Preparation of Helical Polyelectrolyte Networks by Polymerization of Hydrogen-Bonding Liquid Crystalline Monomers

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Many studies have been reported on solid polymeric films having cholesteric order, in which the molecules are arranged in a helical structure along an axis perpendicular to their longitudinal axes.[1−8] It is well-known that the cholesteric phase can be induced by adding nonmesogenic chiral molecules in nonchiral liquid crystals (LCs).[9] 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.[10] In addition, Broer et al. reported the preparation of cholesterically ordered polymer networks by polymerization of monomeric liquid crystalline diacrylate doped with small amounts of chiral molecules, resulting in the induced cholesteric (Ch) phase.[11] Recently, we described the preparation of helical polymer networks by polymerization of LC monomers at the induced Ch phase and hydrolysis of the helical polymer networks to develop helical polyelectrolyte networks with carboxylate groups as ionic species in the helix.[12] However, it was difficult to introduce large amounts of carboxylate groups in the helical networks, because the excessive hydrolysis resulted in the deformation of the helical structure.

On the other hand, Kato et al. have revealed that mesogenic structures could be obtained by self-assembly of pyridine and carboxylic acid derivatives.[13−15] In addition, Kato et al. also reported a formation of liquid cystalline polymer network through the intermolecular hydrogen bonding between polyacrylate and 4,4′-bipyridine.[16] Thus, it is expected that polymer networks with carboxylic acid groups can be prepared by polymerization of hydrogen-bonding LC monomers and subsequent removal of pyridine derivatives from the polymer networks. In this study, we describe the preparation of hydrogen-bonding nematic monomers and polymerization in the Ch phase induced by addition of chiral molecules in the hydrogen-bonding nematic monomers.

Two benzoic acid derivatives with acryloyloxy and methacryloyloxy groups at 4-position (AB and MB in Figure 1) were synthesized by reaction of acryloyl chloride (methacryloyl chloride) and 4-hydroxybenzoic acid in the presence of *N*,*N*-dimethylaniline in dioxane. The structures of the benzoic acids with vinyl groups were confirmed by NMR, IR spectra and elemental analysis. 4,4′-Bipyridine (BPy) was used as the rigid hydrogen-bonding acceptor at both ends of bipyridyl moieties. [2:1] complexes of benzoic acids and BPy were prepared by evaporation from tetrahydrofuran (THF) solutions. The [2:1] complexes are abbreviated as $(AB)_2$−BPy and $(MB)_2$−BPy. Figure 2 shows the IR spectra of AB and $(AB)_2$−BPy in the crystalline state.

Two broad bands centered around 2500 and1900 cm^{-1} are observed in the IR spectrum of the $(AB)_2$−BPy complex, indicating the formation of hydrogen bonding between AB and BPy molecules.[17] A similar IR spectrum was obtained for the $(MB)_2$−BPy complex. Thermal properties are given in Figure 1. The thermal properties were examined by differential scanning calorimetry (DSC) and polarizing optical microscopy. The phase transition temperatures given in Figure 1 were determined by DSC on heating or cooling at a rate of 5 °C/min. Both AB and MB exhibit only a melting point from a crystalline to an isotropic phase. Significant polymerization of AB and MB was caused by heating above their melting points. On the other hand, a nematic phase is observed for the $(AB)_2$−BPy complex in a temperature range of 134−157 °C, whereas both smectic and nematic phases are observed for the $(MB)_2$−BPy complex in the temperature ranges of 129−144 and 144−158 °C.

Polymerizable Ch LCs were prepared by adding S811 and A6PB6A at the concentrations of 1 and 5 mol %, and followed by adding 2,2-dimethoxy-2-phenylacetophenone as photoinitiator at the concentration of 0.5 wt % to the mixtures. A6PB6A is a monotropic LC and is used as cross-linking agent to hold macroscopically helical structure after removal of BPy and S811. Both mixtures, $(AB)_2$−BPy−S811−A6PB6A and $(MB)_2$−BPy−S811−A6PB6A, exhibit only the Ch phase in the temperature ranges of 130−154 and 128−152 °C on cooling, respectively. Polymerization was carried out by UV irradiation at the induced Ch phase (135 °C). Polarized micrographs of both LC mixtures after polymerization are shown in Figure 3. Fingerprint texture indicative of the helical structure is observed for both samples after polymerization, although a little decrease in the helical pitch is caused by polymerization, e.g., the helical pitches of $(MB)_2$−BPy−S811−A6PB6A are 1.71 and 1.47 μm before and after polymerization.[18] It is assumed that a C−C bonding distance formed in the polymer main chain through polymerization is smaller than a distance between two adjacent LC molecules before polymerization. The decrease in the helical pitch by polymerization is related to the decrease in the distance between two adjacent LC molecules. In addition, formation of polymer segments as well as cross-linking decreases mobility of the polymer segments and consequently depresses relaxation of the polymer segments to the relevant morphology of the cholestric systems. Although a little change in the IR spectra before and after polymerization was recognized for both mixtures, the broad bands around 2500 and 1900 cm-1 were observed even after polymerization. Namely, the hydrogen bonding can be assumued to be hold even after polymerization.

The poly[$(MB)_2$−BPy−S811−A6PB6A] network obtained by polymerization of $(MB)_2$−BPy−S811−A6PB6A was found to exhibit a reversible thermal phase transition between Ch and an isotropic phases. Namely, the fingerprint texture appeared by heating and subsequent cooling from the isotropic phase. However, the texture of the poly[$(AB)_2$−BPy−S811−A6PB6A] network, which

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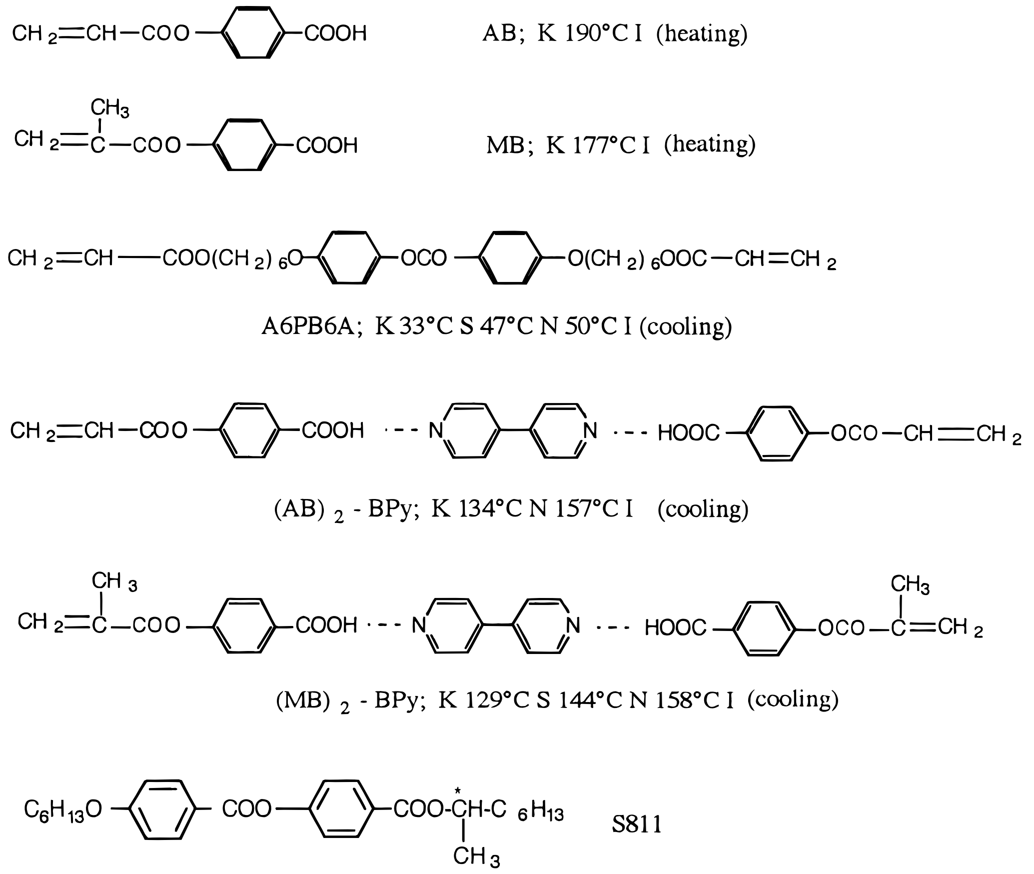

Figure 1. Structures of compounds used in this study.

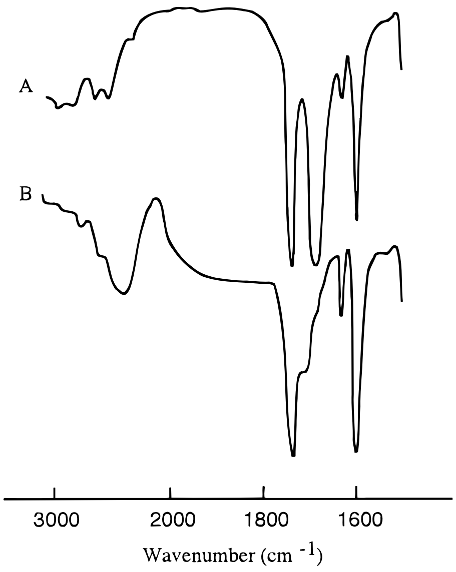

Figure 2. Infrared spectra of AB (a) and $(AB)_2$−BPy (b).

was obtained by polymerization of $(AB)_2$−BPy−S811−A6PB6A, transformed from the fingerprint texture to a schlieren texture by cooling from the isotropic phase. A similar transformation of the texture was caused by removal of BPy and S811 from the poly[$(AB)_2$−BPy−S811−A6PB6A] network. The polymer networks were immersed in THF to remove BPy, S811, and unreacted monomers to give poly[$(AB)_2$−A6PB6A] and poly[$(MB)_2$−A6PB6A] networks. The data of elemental analysis (N content: 0%) indicate that BPy molecules are removed completely by extraction with THF. In addition, both broad bands around 2500 and 1900 cm^{-1} due to the hydrogen bonding disappeared after extraction with THF.

Figure 4 shows the polarized micrographs of samples after extraction with THF. It is found that the fingerprint texture is clearly observed for the poly[$(MB)_2$−A6PB6A] network even after extraction, whereas the poly[$(AB)_2$−A6PB6A] network exhibits the schlieren texture after extraction, indicating transformation of the helical structure to the nematic phase in the case of the poly[$(AB)_2$−A6PB6A] network. To discuss the macroscopic stability of helical structure, molecular weights were determined by gel permeation chromatography. Number-averaged molecular weights (M_n) of polymers of the $(AB)_2$−BPy−S811 and the $(MB)_2$−BPy−S811 mixtures without A6PB6A are given in Table 1. The M_n of poly[$(AB)_2$−BPy−S811] is much smaller than that of poly[$(MB)_2$−BPy−S811]. The cross-linking densities of both poly[$(AB)_2$−A6PB6A] and poly[$(MB)_2$−A6PB6A] networks are approximately 5 mol % based on the amounts of A6PB6A fed in the monomer mixtures. Therefore, it is assumed that an averaged number of the cross-linking sites per poly[$(AB)_2$−BPy−S811] polymer chain is less than one, because the degree of polymerization is nine for poly[$(AB)_2$−BPy−S811]. The transformation of the macroscopically molecular orientation by removal of BPy and S811 is closely related to the molecular weight and cross-linking density of the polymer segments in the polymer networks. In addition, the glass transition temperatures (T_g's) of methacrylate polymers are generally higher than those of acrylate polymers. The difference in the mobility of polymer segments may be one of the factors influencing the stability of the macroscopically molecular orientation.

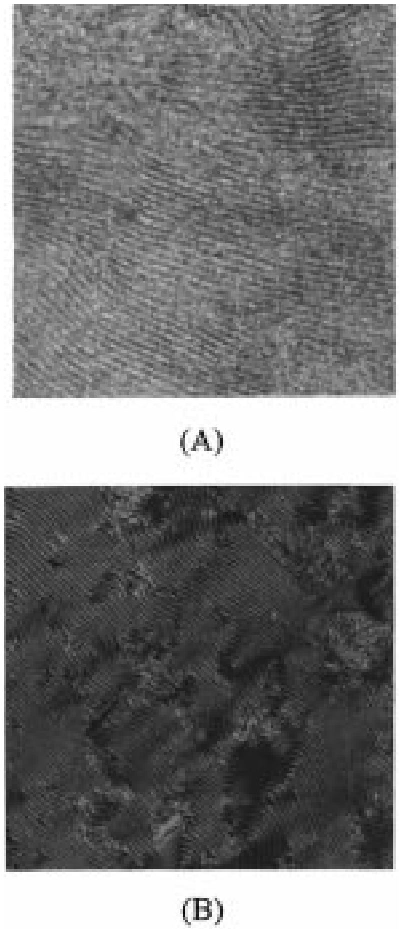

Figure 3. Optical textures of poly[$(AB)_2$−BPy−S811−A6PB6A] (A) and poly[$(MB)_2$−BPy−S811−A6PB6A] (B) obtained by polymerization in the Ch phase. The polarized micrographs were taken at 30 °C.

Table 1. Polymerization Behavior of $(AB)_2$−BPy and $(MB)_2$−BPy containing 1 mol % of S811

	convn (%)	M_n[c]	deg of polymerization
$(AB)_2$−BPy−S811[a]	78	1700	9
$(MB)_2$−BPy−S811[b]	80	11000	55

[a] $(AB)_2$−BPy−S811 was polymerized upon UV irradiation for 15 min at 135 °C. [b] $(MB)_2$−BPy−S811 was polymerized upon UV irradiation for 1 min at 135 °C. [c] M_n is the number-averaged molecular weight determined by gel permeation chromatography (calibration, polystyrene; solvent, tetrahydrofuran).

The extraction of S811 and BPy with THF affects also the properties of the poly[$(MB)_2$−BPy−S811−A6PB6A] network; e.g., the Ch−isotropic phase transition temperature is increased slightly from 250 to 263 °C, and the helical pitch is also increased from 1.47 to 2.05 μm. In addition, the helical pitch in water is decreased with increasing pH: 1.95 μm at pH 3, 1.80 μm at pH 6, and 1.65 μm at pH 11.

In summary, we prepared the helical polyelectrolyte networks by polymerization of the hydrogen-bonding nematic monomers in the induced Ch phase and subsequent extraction of BPy and S811 with THF. The pitch length as well as a helical sense is expected to be controlled easily by varying polymerization temperature, solvent, ph, and chirality of the chiral dopants. Studies on the properties of helical polyelectrolyte networks with respect to adsorption and molecular recognition of chiral compounds are now in progress.

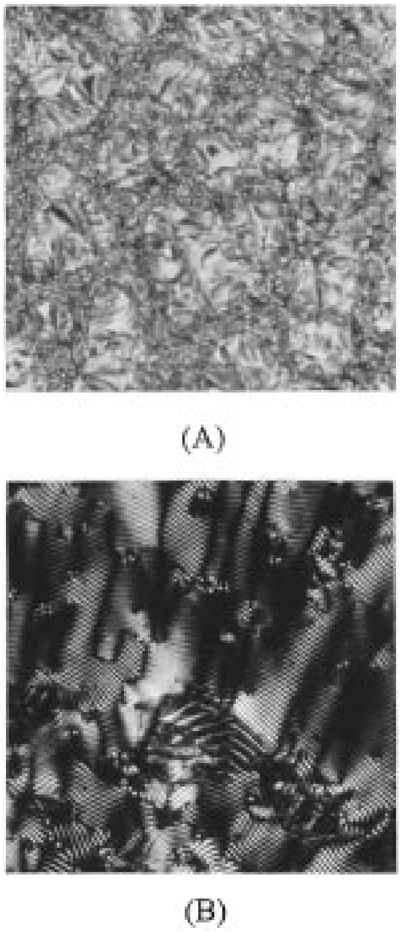

Figure 4. Optical textures of poly[$(AB)_2$−A6PB6A] (A) and poly[$(MB)_2$−A6PB6A] (B) which were obtained by immersion of poly[$(AB)_2$−BPy−S811−A6PB6A] and poly[$(MB)_2$−BPy−S811−A6PB6A] with shaking in THF. The polarized micrographs were taken at 30 °C.

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(18) The helical pitch is estimated based on the fingerprint textures.

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