

Preparation of Polymer Thin Films with Chiral Structure by Polymerization of Liquid Crystalline Monomers

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Liquid crystalline mono- and diacrylate monomers which showed a nematic phase were synthesized. By doping small amounts of a chiral dopant in acrylate mixtures, a induced cholesteric phase was observed. The helical structure in the induced cholesteric phase was frozen in the polymeric films by photopolymerization. The helical polymer networks with an ionic species could be prepared by alkaline hydrolysis of the polymer films.

1. Introduction

Much attention have been focused on the polymerization of liquid crystalline(LC) monomers with respect to preparation of polymer thin films having an anisotropic molecular orientation. Anisotropically oriented films could be obtained by polymerization of the LC monomers on a substrate with rubbing treatment in one direction, in a magnetic field and in an electric field [1-6].

On the other hand, it is well known that the cholesteric phase can be induced by adding non-mesogenic chiral molecules in non-chiral mesogenic liquid crystals [7, 8]. Finkelmann et. al. have studied on the formation of a chiral nematic polymer network by cross-linking reaction of the mixture of chiral comonomer and nematic LC monomers[9]. Recently, Broer et. al. reported the preparation of cholesterically ordered polymer networks by polymerization of LC diacrylate monomers doped with small amounts of a chiral molecule[10, 11]. In this paper, we describe the preparation of the helical polymer networks with carboxyl groups as an ionic species by polymerization of LC monomers at the induced cholesteric phase and hydrolysis under an

alkaline condition.

2. Experimental

2.1 Materials

Structures of the compounds used are shown in Fig.1. Difunctional acrylate monomer, A6P6A was synthesized according to the Broer's method[6]. Monoacrylate monomer, APB6 was synthesized in a similar manner as A6P6A. The chiral dopant, S811(S) was purchased from Merck co..

2.2 Liquid crystalline properties

Thermotropic properties of the mono- and diacrylate monomers and their mixtures were investigated by differential scanning calorimetry and polarizing microscopic observation. Helical pitch in the induced cholesteric phase by adding S811 to the LC monomers was measured by Cano wedge method using a wedge cell.

2.3 Alignment treatment

A glass cell with homogeneous alignment treatment was composed of two glass slides, which coated with polyvinyl alcohol and rubbed in one

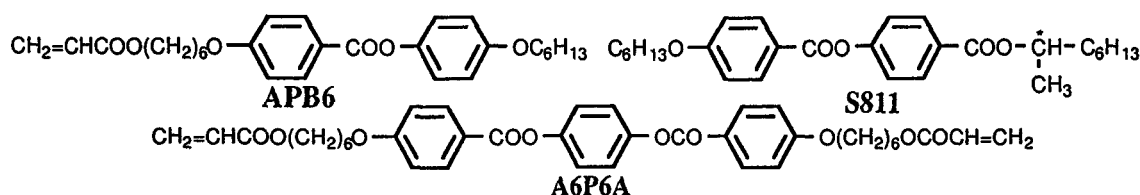


Fig.1 Structure of compounds used in this study

Table 1 Thermotropic properties of liquid crystalline monomers on cooling

samples	Phase transition temperature(°C)				$\Delta H / \text{kJ} \cdot \text{mol}^{-1}$			$\Delta S / \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$		
	K	S	N	I	ΔH_{K-S}	ΔH_{S-N}	ΔH_{N-I}	ΔS_{K-S}	ΔS_{S-N}	ΔS_{N-I}
APB6	• 32	• 50	• 57	•	28	1.4	1.2	92	4.2	3.5
A6P6A	• 75	• 80	• 155	•	68	0.9	1.0	178	2.4	2.3

K:crystalline, S:smectic, N:nematic, I:isotropic

direction. On the other hand, a glass cell with homeotropic alignment treatment was composed of two glass slides which coated with cetyltrimethylammonium bromide. The cell gap was 25 μm .

2.4 Photopolymerization and hydrolysis

Photopolymerization was carried out by irradiation with a 75 W high pressure mercury lamp on the monomer mixtures, which doped with 1 mol% of 2,2-dimethoxy-2-phenylacetophenone as a photo-radical initiator, for 10 min at various temperatures. After removal of the unreacted monomers and the chiral dopant S811 by immersing the polymeric films for 3 days in tetrahydrofuran with stirring, the polymeric films were hydrolysed by reaction with sodium hydroxide (NaOH) for 24 h, resulting desired degrees of alkaline hydrolysis.

3. Results and Discussion

3.1 Liquid crystalline properties

Thermotropic properties of the LC monomers are given in Table 1. The peaks in the DSC thermograms on the second heating or cooling scan

were taken as the phase transition temperatures. The phase structures of the LC monomers and mixtures were assigned on the basis of the DSC measurements and the polarizing microscopic observation. Both the LC monomers showed the nematic phase on heating, whereas a smectic phase as well as the nematic phase were observed as the LC phases on cooling.

By adding various amounts of the chiral dopant, S811, to the LC monomer, APB6 and APB6/A6P6A mixtures, the chiral properties which characterized by a helical pitch p of the induced cholesteric phase were investigated on cooling. In general, p depends on a temperature and the reciprocal pitch p^{-1} shows a linear dependence of the concentration of the chiral dopant in a low concentration range. As shown in Fig.2, p of APB6 containing various concentrations of S811 decreased slightly with increasing temperature. In addition, p decreased with increasing the concentration of S811. However the cholesteric phase disappeared when S811 was added more than 5 mol%.

The phase diagram for the mixtures of APB6

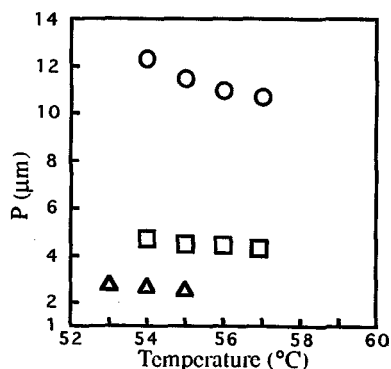


Fig.2 Temperature dependence of the helical pitch (P) of APB6 doped with various concentrations of S811: (○) 1mol%, (□) 3mol%, (△) 5mol%.

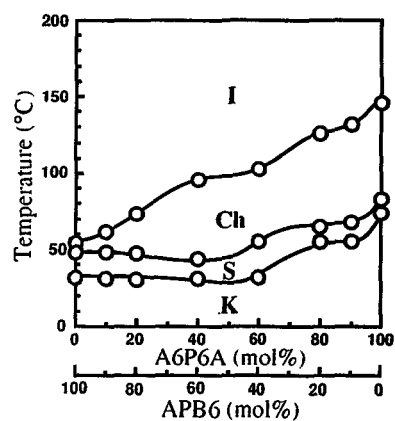


Fig.3 Phase diagram of the mixture of APB6 and A6P6A containing 5mol% of S811

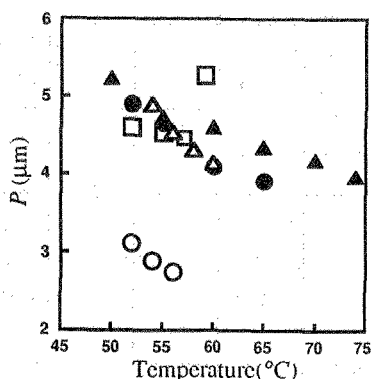


Fig.4 Temperature dependence of the helical pitch (P) of the mixture of APB6 and A6P6A containing 5mol% of S811:(○) [99:1], (△) [98:2], (□) [95:5], (●) [90:10], (▲) [80:20]

and A6P6A containing 5mol% of S811 is shown in Fig.3. The isotropic-cholesteric-smectic-crystal phase transition was observed on cooling at any given concentration of A6P6A in the mixtures. In addition, the phase transition temperatures shifted to higher temperatures with increasing the concentration of A6P6A in the mixtures. Fig.4 shows the temperature dependence of p of the mixtures doped with 5 mol% of S811. The p^{-1} of all the mixtures also decreased with increasing temperature. Unless otherwise stated, all the experiments were carried out by using the samples doped with 5 mol% of S811 in the following experiments.

3.2 Photopolymerization of LC mixtures

Fig.5 shows the polarized optical micrographs of the planar texture (a) obtained in the homogenous cell and the finger print texture (b) obtained in the homeotropic cell after photopolymerization of the [80:20] mixture at 70 °C, at which the [80:20] mixture exists in the cholesteric phase. The mixtures of APB6 and A6P6A are abbreviated as [m:n], where m and n are mol % of APB6 and A6P6A, respectively. The polymer film with helical structure could be prepared by polymerization of the LC mixtures at the cholesteric phase. In addition, the direction of helical axis in the polymer film could be controlled by the surface treatment as shown in Fig.5. No changes in the helical structure were recognized before and after polymerization. The polymer films

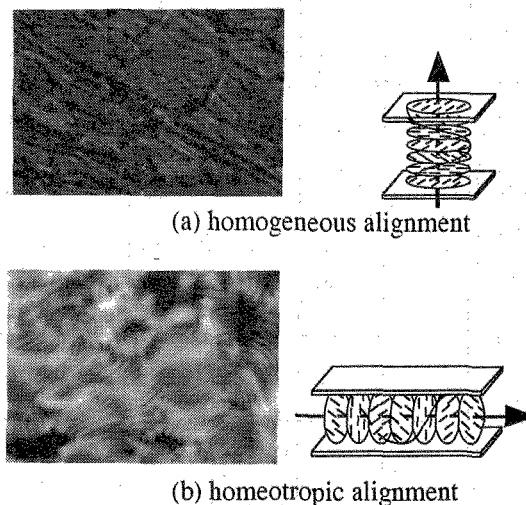


Fig.5 Polarized optical micrographs of optical textures of [80:20] polymerized at 70°C

exhibited reversible phase transition from the cholesteric phase to an isotropic phase. The phase transition temperature increased with increasing the concentration of A6P6A. Although the polymerization of APB6 without A6P6A as a cross-linker also gave the helical structure, the helical structure disappeared irreversibly by heating above 120 °C. The results imply that the cross-linker is required to fix the helical structure.

3.3 Alkaline hydrolysis

It is interesting here to hydrolyze the polymer film with the helical structure. The hydrolysis is expected to provide carboxyl groups as an ionic species in the helical structure. As described above, the direction of the helical axis in the polymer films can be controlled by the surface treatment. Therefore, one can obtain the helical polymer networks with the ionic species, where the direction of the helical axis is oriented either parallel or perpendicular to the surface of the films.

The polymer film obtained by polymerization of the [80:20] mixture at 70 °C, was hydrolyzed with NaOH. Fig.6 shows the infrared spectra (IR) of [80:20]-xNa, where x is a calculated mol% of NaOH relative to a total amount of the molecules, APB6 and A6P6A (20 mol% and 80 mol%). The formation of the sodium salt of benzoic acid by the hydrolysis of the [80:20]

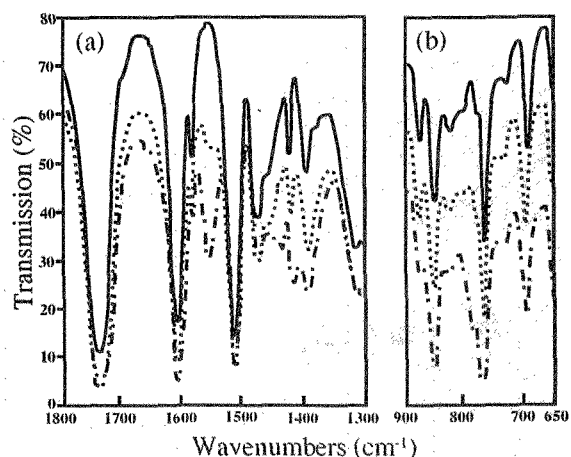


Fig.6 IR spectra, in the 1800-1300 cm^{-1} (a) and 900-650 cm^{-1} (b) range of [20:80]-0Na(—), -20Na(---), -50Na(· · ·)

mixture was revealed by a shift of the band at 770-760 cm^{-1} , which is attributed to the out-of-plane bending of the carbonyl group of the benzoate moiety, to the higher frequencies, and an increase in the absorbance at 1550 cm^{-1} due to the carboxylate anion.

Fig.7 shows the polarized optical micrographs of [80:20]-0Na (a), -20Na (b), -50Na (c). It is clearly seen that the helical structure was remained for [80:20]-20Na after alkaline hydrolysis. Although the degree of hydrolysis could not be determined, the hydrolysis afforded the helical polymer networks with the ionic species. On the other hand, the significant change in the morphology of the network was recognized for [80:20]-50Na. The excessive hydrolysis destroyed the helical structure due to hydrolysis of the cross-linking sites.

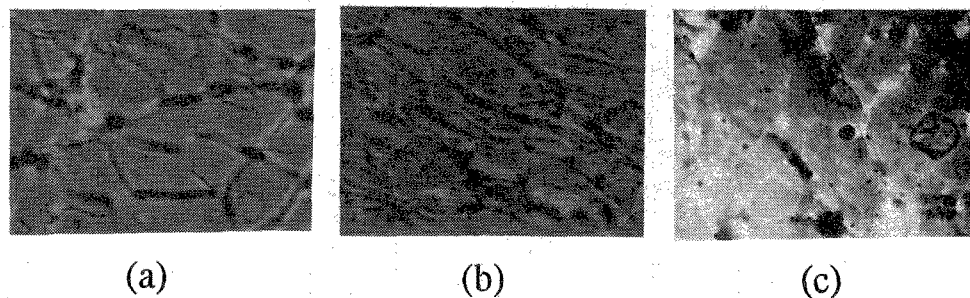


Fig.7 Polarized optical micrographs of [80:20]-0Na(a), -20Na(b), -50Na(c)

4. Conclusion

The helical structure was induced by doping the chiral compound in the non-chiral nematic LC monomer mixtures of APB6 and A6P6A. The diacrylate monomer, A6P6A, was required to fix the helical structure of the polymer networks. The helical axis in the polymer films was controlled by the surface treatment. In addition, the helical polymer networks with the ionic species could be obtained by partial alkaline hydrolysis of the polymer films.

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