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Notes

Novel Preparations of Helical Polymer and Ionomer Networks

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Introduction

Several studies on solid polymeric films having cholesteric order, in which the molecules are arranged in a helical structure along an axis perpendicular to their longitudinal axis, have been reported by solvent evaporation from lyotropic liquid crystalline phases,[1−4] by cross-linking of cellulose derivatives[5−7] and poly(γ-benzyl L-glutamate),[8] and by polymerization of chiral nematic diacrylate.[9,10] On the other hand, it is known that the cholesteric phase can be induced by adding nonmesogenic chiral molecules in nonchiral liquid crystals.[11] Finkelmann et al. have described the formation of a chiral nematic polymer network by cross-linking of the mixture of a chiral comonomer and a nematogenic monomer.[12] Recently, Broer et al. reported the preparation of cholesterically ordered polymer networks by polymerization of monomeric liquid crystalline (LC) diacrylate doped with small amounts of chiral molecules, resulting in the induced cholesteric phase.[13]

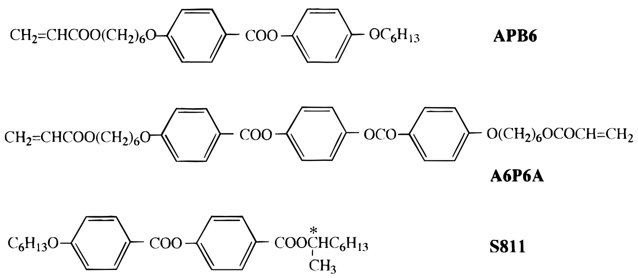
Zhao et al. reported the preparation of side-chain LC ionomers prepared through alkaline hydrolysis of side-chain LC polymers.[14] The introduction of the ionic species was found to affect the thermotropic properties of the side-chain LC polymers. We believe that a combination of helical structure and ionic properties will offer an interesting route for making materials showing molecular recognition, ionic conduction, and so on. In this paper, we describe the preparation of helical polymer networks by polymerization of LC monomers at the induced cholesteric phase and hydrolysis of the helical polymer networks to develop helical ionomer networks with carboxyl groups as ionic species in the helix.

Results and Discussion

Structures of LC acrylate, **APB6**, and LC diacrylate, **A6P6A**, used in this study are shown in Chart 1. Both LC monomers were prepared according to a method reported previously.[13] L-4-[[4-(Hexyloxy)benzoyl]oxy]benzoic acid 2-octyl ester (**S811**, Merck) was used as a nonmesogenic left-handed chiral compound.

Thermotropic phase behavior was examined by differential scanning calorimetry (DSC, SEIKO I&E SSC-5020) and polarized optical microscopy (Olympus BHSP; Mettler FP80 and FP82). Both monomers show only a nematic phase on heating, while smectic (S_A for **APB6** and S_c for **A6P6A**) phases as well as the nematic phase were observed on cooling. The phase behavior obtained on cooling is given in Table 1. Both the nematic and smectic phases were found not only for the monomer, but also for any mixtures of **APB6** and **A6P6A**.

Chart 1



By adding the nonmesogenic chiral compound, **S811**, the cholesteric phase (**Ch**) was induced for each monomer. The induced **Ch** phase was characterized by measuring the helical pitch p on cooling. The helical pitch was measured by the Cano wedge method, which is based on the observation of the disclination lines occurring in a wedge-shaped cholesteric sample under homogeneous planar boundary conditions.[11] It is well-known that p depends on temperature, and the reciprocal pitch p^{-1} shows a linear dependence on the concentration of the chiral dopant in the low-concentration region. Actually, the p of **APB6** containing **S811** decreases slightly with increasing temperature. In addition, p decreases with increasing concentration of **S811**. The **Ch** phase, however, disappears when **S811** is added to more than 5 mol %. The **Ch** phase is also induced by adding **S811** to any mixtures of **APB6** and **A6P6A**. The phase behavior of three eutectic mixtures of **APB6** and **A6P6A**, which contain 5 mol % of **S811** relative to the total amount of **APB6** and **A6P6A** in the mixtures, is given in Table 1; the molar ratio of **APB6** and **A6P6A** was varied as 98:2, 95:5, and 80:20, indicated as [98:2], [95:5], and [80:20]. The addition of S811 lowers the phase transition temperatures by several degrees. Figure 1 shows the temperature dependence of p of the mixtures containing 5 mol % **S811**. p decreases with increasing temperature in a way similar to that for **APB6**. Although the p of the mixtures is longer than that of **APB6**, no distinct composition effect on the pitch was observed for the mixtures.

The photopolymerization of the three mixtures of **APB6** and **A6P6A** ([98:2], [95:5], and [80:20]) containing 5 mol % of **S811** was performed to explore the influences of polymerization on the phase behavior, and to make polymer networks with helical structure. The samples were prepared by adding 1 mol % of 2,2-dimethyl-2-phenylacetophenone as a photoinitiator in the monomer mixtures and injecting the samples into two kinds of glass cells with 25 μm cell gaps; one glass cell was a homogeneous alignment glass cell, and the other was a homeotropic alignment glass cell. According to the direction of the helical axis, the oily streak texture and fingerprint texture were observed in the homogeneous

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Table 1. Thermotropic Properties of the LC Monomers and the APB6/A6P6A Mixtures Containing 5 mol % S811

	phase transition temp (°C)[b]						
APB6[a]	K	32	S	50	N	57	I
A6P6A[a]	K	75	S	80	N	155	I
APB6/A6P6A ([98:2])	K	30	S	50	Ch	59	I
APB6/A6P6A ([95:5])	K	31	S	48	Ch	60	I
APB6/A6P6A ([80:20])	K	30	S	47	Ch	73	I

[a] Without S811. The smectic phases for APB6 and A6P6A are monotropic. [b] The phase transition temperatures were determined by DSC measurement on cooling. Peak temperatures were taken as the phase transition temperatures.

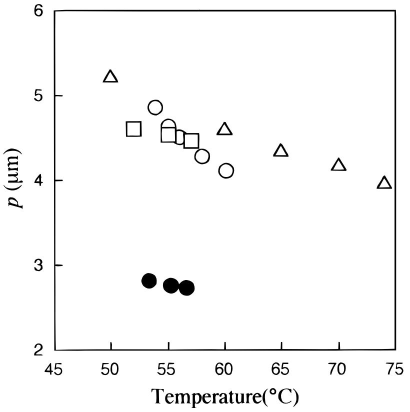


Figure 1. Temperature dependence of the helical pitch p of APB6 and mixtures of APB6 and A6P6A: (●) APB6; (○) [98:2]; (□) [95:5]; (△) [80:20].

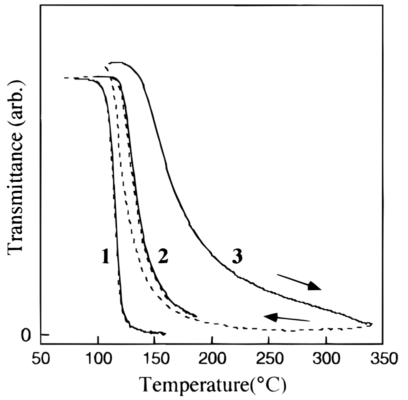


Figure 2. Changes in transmittance of the polymerized mixtures of APB6 and A6P6A containing 5 mol % S811 between crossed polarizers observed by heating (solid lines) and cooling (dashed lines): (1) [98:2]; (2) [95:5]; (3) [80:20].

glass cell and in the homeotropic glass cell, respectively, indicating formation of the helical structure in the monomeric state. The samples were irradiated with a 75 W high-pressure mercury lamp at the induced **Ch** phase for 10 min. The conversions of the monomers in the mixtures were higher than 90%, estimated by gel permeation chromatography of the unreacted monomers extracted with tetrahydrofuran (THF) after polymerization, because of insolubility of the resulting polymers due to cross-linking. No significant change in the texture was brought about during photopolymerization. Figure 2 shows the changes in the transmittance of the three polymerized samples between crossed polarizers as a function of temperature. Below 110 °C, the [98:2] sample is in the **Ch** phase; thus birefringence was detected. A decrease in the transmittance was observed by heating above 110 °C; for the two samples with the least cross-linking, the transmittance reached zero, indicating a phase transition from the **Ch** phase to the isotropic (**I**) phase. The birefringence appeared by cooling below 110 °C. In addition, the fingerprint texture turned dark and reappeared by heating and cooling, respectively. In this way, the thermotropic reversible **Ch**−**I** phase transition was demonstrated. The phase transition temperature increases with the increasing content of **A6P6A**. For the [80:20] sample, however, the fingerprint texture remained even at temperatures higher than 300 °C. Although heating caused a decrease in transmittance, the **Ch**−**I** phase transition did not occur completely. In addition, the [80:20] sample was found to show a significant hysteresis of the change in the transmittance, as can be seen clearly in Figure 2. The hysteresis may be interpreted in terms of a restricted motion of mesogens in the highly cross-linked networks and by a partial decomposition of the networks, as indicated by a slight coloration upon heating above 300 °C. The fingerprint texture was maintained after the photopolymerization of **APB6** without **A6P6A**, while the texture disappeared irreversibly by heating above 110 °C. Therefore, **A6P6A** as the cross-linker is required to freeze the helical structure in the networks. In addition, the phase behavior of the networks is closely related to the cross-linking density.

It is possible to hydrolyze the polymer networks with the helical structure to develop helical ionomer networks. The hydrolysis is expected to provide carboxyl groups as ionic species in the helical structure. As indicated above, the direction of the helical axis in the polymer films can be controlled by the surface treatment. Thus, one can obtain helical ionomer networks, where the direction of the helical axis is oriented either parallel or perpendicular to the surface of the films. The helical polymer network obtained by photopolymerization of the [80:20] sample in the homogeneous alignment glass cell at 70 °C, at which the [80:20] sample was in the induced **Ch** phase, was immersed in THF to tear off the helical polymer network films from the glass plates. The films obtained were subsequently immersed in THF for 3 days at room temperature with stirring to remove unreacted monomers and the chiral dopant **S811**. The immersion of the films in THF for 3 days resulted in no significant change in the morphology of the helical polymer networks on the basis of polarized optical microscopy, while a slight increase in the **Ch**−**I** phase transition temperature was observed, e.g., 121 and 125 °C for the polymerized [98:2] sample before and after immersion in THF, respectively. After removal of the unreacted monomers and **S811**, the films were hydrolyzed by reacting with sodium hydroxide (NaOH) for 24 h at room temperature, resulting in the desired degrees of alkaline hydrolysis.

Infrared spectra (IR) of [80:20]-mNa (m = 0, 6, 10), where m is the estimated degree of hydrolysis (mol %) relative to the total amount of the monomers in the helical polymer network films, are shown in Figure 3. Zhao et al. reported the preparation of side-chain LC ionomers through alkaline hydrolysis of the side-chain LC polymer having two different types of ester bondings and stated that the alkaline hydrolysis of the phenyl ester occurred easily compared with that of the alkyl ester due to stability of the liberated oxanion and a steric effect.[14] They also showed that the degrees of hydrolysis were roughly compatible with those expected on the basis of the amounts of NaOH. The formation of the sodium salt of benzoic acid in the helical network films was verified in our films by a shift of the band at 760 cm^{-1}, due to the out-of-plane bending of the ben-

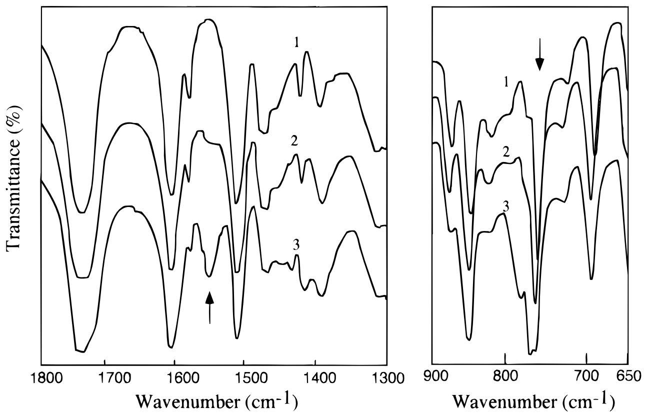
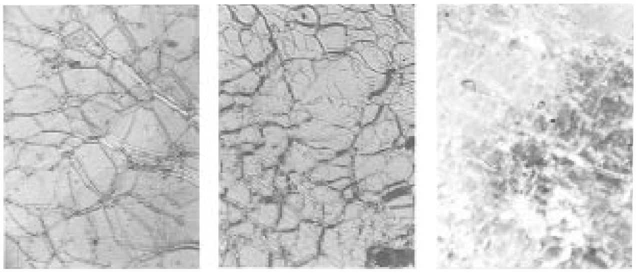


Figure 3. Infrared spectra of a hydrolyzed mixture of APB6 and A6P6A: (1) [80:20]-0Na; (2) [80:20]-6Na; (3) [80:20]-10Na.

zoate carbonyl group, to higher frequencies, as well as an increase in the absorbance at 1550 cm^{-1} due to the carboxylate anion with increasing concentration of NaOH for alkaline hydrolysis. In our case, however, an estimation based on the absorbance around 300 nm of the THF solution after alkaline hydrolysis revealed that the degrees of hydrolysis were much lower than those expected. Namely, the hydrolysis of the [80:20] film with 20 and 50 mol % NaOH compared to the total amount of monomers in the film provided [80:20]-6Na and [80:20]-10Na films, respectively. The lower degrees of hydrolysis of the helical network films may be related to insufficient swelling of the films and diffusion of the hydroxide ions into the films because of their high cross-linking density.

Figure 4 shows the polarized optical micrographs of [80:20]-0Na, -6Na, and -10Na. The [80:20]-0Na sample shows an oily streak texture, resulting from the helical structure in homogeneous alignment. No change in the oily streak texture was observed for the [80:20]-6Na sample after alkaline hydrolysis. The results based on the IR spectroscopy and the microscopic observation demonstrate that helical ionomer networks can be obtained by polymerization and alkaline hydrolysis. Contrary to the above result, the oily streak texture disappears for [80:20]-10Na. Although a partial dark region was observed for the [80:20]-10Na film, most of the film exhibits birefringence, as shown in Figure 4c. On the other hand, scanning electron micrographs of the three samples were little affected by hydrolysis. Therefore, no physical disintegration of the polymer networks appears to have been induced even by excessive hydrolysis. The birefringence of the samples is closely related to the anisotropic orientation of phenylbenzoate mesogens along the helical axis. Interference of the intermolecular interaction between mesogens due to ionic interactions as well as a decrease in the amount of cross-linking sites due to the excessive alkaline hydrolysis results in deformation of the helical structure.



(a) (b) (c)

Figure 4. Polarized optical micrographs of a hydrolyzed mixture of APB6 and A6P6A: (a) [80:20]-0Na; (b) [80:20]-6Na; (c) [80:20]-10Na.

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