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Polymerization of Liquid-crystalline Monomers with Biphenyl Moiety

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To explore the effect of orientation of monomers and polymerization procedure on polymerization behavior, thermal polymerization and photopolymerization of vinyl monomers having a biphenyl structure were conducted at various temperatures. It was found that the initial rate of polymerization and conversion increased with temperature despite phases of the monomer. It was also observed that Arrhenius plots for the initial rates of photopolymerization fell on a straight line, while those of thermal polymerization changed the slope at the smectic-isotropic or nematic-isotropic phase transition temperature. The number-average molecular weight of the polymer produced in the thermal polymerization in the smectic phase was higher than that in the isotropic phase, whereas that of the polymer obtained by photopolymerization in the smectic phase was lower than that in the isotropic phase. These results suggest that polymerization behavior is affected by the initiation method in the polymerization of liquid-crystalline monomers.

Keywords: Liquid crystal; biphenyl; polymerization; orientation; diffusion

INTRODUCTION

Most of the nematic liquid crystals (NLCs) which showed the LC phase at low temperatures were Schiff-base compounds in the early stage of the history of LC materials. However, the LCs having the Schiff-base structure showed some drawbacks in that they tend to be hydrolyzed not only in water but also in organic acids [1]. In contrast, LCs having biphenyl or

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bicyclohexyl moiety showed several advantages: they are chemically stable, and they show an LC phase with a lower viscosity at lower temperatures than those of the Schiff-base LC materials. These lead to rapid response of the materials to external stimulus. In addition, the compounds containing the bicyclohexyl structure show no absorption in the UV region, extremely small birefringence and small wavelength dispersion of the refractive index. These are advantageous for optical materials.

Highly oriented polymers exhibit anisotropy in optical, electrical and thermomechanical properties. Many works have recently been reported on polymer films with anisotropic molecular alignment obtained by bulk polymerization of LC monomers such as acrylate [2–11], methacrylate [12–15], vinyl ether [16–18], epoxide [19, 20] and styrene [21, 22] derivatives. These monomers are interesting in view of the possibility of studying polymerization kinetics in the mesomorphic phase. The smectic (*S*), the nematic (*N*) and the isotropic (*I*) phases differ in the orientation, viscosity and mobility of mesogens. Any orientation and configuration such as a twisted *N* can be induced by shear stress, electric or magnetic fields and at specially treated surfaces. Orientation of the molecules can also be varied locally, and patterned structures can be prepared.

Monomer organization may affect the polymerization kinetics, the polymer structure and microstructure of polymers. The effect of LC ordering on the polymerization behavior of mesomorphic vinyl monomers has been examined extensively. We also reported the polymerization behavior of LC monomers with a highly oriented ferroelectric smectic *C* phase [11]. However, there is little agreement concerning the influence of the two basic properties of LC materials, ordering and diffusion, on polymerization behavior. There are at least three types of LC monomers reported previously. First, the polymerization rate of some monomers increased with temperature and the polymerizability in the *I* phase was higher than that in the LC phase [23, 24]. In the second type of the LC monomers, the polymerizability in the LC phase was higher than that in the *I* phase [25–30]. In the third group of the LC monomers, the polymerization behavior was not affected by phase structure and external forces [31, 32].

The rate of initiation (R_i) changes with temperature in the thermal polymerization, while R_i is constant regardless of temperature in the photopolymerization. Therefore, it is expected that the polymerization behavior is affected by the polymerization method, depending on either thermal polymerization or photopolymerization. In addition, there are some problems regarding the solubility of polymer in monomer. The number-average molecular weight (M_n) of the polymer obtained by polymerization

of (4-acryloyloxybenzylidene)-4-butoxyaniline (**ABBA**) was constant at any temperature [33]. It was revealed that poly(**ABBA**) precipitated after the polymer grew to a certain degree of polymerization. In the system where precipitation occurs during polymerization, we could not evaluate the effect of phase structure on the polymerization procedure precisely. In order to compare the polymerization behavior, especially M_n of the sample by thermal polymerization and photopolymerization, LC monomers possessing a biphenyl structure, in which the corresponding polymer was soluble in the monomer, were used in this study.

EXPERIMENTAL

Materials

Three monomers, 4-acryloyloxy-4'-cyanobiphenyl (**ACB0**), 4-acryloyloxy-4'-decylbiphenyl (**ADB**), 4-acryloyloxy-4'-butylbicyclohexane (**ABBC**), were used in this study and the structure and transition temperatures are shown in Figure 1. **ACB0** was synthesized as reported previously [34, 35]. It was recrystallized from a mixture of hexane and ethanol (5:1). The compound was characterized by means of $^1\text{H-NMR}$ (Brucker AC200, 200 MHz), IR (Hitachi 260-10) and elemental analysis. **ADB** and **ABBC** were obtained from Dainippon Ink & Chemicals, Inc. The phase transition temperature

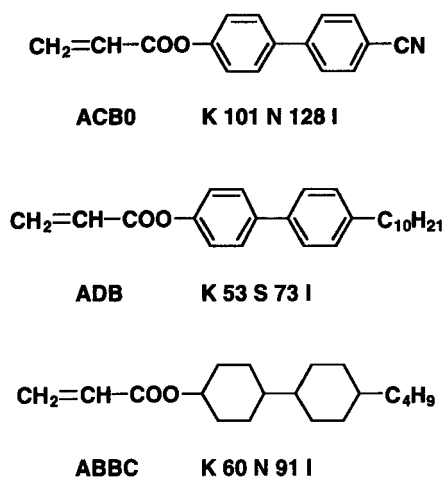


FIGURE 1 Structures and phase transition temperature of monomers used in this study. Abbreviations: *K*, crystal; *S*, smectic; *N*, nematic; *I*, isotropic.

and the phase structure were determined by differential scanning calorimetry (DSC; Seiko I&E SSC-5200 and DSC220C; heating and cooling rate, 5°C/min) and optical polarizing microscopy (Olympus Model BH-2; Mettler FP82HT hot stage and Mettler FP90 central processor).

Polymerization Procedure

It was confirmed that spontaneous thermal polymerization occurred during injection of **ACB0** into the glass cell. **ACB0** was thermally polymerized without an initiator. However, no thermal polymerization occurred spontaneously during injection of **ADB** into the glass cell. Therefore, a mixture of **ADB** and an initiator (1 mol%) was prepared by dissolving each component in acetone and subsequent evaporation of the solvent under vacuum. Benzoin was added as a photoinitiator and 2,2'-azobis(isobutyronitrile) (AIBN) was used as a thermal initiator. The *I*–*S* phase transition temperature of **ADB** with 1 mol% AIBN and that with 1 mol% benzoin was 71°C and 68°C, respectively.

The thermal polymerization of the monomers was carried out isothermally at various temperatures within the range of 55°C to 150°C. Monomer samples (9–10 mg) were placed in indented DSC pans and sealed, and they were kept in the *I* phase for 10 min in the calorimeter. For **ADB**, AIBN (1 mol%) was added in the sample. Then, they were slowly cooled down to polymerization temperature. The conversion was determined by calculating the enthalpies from the area under the DSC curve [26, 36]. 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 **ADB** containing benzoin as a photoinitiator (1 mol%) into the glass cell in the *I* phase. After the samples were kept in the *I* phase for 10 min, they were slowly cooled down to polymerization temperature. Photoirradiation was performed at 366 nm (intensity, 3 mW/cm²) isolated with glass filters from a 500 W high-pressure mercury lamp. The course of the polymerization was followed by gel permeation chromatography (GPC; Toyo Soda HLC-802; column, GMH6 × 2 + G4000H8; eluent, chloroform). The conversion was estimated from Eq. (1).

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

where *P* is the peak area in the GPC chart corresponding to the polymers produced and *M* is that corresponding to the unreacted monomers. The

Mn of the polymers was determined by GPC calibrated with standard polystyrenes.

RESULTS AND DISCUSSION

Polymerization Behavior

Polymerization was performed in three distinct temperature regions: (a) in the crystalline (*K*) phase, (b) in the LC phase, and (c) in the *I* phase. No polymerization occurred in the *K* phase of the monomers used in this study. The spontaneous thermal polymerization of **ACB0** occurred and the resulting polymer was insoluble in chloroform but soluble in dimethylformamide. Gel was formed after 300-s photoirradiation of **ADB** with 1 mol% benzoin. The excited triplet state (T_1) of benzoin abstracts hydrogen from hydrogen-donating molecules such as polymers produced and monomers [37]. When hydrogens of the polymers are abstracted, polymer radicals are produced and the resulting polymer radicals are readily recombined to form crosslinking. It was reported that when a polymer was irradiated in the presence of benzil, gel was formed [33]. However, no gel was produced within 60-s photoirradiation in the present system and then photopolymerization of **ADB** was conducted within 60 s at various temperatures. **ABBC** in the *I* phase was thermally polymerized without an initiator, although no thermal polymerization of **ABBC** in the *N* phase occurred spontaneously. Therefore, photopolymerization of **ABBC** could be conducted only in the *N* phase. However, gel was formed in photopolymerization of **ABBC** in the *N* phase.

Figure 2 shows the final conversion of **ACB0** as a function of the polymerization temperature. The final conversion increased with temperature. This is understandable because the propagation process predominates over the termination process such as the recombination reaction and the disproportionation reaction with rising temperature. In other words, viscosity decreases as temperature increases and then the addition of monomers to the propagating radicals becomes favorable due to the enhanced diffusion of each species. This result suggests that diffusion of monomers affects the polymerization behavior.

The relation between the initial rate of polymerization and the polymerization temperature is shown in Figures 3 (**ACB0**) and 4 (**ADB**). It was found that the initial rate of polymerization increased monotonously with temperature despite the molecular structure of the monomers, phase of

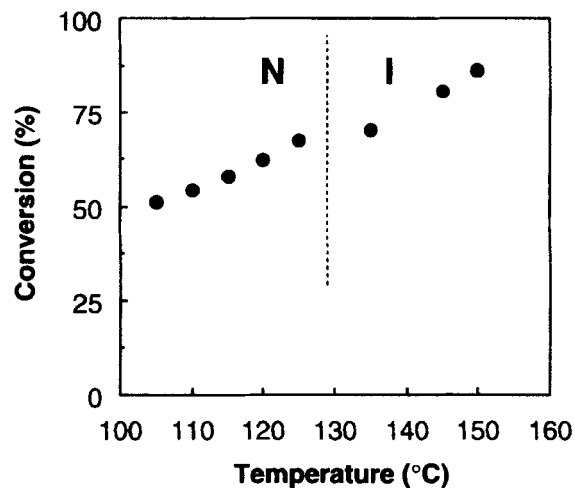


FIGURE 2 Final conversion in thermal polymerization of ACB0 at various temperatures. Initiator was not used in the polymerization.

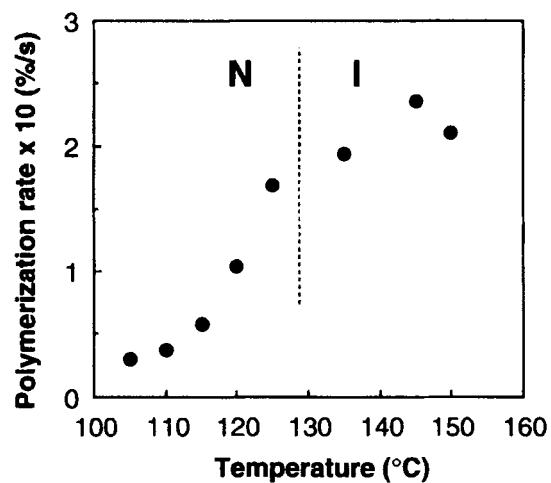


FIGURE 3 Initial rates of thermal polymerization of ACB0 at various temperatures. Initiator was not used in the polymerization.

the monomers and initiation method, either thermal polymerization or photopolymerization. The rate of polymerization (R_p) is expressed by Eq. (2).

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

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. The terms of $k_i^{1/2}$ in the thermal polymerization and k_p are expected to increase with temperature although k_t is not dependent much on temperature. It may be reasonable, therefore, that R_p increased with temperature.

Figures 5 and 6 show Arrhenius plots for the initial rates of polymerization of **ACB0** and **ADB**, respectively. It was observed that in the thermal polymerization the activation energy was larger in the LC phase than in the *I* phase (Figs. 5 and 6(a)). The thermal polymerization in the LC phase occurs simultaneously with the alignment of the monomers, so polymerization competes with the alignment process. It is expected that the alignment

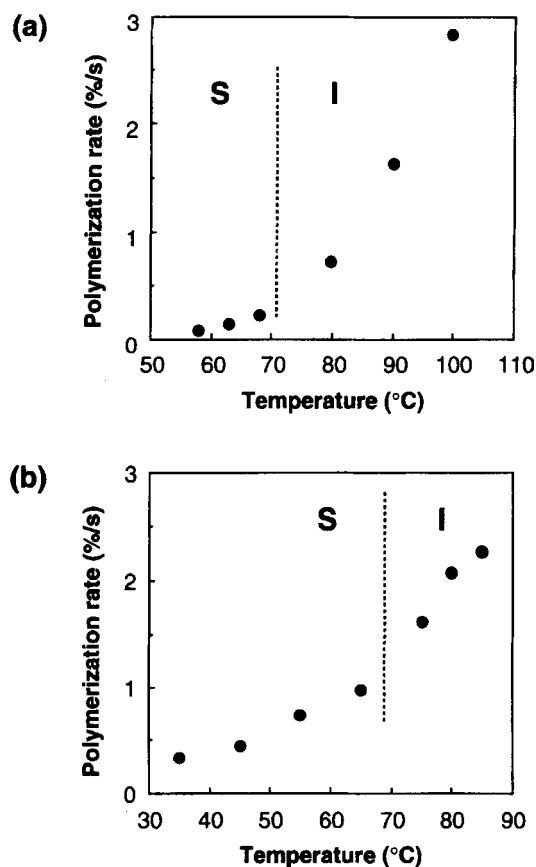


FIGURE 4 Initial rates of polymerization of **ADB** at various temperatures. (a), thermal polymerization with 1 mol% AIBN; (b), photopolymerization with 1 mol% benzoin.

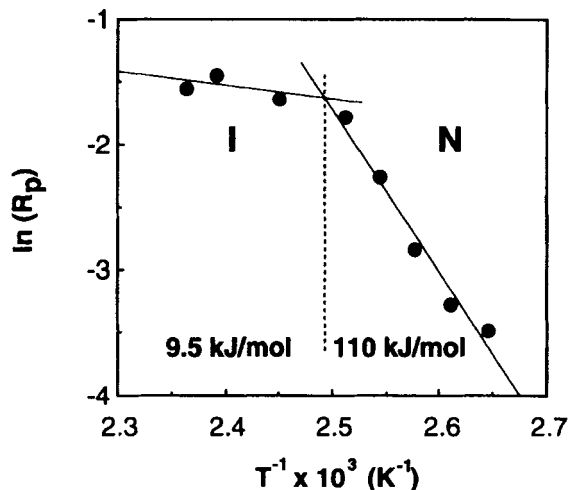


FIGURE 5 Arrhenius plots for the initial rates of thermal polymerization of **ACB0**. Initiator was not used in the polymerization. The values of the activation energy are shown in the figure.

process of monomers interferes with the propagation process in the polymerization. It is reasonable, therefore, that the activation energy of the thermal polymerization in the LC 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 (Fig. 6(b)). This is presumably because photopolymerization can be carried out after the state of the monomer is completely in equilibrium with its intrinsic phase structure. Similar results were obtained for Schiff-base monomers [33].

Figure 7 shows the relation between M_n of the polymer obtained and the polymerization temperature. Surprisingly, profiles of M_n vs. temperature in thermal polymerization were different from those in photopolymerization. M_n of the polymer produced by thermal polymerization of **ADB** in the *S* phase was higher than that in the *I* phase (Fig. 7(a)). In contrast, M_n of the polymer produced by photopolymerization of **ADB** in the *S* phase was lower than that in the *I* phase, and M_n increased discontinuously at the *S*–*I* phase transition temperature (Fig. 7(b)). At that temperature, the orientation of the monomer is absent macroscopically, but it remains microscopically, so this microscopic orientation of monomers might be advantageous for the reaction between propagating radicals and monomers.

It is well known that M_n is proportional to the kinetic chain length (ν) [38]. The term of ν is proportional to R_p and is inversely proportional to the rate of initiation (R_i). In the photopolymerization, the generation of the

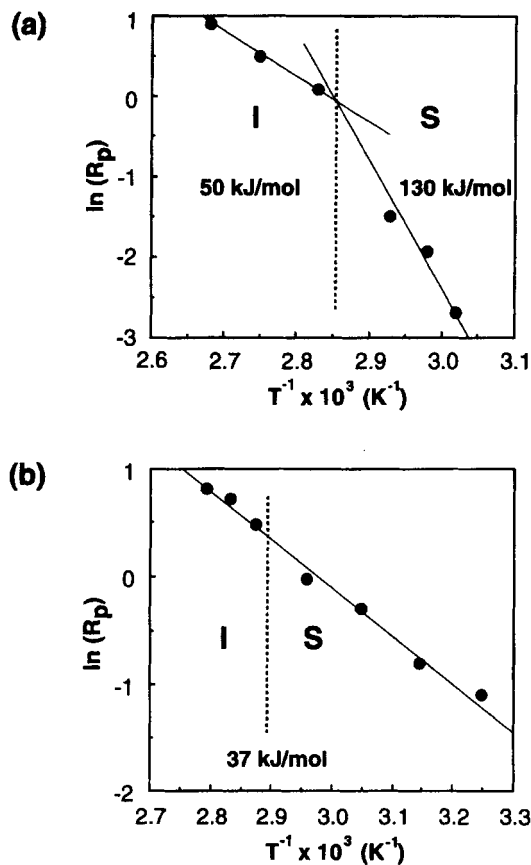


FIGURE 6 Arrhenius plots for the initial rates for polymerization of ADB. (a) thermal polymerization with 1 mol% AIBN; (b) photopolymerization with 1 mol% benzoin. The values of the activation energy are shown in the figure.

radicals is dependent only on the absorbed light, so that R_i is constant at any polymerization temperature. However, R_p increased with temperature as shown in Figure 4(a). Therefore, it may be reasonable that M_n increased as temperature increased. On the other hand, since the radicals are thermally produced in thermal polymerization, the number of radicals produced for a certain period increases with temperature, and then R_i increases with temperature. Although R_p also increased with temperature, it is expected that the rate of increase of R_i is larger than that of R_p in thermal polymerization. Consequently, M_n decreased as temperature increased.

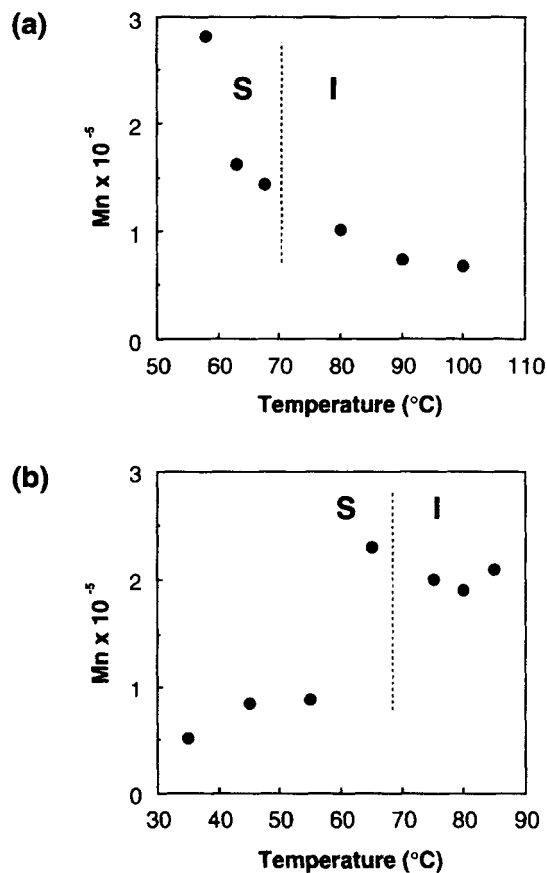


FIGURE 7 M_n of polymers of ADB obtained by polymerization with an initiator at various temperatures. (a) thermal polymerization with 1 mol% AIBN; (b) photopolymerization with 1 mol% benzoin.

Alignment of Polymer Produced

The molecular alignment of the polymers was explored by optical polarizing microscopy. To investigate the orientation of polymers produced by photopolymerization, ADB was polymerized in the *S* phase in cells with a $20\text{ }\mu\text{m}$ gap. After polymerization, the cells were opened and the polymerization mixture was thoroughly washed with methanol to remove unreacted monomers and the initiator. Washing of the product was repeated until no absorption of the monomer and the initiator was detected in the washings by UV absorption spectroscopy. The sample was then dried and examined with a polarizing microscope regarding the optical anisotropy.

The optical texture observed before polymerization at 60°C in the *S* phase is shown in Figure 8(a). As is clearly seen, the sample exhibited a focal-conic texture. Figure 8(b) shows that the polymers prepared in the *S* phase showed a focal-conic texture. It is well known that orientation of LC molecules is strongly affected by the interface between the LC molecules and the substrate [39, 40]. In fact, in LC display devices, alignment layers (usually polyimides) are always employed to obtain better orientation of the

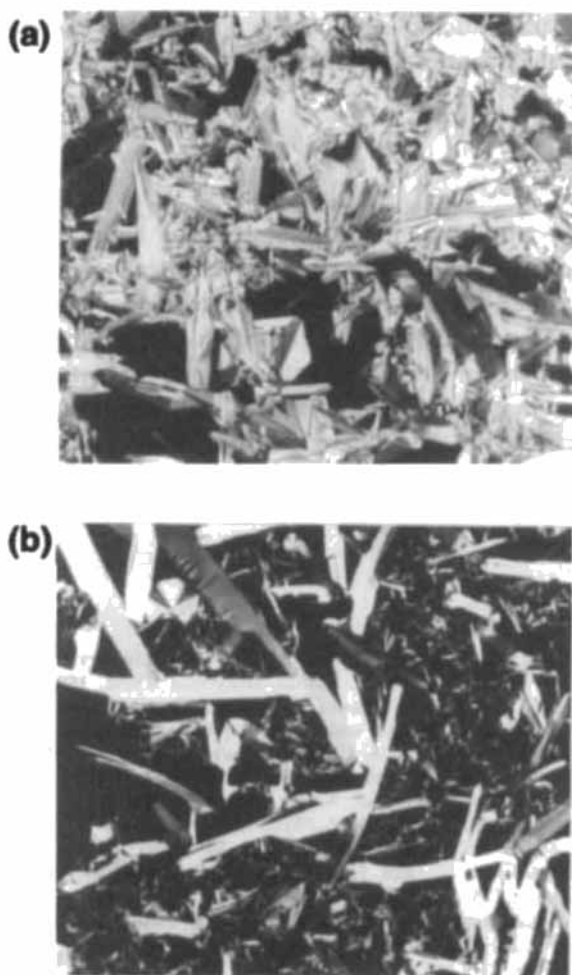


FIGURE 8 Textures observed before and after photopolymerization of **ADB** in the *S* phase. (a) before irradiation; (b) after irradiation. The sample after irradiation was thoroughly washed with methanol to remove unreacted monomers and initiator. (See Color Plate XI).

mesogens. In the present system, the monomers are aligned due to the LC nature and good orientation is enhanced at the interface compared with that of polymers by solution polymerization. On polymerization of the aligned monomers, mesogens may still be oriented owing to the effect of interface. If this is the case, the polymer produced by photoirradiation with benzoin as the initiator should show good orientation of mesogens because in the photopolymerization one can polymerize the LC monomers after they are completely oriented. Furthermore, it is possible to enhance further the orientation in the photopolymerized polymer. As described before, gel was formed after 300 s irradiation. It is highly possible that crosslinking enables a more stable alignment of the mesogens.

CONCLUSION

Polymerization of vinyl monomers having a biphenyl structure was conducted in different phases of monomers in the cells. The final conversion and the initial rate of polymerization of the monomer having biphenyl moiety increased with temperature regardless of phases of the monomer. The M_n of the polymer produced in thermal polymerization in the *S* phase was higher than that in the *I* phase, whereas that of the polymer obtained by photopolymerization in the *S* phase was lower than that in the *I* phase. The M_n of the polymer is mainly affected by the initiation method of polymerization.

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