Induced Smectic Phase Formed by New Liquid Crystalline Binary Systems Consisting of Main Chain Polymer and Twin Compound

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The thermal and mesomorphic properties of the new liquid crystalline binary systems, consisting of a nematic main chain liquid crystalline polymer and a nematic twin liquid crystal, have been studied. The liquid crystalline binary systems formed an induced smectic A phase, which was characterized by a uniaxial conoscopic figure, a fan texture, and a broad X-ray scattering peak at the wide angle.

The use of noncovalent interactions between distinct components can provide significantly potential producing a supramolecular structure in the liquid crystalline field and act effectively in forming the new liquid crystalline systems which are of considerable interest in both fundamental and technological viewpoints.[1-10] The mixing two or more liquid crystals allows to vary the properties of the liquid crystalline systems and can enhance the liquid crystallinity.[1,2,6,8-10] In general, this is due to the interactions between different components.

In this work, we found that the new binary systems consisting of a nematic main chain liquid crystalline polymer and a nematic twin liquid crystal exhibit an induced smectic A phase. We used a polycarbonate type of the main chain liquid crystal polymer consisting of azobenzene mesogenic and tri(oxyethylene) units and the twin liquid crystal with nitroazobenzene mesogenic units on both sides of an octamethylene chain (Figures 1, 2). The liquid crystalline polycarbonate (Mn=5, 400, Mw/Mn=1.4) was synthesized by interfacial polymerization of 4,4'-dihydroxyazobenzene and triethylene glycol bis(chloroformate). The purification of the liquid crystalline polycarbonate was performed by adding methanol to the tetrahydrofuran-polymer sample solution. The molecular weight of the liquid crystalline polycarbonate was determined by GPC measurement, calibrated with standard polystyrenes. The twin liquid crystal was obtained by the reaction of sebacoyl chloride and 4-(4-(nitro)phenylazo)phenol. The chemical structure of the twin liquid crystal was identified by ^{1}H NMR measurement: ^{1}H NMR (CDCl$_3$) δ =1.44(m 8H), 1.8(t 4H), 2.6(t 4H), 7.26(d 4H), 7.98(d 8H), 8.28(d 4H).

The phase transitions of the liquid crystalline systems prepared in this work were examined by the combination of DSC measurement, polarizing microscopy, and X-ray diffraction measurement. The phase transition temperatures are summarized in Figure 3. Figure 4 shows the DSC curves of the twin liquid crystal, the main chain liquid crystalline polycarbonate, and the liquid crystalline binary system with X=0.5. Both the twin liquid crystal and the liquid crystalline polycarbonate formed an enantiotropically nematic phase with a schlieren texture and exhibited the solid-nematic and nematic-isotropic phase transitions as shown in Figure 4. The liquid crystalline binary systems with X=0.2, 0.3, 0.5, and 0.7 clearly showed an enantiotropically smectic A phase with a fan texture (Figure 5). In addition, the liquid crystalline binary systems with X=0.2 or 0.3 exhibited the solid-smectic A and smectic A-isotropic phase transitions in the same manner as PC/TNO$_2$(0.5) (Figure 4). In PC/TNO$_2$(0.7) with X=0.7, however, the nematic and smectic A phases were produced. The formation of the induced smectic A phase in the liquid crystalline binary systems is due to the noncovalent interactions between the twin and main chain polymeric molecules. In addition, these data obtained by DSC measurement (Figure 4) and polarizing microscopy (Figure 5) indicate that the twin liquid crystal and the liquid crystalline polycarbonate are miscible.

Figure 5 shows the optical textures of PC/TNO$_2$(0.5). The liquid crystalline binary systems with X=0.2, 0.3, and 0.5 formed batonnets at the isotropic-smectic phase transition temperature on cooling the isotropic liquid and a fan texture on cooling the state with the batonnets. Furthermore, the uniaxial conoscopic figures were observed for the homeotropic structures produced by the liquid crystalline binary systems as shown in Figure 6. The homeotropic structure was obtained in a sample sandwiched between glass plates with perpendicular surface treatment, using a carboxylatochromium complex

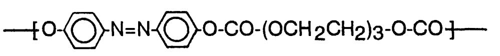


Figure 1. Structure of polycarbonate type of main chain liquid crystalline polymer.

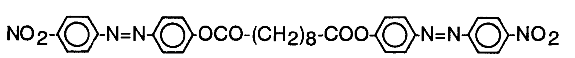


Figure 2. Structure of twin liquid crystal.

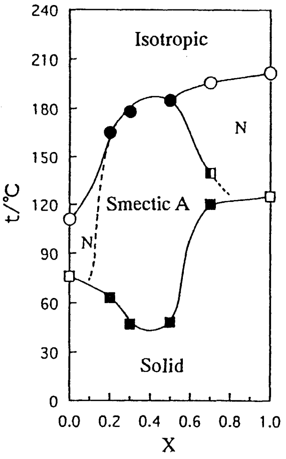


Figure 3. Phase transition temperatures of liquid crystalline systems: N; nematic: X: molar fraction of twin liquid crystal component: 1-X; unit molar fraction of liquid crystalline polycarbonate component.

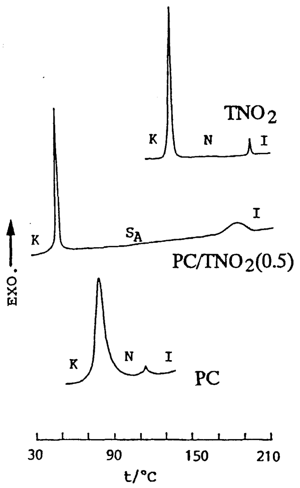
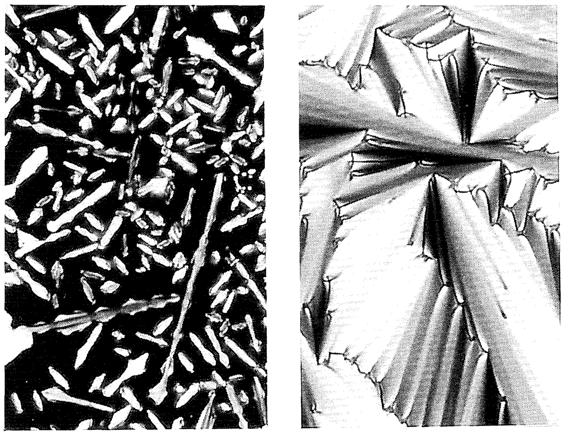


Figure 4. DSC curves of twin liquid crystal (TNO$_2$), main chain liquid crystalline polycarbonate (PC), and liquid crystalline binary system [PC/TNO$_2$(0.5)].



Batonnets (183.2℃) Fan shaped texture (96.0℃)

Figure 5. Optical textures exhibited by PC/TNO2(0.5).

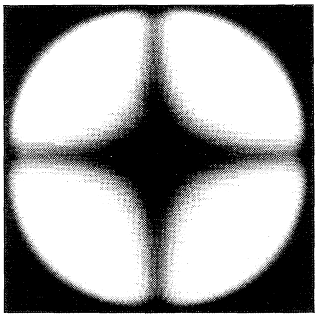


Figure 6. Conoscopic figure of PC/TNO2(0.5).

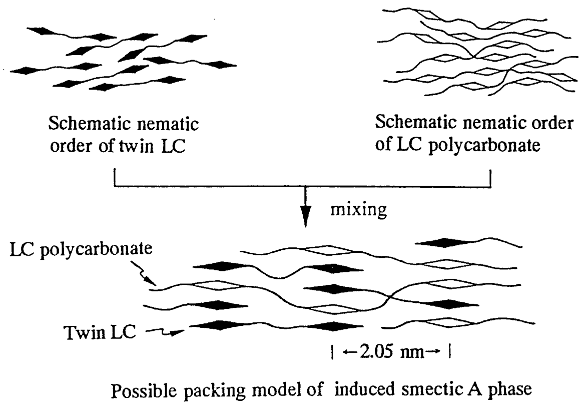


Figure 7. Formation of induced smectic A phase.

agent.[11]

The orientational behavior of the induced smectic A phase was examined at various temperatures by X-ray diffraction measurement. The measuring temperature was controlled with a Mettler hot stage FP82 equipped with a Mettler temperature controller FP80. In the liquid crystalline binary systems, the sharp scattering peak corresponding to the smectic A layer spacing was on the small angle. In addition, the broad scattering peak, which indicates the absence of the long-range orientational order in the smectic layer, was on the wide-angle region.

The smectic A layer spacing was 2.05 nm in every liquid crystalline binary system. The smectic layer spacing of 2.05 nm corresponds to the distance between centers of the mesogenic cores in the extended twin molecule. In this case, the possible packing model is schematically illustrated in Figure 7. As shown in Figure 7, the twin liquid crystal and the liquid crystalline polycarbonate have the nematic orientational orderings. The interactions between the twin and polymeric molecules allow the liquid crystalline binary systems to produce the smectic A orientational ordering. The mesogenic moieties in both the twin liquid crystal and the liquid crystalline polycarbonate overlap each other and the distance between the mesogenic moieties along the director corresponds to the smectic A layer spacing. In this case, the nitroazobenzene-nitroazobenzene, nitroazobenzene-dioxyazobenzene, and dioxyazobenzene-dioxyazobenzene interactions can act effectively in producing the induced smectic A phase.

Furthermore, we measured the UV-visible spectra of PC/TNO2(0.5), the twin liquid crystal, and the liquid crystalline polycarbonate. In the liquid crystalline state, the twin liquid crystal and the liquid crystalline polycarbonate displayed the absorption of the transform azobenzene at 460 nm and 350 nm, respectively. PC/TNO2(0.5) exhibited the absorption at 393 nm, which is absent in the twin liquid crystal and the liquid crystalline polycarbonate, in addition to the absorption at 350 nm and 460 nm. The absorption at 393 nm in PC/TNO2(0.5) corresponds to the presence in the interactions between nitroazobenzene and dioxyazobenzene units.[9] Also, these interactions are strongly related to the formation of the induced smectic A phase.

References and Notes

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