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Liquid-Crystalline Binary Systems with Nonmesomorphic Comb-Shaped Polymer Component

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Binary liquid-crystalline systems were prepared by mixing a nonmesomorphic comb-shaped polymer (CSP) and low-molecular-weight liquid crystal. CSP exhibited a glass-isotropic phase transition. The binary liquid-crystalline systems consisting of CSP and polar molecule formed smectic A and smectic B phases. The induction of liquid crystalline phases is due to interactions between the side chain of CSP and low-molecular-weight liquid crystals.

Keywords Amorphous polymer; induced smectic phase; liquid-crystalline binary system; polar molecule

Introduction

Thermotropic liquid-crystalline systems are formed by mesogenic compounds and mixtures. One of a method to improve liquid-crystalline properties is to mix two or more components [1,2]. It is known that the noncovalent interactions between distinct molecules can lead to the formation of liquid-crystalline phases with enhanced thermal stability [3,4]. For instance, a binary mixture of electron-donor and electron-acceptor molecules can form induced smectic phases by a charge-transfer effect even if the components show only a nematic phase or no liquid-crystalline phase [1,2, 5–10].

In this study, binary liquid-crystalline systems consisting of a nonmesomorphic comb-shaped polymer and a nematic liquid crystal were prepared. Their thermal and orientational properties were examined. This paper describes the formation of induced smectic A and smectic B phases in the liquid-crystalline binary systems.

Experimental

Materials

The structures of mixing components are shown in Fig. 1. A methacrylate monomer was synthesized following the previous method [11,12].

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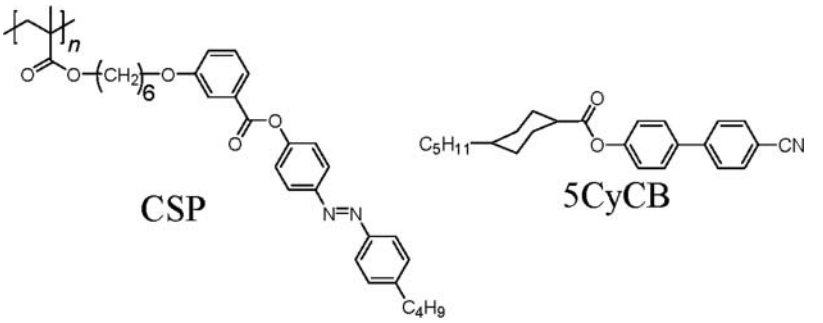

Figure 1. Structures of CSP and 5CyCB.

3(1-(Hydroxy)hexyloxy)benzoic acid (m6B)

3-Hydroxybenzoic acid, 6-chloro-1-hexanol and potassium hydroxide were dissolved in ethanol, and the solution was refluxed for 24 h. After the reaction, ethanol was evaporated and a crude product was obtained. The crude product was dissolved in water, and the solution was acidized with hydrochloric acid. 3-(1-(Hydroxy)hexyloxy)benzoic acid (*m*6B) was filtered off.

3-(1-Methacryloyloxy)hexyloxy)benzoic acid (MABA)

*m*6B and excess methacrylic acid were dissolved in chloroform at 60°C, and the solution was refluxed for 15 h. After the reaction, the chloroform solution was washed with water, and the chloroform solution was dried with magnesium sulfate. Chloroform was evaporated, and the crude product of 3-(1-methacryloyloxy)hexyloxy)benzoic acid (MABA) was purified by recrystallization using ethanol.

4-(3-(6-Methacryloyloxy)hexyloxy)benzoyloxy-4′-butylazobenzene (mBu)

MABA was reacted with excess thionyl chloride, and after the reaction, thionyl chloride was evaporated. The crude product was dissolved in tetrahydrofuran, and the solution was added in the tetrahydrofuran solution of 4-(4-(butyl)phenylazo)phenol and triethylamine. The solution was reacted at room temperature for 12 h. After the reaction, tetrahydrofuran was evaporated, and the crude was dissolved in chloroform. The chloroform solution was washed with water, and the chloroform solution was dried with magnesium sulfate. Chloroform was evaporated, and crude product was recrystallized from 2-propanol. The methacrylate monomer 4-(3-(6-methacryloyloxy)hexyloxy)benzoyloxy-4′-butylazobenzene (*m*Bu) was obtained.

^{1}H NMR($CDCl_3$), δ: 7.99 (d, 2H, Ar-***H***), 7.83 (m, 4H, Ar-***H***), 7.71 (s, 1H, Ar-***H***), 7.42 (t, 1H, Ar-***H***), 7.35 (m, 4H, Ar-***H***), 7.18 (d, 1H, Ar-***H***), 6.10 (s, 1H, C***H***$_2$=C), 5.54 (s, 1H, C***H***$_2$=C), 4.17 (t, 2H, -COOC***H***$_2$-), 4.03 (t, 2H, -CH_2C***H***$_2$O-), 2.70 (t, 2H, Ar-C***H***$_2$-), 1.94 (s, 3H, CH_2=C(C***H***$_3$)-), 1.84-1.38 (m, 12H, -C***H***$_2$-), 0.95 (t, 3H, -CH_2C***H***$_3$).

4-Pentyl-4′-cyanobiphenylyl cyclohexanoate (5CyCB)

4-Pentyl-4′-cyanobiphenylyl cyclohexanoate (5CyCB) was synthesized by esterification. *trans*-4-Pentylcyclohexanecarboxylic acid reacted with excess thionyl chloride, and after the reaction, thionyl chloride was evaporated. The crude product was dissolved in tetrahydrofuran, and the solution was added in the tetrahydrofuran solution of 4-cyano-4′-hydroxybiphenyl and triethylamine. The solution was reacted at room temperature for 12 h. After the reaction, tetrahydrofuran was evaporated, and the crude was dissolved in chloroform. The chloroform solution was washed with water, and the chloroform solution was dried with magnesium sulfate. Chloroform was evaporated, and crude product was recrystallized from methanol.

^{1}H NMR($CDCl_3$), δ: 7.73-7.56 (m, 6H, Ar-***H***), 7.17 (d, 2H, Ar-***H***), 2.51 (m, 1H, -C***H***(AX)), 2.13 (m, 2H, -C***H***(AX)), 1.87 (m, 2H, -C***H***(EQ)), 1.62-1.51 (m, 2H, -C***H***(EQ)), 1.32-1.22 (m, 9H, -C***H***(AX), -C$\boldsymbol{H}_2$-), 1.01 (m 1H, -C***H***(EQ)), 0.92 (t, 3H, -CH_2C$\boldsymbol{H}_3$).

Side Chain Polymer (CSP)

*m*Bu and AIBN were dissolved in tetrahydrofuran, and dry nitrogen gas. The mixture was maintained at 60°C for 24 h. After the reaction, the solution was poured into methanol, and the precipitate was filtered off. The purification of the polymer was carried out by soxhlet extraction using methanol for 24 h, and gave rise to the comb-shaped polymer (CSP: poly(4-(3-(6-methacryloyloxy)hexyloxy)benzoyloxy-4′-butylazobenzene)).

Binary Liquid Crystals

Binary liquid-crystalline systems were prepared by mixing CSP and nematic liquid crystal (5CyCB).

Measurement

The liquid-crystalline properties and phase transition temperatures were examined by polarizing microscopy (a Nikon polarizing microscope with a Mettler thermosystem 900 equipped with a Mettler hot stage HT84) and DSC measurement (a Shimadzu DSC60). The orientational behavior was examined by the temperature-variable X-ray diffraction measurement (a Shimadzu XRD 6100 with an Anton Parr heating system). The molecular weight was measured by GPC measurement (a Shimadzu CTO-20A), calibrated standard polystyrenes.

Results and Discussion

Phase Transitions

A side chain polymer (CSP : $Mn = 22900$, $Mw/Mn = 2.20$), having 4-(4-(butyl)phenylazo)-phenylbenzoate (BAB) side groups, exhibited only a glass transition and did not reveal a liquid-crystalline phase (see Fig. 2). A low-molecular-weight 5CyCB with a cyanobiphenyl group is a nematic liquid crystal. The binary liquid crystals (CSP/5CyCB(X), X: mole fraction of 5CyCB), consisting of CSP and 5CyCB, show induced smectic A and smectic B phases, which were formed by CSP or 5CyCB (see Fig. 2). It is expected that an interaction between 4-cyanobiphenylylbenzoate (strong polar group) of 5CyCB and BAB

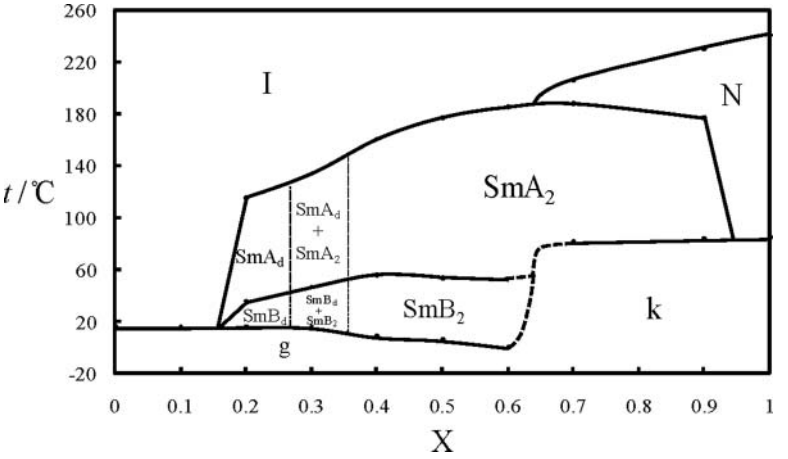

Figure 2. Phase diagram of binary liquid crystals CSP/5CyCB(X). X : mole fraction of 5CyCB, g : glassy, k : solid, SmB : smectic B, SmA : smectic A, I : isotropic. d and 2 denote interdigitated bilayer and bilayer structures, respectively.

side group (nonpolar group) of CSP led to the formation of the induced smectic phases. In previous researches, the formation of induced smectic phases was reported in the binary mixtures, consisting of a strong polar compound and a nonpolar compound [1,2].

In the smectic A and smectic B phases of CSP/5CyCB(X), fan textures were observed (Fig. 3). However, the fan texture in the smectic A phase is not obviously different from the fan texture in the smectic B phase. Therefore, it is difficult to determine the smectic A-smectic B phase transition by polarizing microscopy. However, DSC and X-ray diffraction measurements clearly revealed the existence of the smectic A-smectic B phase transition in CSP/5CyCB(X) except CSP/5CyCB(0.3). The smectic phases formed by CSP/5CyCB(0.3) are a frustrated smectic phase. The two types of layer structures were found in the smectic phases of CSP/5CyCB(X). The orientational structures of the smectic phases depended on the composition of low-molecular-weight liquid crystals. An interdigitated bilayer structure (X = 0.2) and a bilayer structure (X is more than 0.4) were formed. Both the interdigitated layer and bilayer structures were coexisted in CSP/5CyCB(0.3). The same coexistence of two smectic layer structures was also found for binary mixtures with polar components [13,14].

X-Ray Diffractions

The temperature-variable X-ray diffraction measurement in the liquid-crystalline phase was performed in order to investigate the orientational behavior of the binary liquid crystals. The X-ray diffraction patterns of CSP/5CyCB(X) were shown in Fig. 4. In the smectic A phase (X = 0.7, 0.9), the inner sharp reflections and the outer broad reflection were measured. The inner sharp reflection corresponds to the layer spacing of the smectic A phase and the outer broad reflection shows a short range order within the smectic layer. On the other hand, the X-ray diffraction pattern of the smectic B phase (X = 0.2, 0.3 and 0.5) are characterized by the sharp inner and outer reflections. The fact that the outer reflection is sharp indicates the existence in a long range order within the smectic layer, having a hexatic packing.

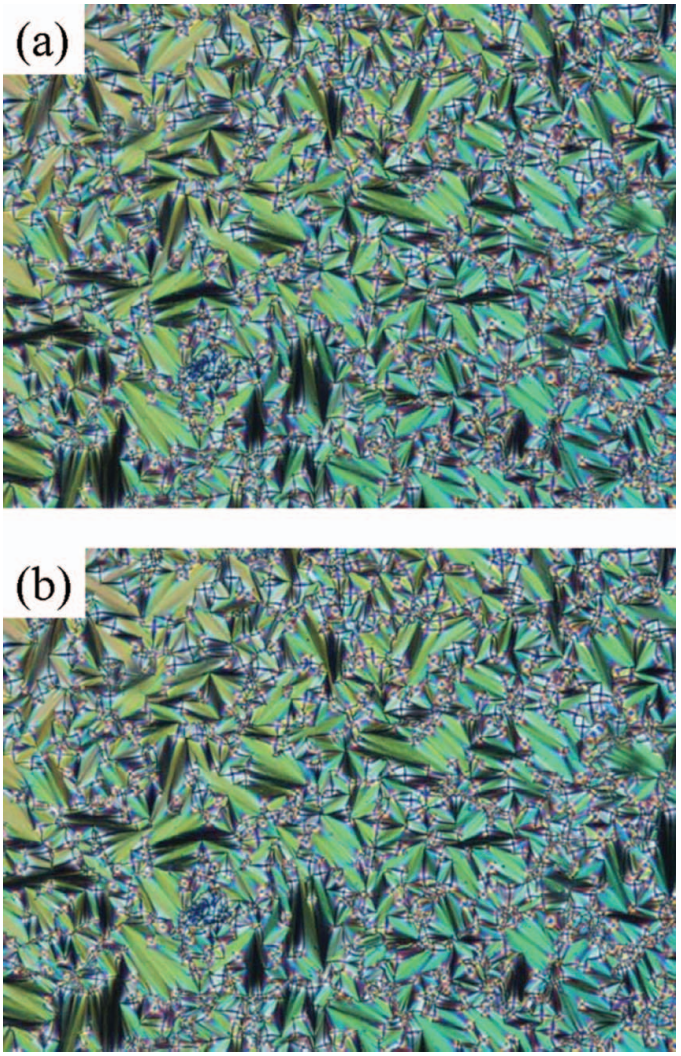

Figure 3. Optical textures observed for CSP/5CyCB(0.5). (a) : smectic A, 150°C, (b) : smectic B, 30°C. The photographs of both (a) and (b) were taken in the same position.

At X = 0.3, the interdigitated layer and bilayer structures coexist, showing the X-ray inner reflections corresponding to the length of interdigitated layer and bilayer periodicities.

From the relationship between a layer spacing and molecular lengths, possible packing models for the smectic phases were proposed (see Fig. 5). In the smectic A phase, there is a segregation between polymer backbones and mesogenic groups. The mesogenic groups have an orientational order and no positional order within the layer. The smectic B phase has the hexatic order within the layer. The intermolecular distance within the smectic B layer is 4.4 Å. The fully-extended side chain length of CSP is 28.4 Å, while the molecular length of 5CyCB is 21.7 Å. In CSP/5CyCB(0.2), the smectic layer spacing is 35.2 Å, corresponding to the interdigitated bilayer structure. In CSP/5CyCB(0.5) and CSP/5CyCB(0.9), the layer spacings were 54.0 Å and 53.9 Å, respectively, corresponding to twice the side chain

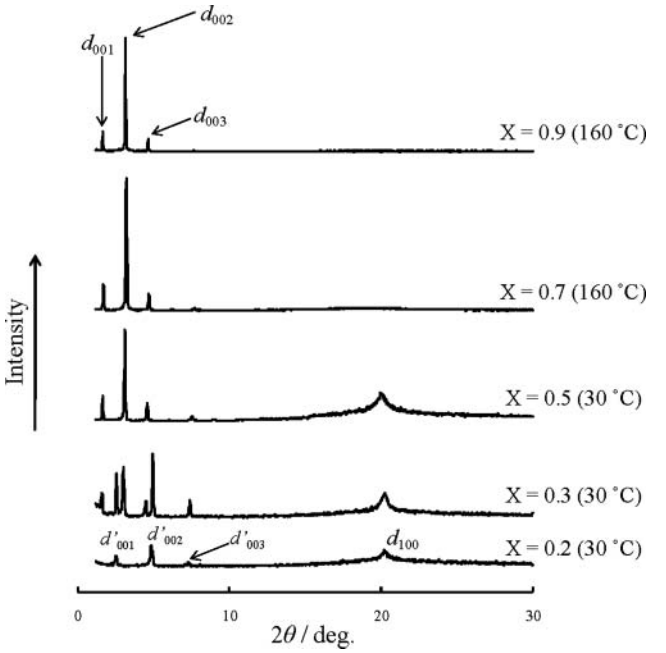

Figure 4. XRD patterns of CSP/5CyCB(X). X = 0.2, 0.3, 0.5 : smectic B, X = 0.7, 0.9 : smectic A.

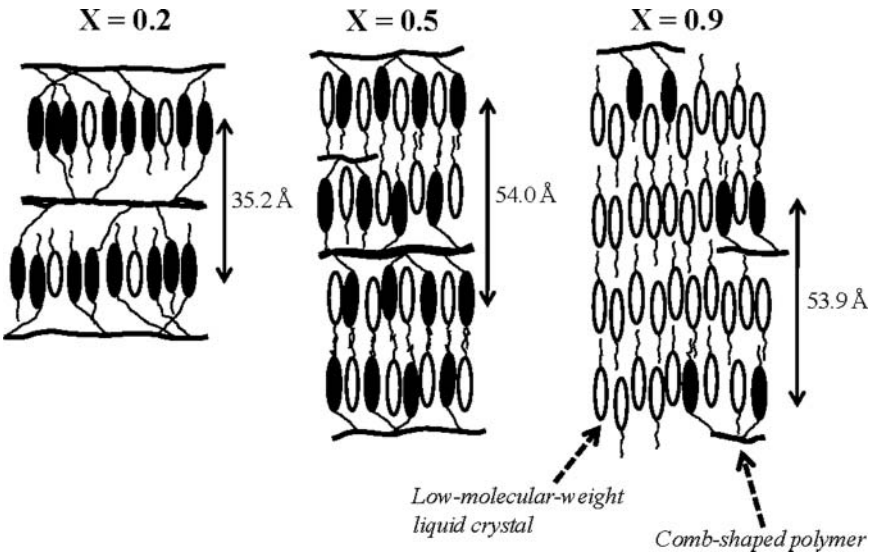

Figure 5. Possible packing models for induced smectic A phases of CSP/5CyCB(X). X = 0.2 : interdigitated bilayer, X = 0.5, 0.9 : bilayer. In the smectic A phases, the position of the center of gravity of the mesogenic groups is random within the layer. The smectic B phase has a hexatic packing within the layer.

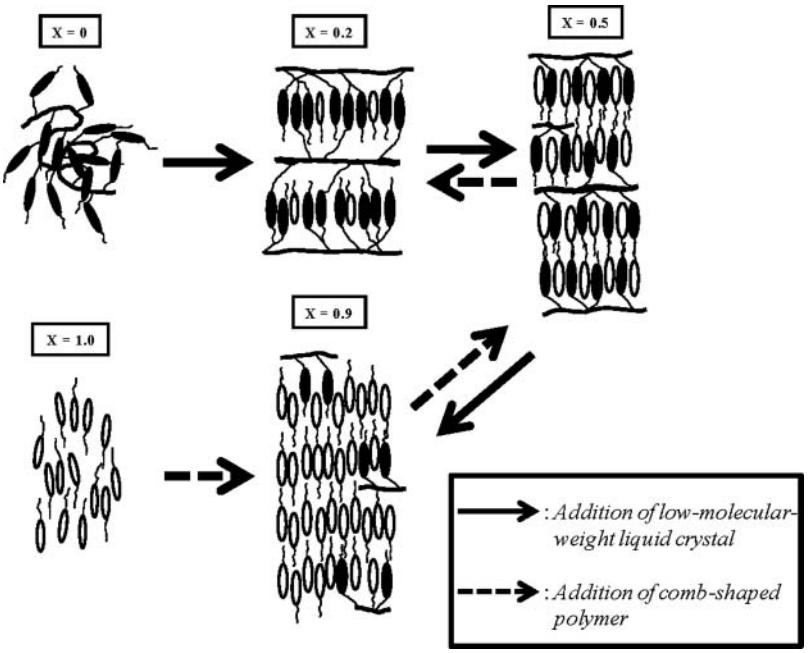

Figure 6. Schematic illustrations for image of liquid crystal formation.

length of CSP. CSP/5CyCB(0.5) and CSP/5CyCB(0.9) formed the bilayer structure that partially overlapped terminal alkyl chains. In the X-ray diffraction patterns for the bilayer structure, the peak intensity of the second order reflection was stronger than that of first order reflection. The distance for the second order reflection corresponds to the periodicity of mesogenic groups. The image of the liquid crystal formation in CSP/5CyCB(X) was schematically illustrated in Fig. 6. The interdigitated layer is formed by an influence of CSP as shown in $X = 0.2$. In contrast, the formation of the bilayer structure is mainly influenced by 5CyCB.

Conclusions

The induced smectic A and smectic B phases were shown in the binary liquid crystals consisting of the nonmesomorphic side chain polymer and the nematic liquid crystal. In the orientational structures of the induced smectic phases, both the interdigitated layer and bilayer structures were formed. Furthermore, even a small amount of CSP acts effectively in forming layer structure.

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