Liquid-Crystalline Polymer Networks: Effect of Cross-Linking on the Stability of Macroscopic Molecular Orientation

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Received December 10, 1998

Revised Manuscript Received February 25, 1999

Introduction

The effect of monomer organization on the polymerization and properties of the polymers has been investigated from both scientific and industrial points of view.[1,2] One of the typical monomer organizations is based on the thermotropic liquid-crystalline (LC) systems. Recently, many studies have been focused on polymer networks with an anisotropic molecular orientation by polymerization of liquid-crystalline monomers in a unidirectional orientation.[3−18] LC monomers having polymerizable groups such as acrylate, methacrylate, vinyl ether, epoxide, and diene derivatives were used in the pursuit. The macroscopically oriented polymer networks were found to exhibit anisotropic mechanical and optical properties. In particular, densely cross-linked polymer networks, which were prepared by bi- or polyfunctional LC monomers, showed excellent transparency and stable anisotropic molecular orientation.[13] However, the dense cross-linking of the polymer networks removed any phase transition due to extreme restriction of molecular motion of the mesogenic groups in the polymer networks. Therefore, the densely cross-linked polymer networks cannot respond to external stimuli such as electric field, magnetic field, temperature, and so on. Contrary to the densely cross-linked polymer networks, the lightly cross-linked polymer networks not only hold the stability of the macroscopic molecular orientation but also show a reversible phase transition between a liquid-crystalline phase and an isotropic phase.[19,20]

On the other hand, many studies on photomodulation of optical properties of LC materials have been reported with respect to the use for various optical devices such as optical switching, optical recording, and optical computing.[21−27] If we can detect enough signal based on the photomodulation of the optical properties of the LC systems such as birefringence and transparency, we will be able to use the LC systems for the optical devices. The lightly cross-linked LC networks can be considered to be a candidate for constructing such LC systems, because they show both the macroscopically stable molecular orientation and reversible phase transition.[28]

We report here the preparation and characterization of LC polymer networks with cross-linking, in particular with respect to the cross-linking effect on the thermal reversibility of the macroscopically molecular orientation of LC polymer networks.

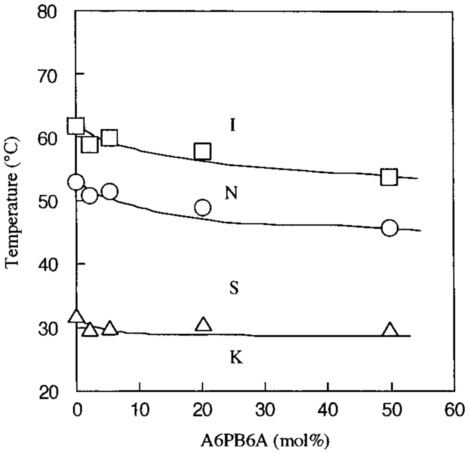
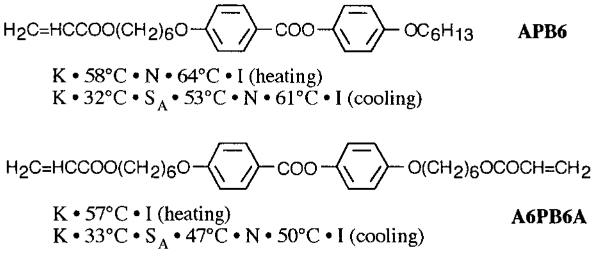


Figure 1. Phase diagram of the binary mixtures of **APB6** and **A6PB6A**.

Scheme 1



K • 58°C • N • 64°C • I (heating)
K • 32°C • S_A • 53°C • N • 61°C • I (cooling)

K • 57°C • I (heating)
K • 33°C • S_A • 47°C • N • 50°C • I (cooling)

Results and Discussion

Two kinds of liquid-crystalline monomers, **APB6** and **A6PB6A**, were synthesized according to a method reported previously (Scheme 1).[13,29−32]

Thermal phase transition behavior of the monomers was examined by means of differential scanning calorimetry (DSC, Seiko I&G SSC-5020) and polarizing optical microscopic observation (POM, Olympus BHSP polarizing optical microscope; Mettler FP80 and FP82 hot stage and controller). Scanning rate of DSC measurements was 5 °C/min, and the peak temperatures obtained were taken as the phase transition temperatures.

Monoacrylate, **APB6**, exhibits only a nematic (N) phase on heating, whereas a smectic (S_A) phase as well as the N phase is observed on cooling. Diacrylate, **A6PB6A**, is a monotropic liquid crystal; namely, both N and S_A phases are observed only on cooling.[13]

Figure 1 shows a phase diagram of binary mixtures of **APB6** and **A6PB6A** in which **A6PB6A** is in a concentration range from 0 to 50 mol %. The phase diagram is based on the DSC thermograms obtained on cooling. All mixtures containing **A6PB6A** up to 50 mol % exhibit the N phase in a temperature range similar to that of **APB6**. Phase separation of each monomer in the mixtures was not recognized in all mixtures studied, although a little depression in the transition temperatures was observed with the increase in the concentration of **A6PB6A**. The similarity in the structures of both monomers resulted in the good mutual solubility.

Polymerizable mixtures were prepared by adding 2 mol % of 2,2-dimethoxy-2-phenylacetophenone to **APB6**/**A6PB6A** mixtures as a photoradical initiator. The

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10.1021/ma9819081 CCC: $18.00

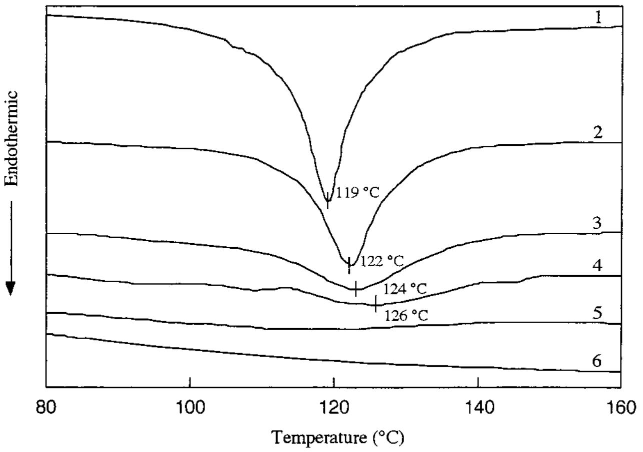

Figure 2. DSC thermograms of poly(**APB6**/**A6PB6A**) on heating: 1, p(100:0); 2, p(98:2); 3, p(95:5); 4, p(90:10); 5, p(85:15); 6, p(80:20). p(*m*:*n*) represents the composition of poly(**APB6**/**A6PB6A**), where *m* and *n* are the contents of **APB6** and **A6PB6A** in mol %, respectively.

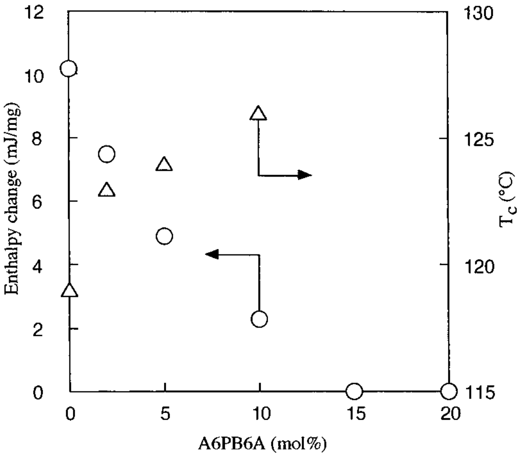

Figure 3. Effect of cross-linking density on enthalpy change and the N−I phase transition temperature (T_c) of poly(**APB6**/**A6PB6A**).

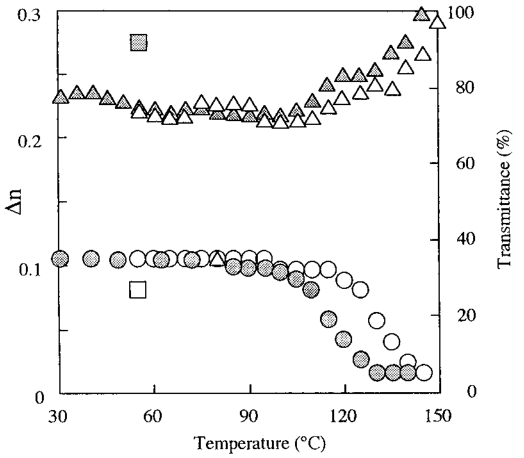

Figure 4. Changes in the birefringence, Δn (○, ●, □), and transmittance (△, ▲, ■) of the poly(**APB6**/**A6PB6A**) (95:5 mol %) network as a function of temperature: (□, ■), before polymerization; (●, △), heating after polymerization; (●, ▲), cooling after heating to the I phase.

amount of **A6PB6A** in the **APB6**/**A6PB6A** mixtures was varied from 0 to 20 mol %. Into two glass plates, 2 mg of each **APB6**/**A6PB6A** mixture containing the photoradical initiator was loaded and was irradiated at 55 °C (N phase). After polymerization, the sample was removed from the glass plates and was subjected to gel permeation chromatography (GPC; JASCO 880-PU; column, Shodex KF-80M + KF-80M; eluent, tetrahydrofuran; standard, polystyrene). The conversion of mixtures was determined by measuring the residual amount of monomers in the samples after polymerization because of insolubility of samples due to cross-linking with the diacrylate, **A6PB6A**. The conversion was found to become higher than 90% by UV irradiation longer than 10 min. Therefore, the polymerization was carried out by UV irradiation for 10 or 15 min in this study.

Figure 2 shows DSC thermograms of poly(**APB6**/**A6PB6A**) containing various amounts of **A6PB6A** obtained on heating. The cross-linking density of the poly(**APB6**/**A6PB6A**)'s was not determined experimentally. It is assumed that the amounts of **A6PB6A** fed in the monomer mixtures are roughly equal to the cross-linking density of the polymer networks, because the conversion of the monomer mixtures was higher than 90%. Therefore, the result shown in Figure 2 indicates the effect of the cross-linking density on the phase transition behavior of the poly(**APB6**/**A6PB6A**)'s. It is clearly seen that the cross-linking density has an influence on the phase transition behavior. An endothermic peak at 119 °C was observed for poly(**APB6**) without **A6PB6A**. It has been reported that the poly(**APB6**) show the S phase as a LC phase.[32] Therefore, the peak can be assigned to the S to I phase transition. The endothermic peak was shifted to higher temperatures and broadened by increasing the cross-linking density. To clarify the effect of the cross-linking density on the phase transition behavior, the change in the phase transition temperature and enthalpy change was plotted as a function of the cross-linking density in Figure 3. As can be seen in Figure 3, the phase transition temperature increased and the enthalpy change decreased with the increase in the cross-linking density. The effect of the cross-linking density is interpreted in terms of extreme depression in the molecular motion of the polymer segments in the polymer network. The higher the cross-linking density increases, the less the molecular motion becomes. No peak was observed on DSC thermograms for poly(**APB6**/**A6PB6A**)'s containing **A6PB6A** higher than 15% due to the depression of the molecular motion.

The poly(**APB6**/**A6PB6A**) networks having cross-linking density lower than 15 mol % still have enough molecular motion to show the phase transitions to the I phase. To explore the effect of cross-linking on both stability and thermal reversibility of macroscopic molecular orientation, transmittance and birefringence of the polymer networks with various cross-linking densities were measured as a function of temperature.

Figure 4 shows changes in both birefringence (Δn) and transmittance of the poly(**APB6**/**A6PB6A**) (95:5 mol %) network by heating and following cooling. The value of Δn was determined by measuring the number of interference lines of the poly(**APB6**/**A6PB6A**) network in the Cano-wedge cell between two crossed polarizers by the use of a probe light from a laser diode (Suruga Seiki Co.; 670 nm; 5 mW). Before polymerization, Δn of the (**APB6**/**A6PB6A**) mixture was 0.08 at 57 °C, which is roughly equal to the value of Δn measured with the Abbe refractometer. Although a little increase in Δn was observed by polymerization as can be seen in Figure 4, the value of the poly(**APB6**/**A6PB6A**) network was

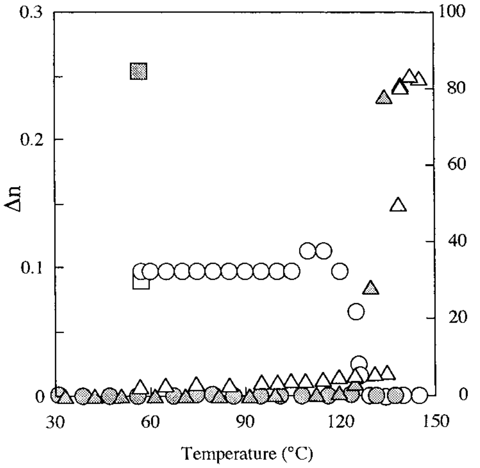

Figure 5. Changes in Δ*n* (○, ●, □) and transmittance (△, ▲, ■) of the poly(**APB6**) network as a function of temperature: (□, ■), before polymerization; (○, △), heating after polymerization; (●, ▲), cooling after heating to the I phase.

around 0.1 and kept constant up to 120 °C. Above 120 °C, Δ*n* decreased rapidly due to the phase transition to the I phase. Subsequently, by cooling Δ*n* was increased again and restored to the initial value. The temperature dependence of the transmittance of the poly(**APB6**/**A6PB6A**) (95:5 mol %) network in the homogeneous glass cell with a 50 μm cell gap is also shown in Figure 4. Although a slight change in the transmittance of the polymer network was induced by polymerization, the transmittance was kept about 80% by heating to 120 °C and cooling. The results shown in Figure 4 clearly demonstrate that the poly(**APB6**/**A6PB6A**) network shows the reversible phase transition between the uniaxial LC phase and the I phase.

On the other hand, the polymerization of **APB6** without **A6PB6A** affected the temperature dependence of both Δ*n* and transmittance in a different way from the poly(**APB6**/**A6PB6A**) network. A significant decrease in the transmittance was observed by polymerization as shown in Figure 5. POM observation revealed that the polymerization resulted in the transformation from the uniaxial monodomain structure to a multidomain structure. As described above, poly(**APB6**) is in the S phase below 119 °C, whereas **APB6** is in the N phase at the irradiation temperature (55 °C). The macroscopically structural transformation to the multidomain structure may be related to the phase transition from the N phase to the S phase during polymerization.[13] In addition, polymerization shrinkage may be one of factors to disorder the macroscopic molecular orientation.[13] Consequently, the multidomain structure was responsible for the significant decrease in the transmittance due to strong light scattering. The Δ*n* of poly(**APB6**) was about 0.9 and kept by heating to 110 °C. However, no restoration of Δ*n* was caused for the poly(**APB6**) by heating above 130 °C and following cooling after the phase transition to the I phase once. After the phase transition to the I phase, the domain size of the multidomain structure became smaller than that immediately after polymerization. The comparison of results obtained for poly(**APB6**/**A6PB6A**) and poly(**APB6**) implies that the cross-linking of the polymer networks with a few mole percent of **A6PB6A** is enough to sustain the macroscopically uniaxial molecular orientation and is responsible for the thermal reversible change in the macroscopic molecular orientation between the uniaxial LC phase and the I phase.

To explore the effect of monomer structure, **APB6** was copolymerized with other monomers such as 1,4-diacryloyloxybiphenyl (**ABA**), tetraethylene glycol dimethacrylate (**4*G***), methylene bis(acrylamide) (**MBA**), and hexamethylene diacrylate (**HA**). The copolymer from the mixture of **APB6** and **ABA** showed stable macroscopic molecular orientation, while the copolymers from the mixtures of **APB6** and **4G**, **MBA**, or **HA** did not. The result can be interpreted in terms of the structure of the monomers. Both monomers, **A6PB6A** and **ABA**, have mesogenic core moiety, whereas the others do not have one. The intermolecular interaction between mesogenic moieties is one of important factors influencing properties of the resulting polymer networks.

In summary, we investigated the stability of macroscopically molecular orientation with respect to the cross-linking density of the LC polymer networks. The increase in the cross-linking density depressed the molecular motion of the mesogenic molecules in the LC polymer networks. Consequently, no phase transition to the I phase was observed for the densely cross-linked LC polymer networks prepared by the cross-linking with the diacrylate, **A6PB6A**, more than 15 mol % in the LC monomer mixtures. On the other hand, the cross-linking with a few mole percent of **A6PB6A** is enough to sustain the macroscopically uniaxial molecular orientation, and the lightly cross-linked LC polymer networks show the reversible macroscopically molecular orientation between the uniaxial LC phase and the I phase. The intermolecular interaction between mesogenic moieties is an important factor influencing the phase transition behavior as well as the stability of macroscopically molecular orientation of the polymer networks.

Acknowledgment. We are grateful to Prof. T. Ikeda and Dr. A. Shishido of Tokyo Institute of Technology for measuring of refractive indices with the Abbe refractometer.

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MA9819081