may account for the difference in the M_n of polymers obtained in the I phase between ME and MBEA. Furthermore, the M_n of the polymer obtained by the thermal polymerization of ABBA was constant at any polymerization temperature examined. It was observed that the polymer produced by the thermal polymerization of ABBA precipitated during the polymerization. Poly(ABBA) is not soluble in its monomer, ABBA, so it is expected that poly(ABBA) precipitates after the polymer attains a certain degree of polymerization. This may be an origin of the constant M_n of the polymer of ABBA for the thermal polymerization.

Fig. 8 shows the conversion for the photopolymerization of ABBA with benzil (2 mol%) at 140°C and the gel fraction in the polymer as a function of time. The conversion

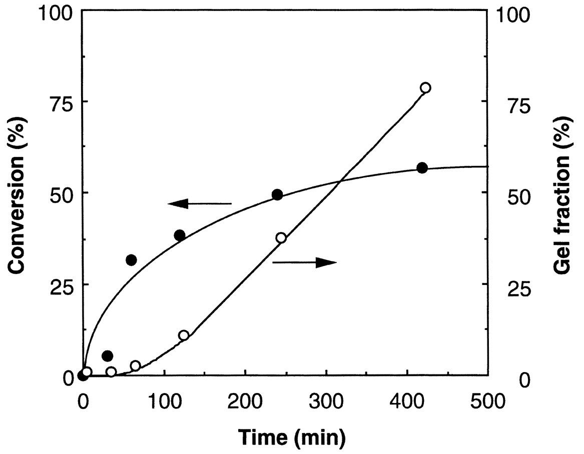

Fig. 8. Time–conversion curve (●) and gel fraction (○) for the photopolymerization of ABBA with benzil (2 mol%) at 140°C.

increased with polymerization time and was saturated at a later stage. Furthermore, gel was produced even at the initial stage of polymerization. It should be noted that the gel fraction in the polymer increased with polymerization time.

The excited triplet state (T_1) of benzil abstracts hydrogen atoms from hydrogen-donating molecules such as the polymers produced and the monomers [32]. When hydrogen atoms of the polymers are abstracted, polymer radicals are produced and the resulting polymer radicals are readily recombined to form crosslinks. To clarify whether this is the case, poly(ABBA) synthesized separately by solution polymerization was irradiated at 366 nm in the presence of benzil (2 mol% with respect to the monomer units in the polymer) in the cell. It was found that a gel was formed.

3.2. Alignment of polymer produced

The molecular alignment of the polymers was explored by optical polarizing microscopy. To compare the orientation of the polymers produced by thermal polymerization and photopolymerization, ABBA was polymerized in the N and I phases in cells with a 20 μm gap. After the polymerization, the cell was opened and the polymerization mixture was thoroughly washed with methanol to remove unreacted monomers and initiator. Washing of the product was repeated until no absorption of the monomer and initiator was detected in the washings by UV absorption spectroscopy. The sample was then dried and examined with the polarizing microscope to determine the optical anisotropy.

The polymers produced in the I phase showed no birefringence either for the thermal polymerization or the photopolymerization. Surprisingly, however, the polymers prepared in the N phase showed birefringence regardless of the polymerization method. The birefringence was very stable and remained unchanged up to 200°C in both samples obtained by thermal polymerization and by photopolymerization. The optical texture observed after the thermal polymerization at 90°C in the N phase is shown in Fig. 9a. Black circular parts were observed in the texture, which presumably resulted from the evolution of nitrogen gas on the decomposition of AIBN. As is seen clearly, the polymer, after polymerization in the N phase, partially exhibited an LC phase. It must be emphasized here that poly(ABBA) obtained by solution polymerization showed no LC phase. This means that poly(ABBA) displays no LC nature even though its monomer is mesogenic. It is well known that the orientation of LC molecules is strongly affected by the interface between the LC molecules and the substrate [33,34]. In fact, in LC display devices, alignment layers (usually polyimides) are always employed to obtain better orientation of the mesogens. In the present system, the Schiff-base monomers are aligned due to their LC nature and the orientation is enhanced at the interface. On polymerization of the aligned monomers, mesogens may still be oriented owing to the effect of the interface, although the polymer itself loses its LC nature. If this is the case, the polymer produced by photoirradiation with benzil as initiator should show better orientation of mesogens, because in the photopolymerization one can polymerize the LC monomers after they are

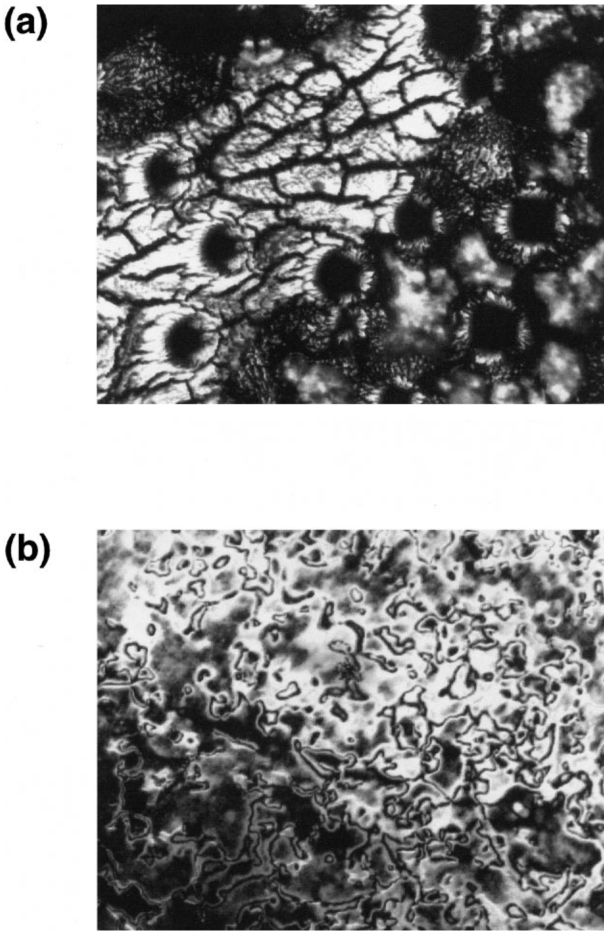

Fig. 9. Textures observed after the polymerization of ABBA in the N phase. The sample was thoroughly washed with methanol to remove unreacted monomers and initiator. (a) Thermal polymerization; (b), photopolymerization.

completely oriented. As is shown in Fig. 9b, the polymer obtained by photopolymerization exhibited much better orientation of mesogens. In the photopolymerized polymer, another factor could enhance further the orientation. As described before, a gel was formed in the photopolymerization. It is highly possible that crosslinking enables the alignment of the mesogens more stable.

4. Conclusion

The polymerization behavior of Schiff-base vinyl monomers in the bulk was explored, and the results showed that the initial rate of polymerization was governed by molecular diffusion and the final conversion may be affected by the molecular alignment. It was also found that the M_n of the polymer obtained by thermal polymerization in the N phase was higher than that in the I phase. The polymer produced by solution polymerization showed no LC phase. However, very surprisingly, the polymer produced in the N phase exhibited an LC phase even after the sample was thoroughly washed with methanol to remove unreacted monomers and initiator. As expected, the crosslinked polymer obtained on photoirradiation of ABBA was better aligned than that produced by thermal polymerization.

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