

# Ordered smectic phase formed by novel binary liquid crystalline systems consisting of low-molecular-weight polar compounds and an amorphous side-chain polymer

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## Abstract

Novel binary liquid crystalline systems were obtained by mixing amorphous side-chain polymethacrylate (SCP) and polar compounds. Their thermal and orientational properties were examined by DSC measurement, polarizing microscopy and temperature-variable X-ray diffraction measurement. SCP exhibited only a glass transition and did not form a liquid crystalline phase. An induced smectic A phase was formed by the binary liquid crystalline systems consisting of SCP and azobenzene derivatives with polar groups over a wide temperature range. In the case of the binary liquid crystalline systems composed of SCP and a cyanobiphenyl derivative, a highly ordered smectic B phase was formed as well as the smectic A phase. The induction of the smectic phases is due to interactions between the side-chains of SCP and the polar molecules.

## Key words

binary liquid crystalline mixture, side-chain polymethacrylate, induced smectic B, phase transition, X-ray

## 1. Introduction

The mixing of two or more liquid crystalline compounds allows to induce the liquid crystalline phases with enhanced thermal properties. This is due to the noncovalent interactions between distinct mesogenic components. Furthermore, the mixing technique is a method for improving the properties of polymers (Benthack and Finkelmann, 1985; George and Porter, 1986; Huh et al., 1983; Kiss, 1987). In this regard, the mixing of different liquid crystalline polymers or low-molecular-weight liquid crystals has been already investigated (Demus et al., 1981; Imrie, 1995; Park et al., 1975; Pelzl et al., 1987). Addition of chiral compounds into liquid crystalline materials leads to the formation of chiral liquid crystalline phases. Furthermore, in mixed systems, self-assembly and self-organization occur via noncovalent interactions between distinct molecules. Noncovalent interactions such as hydrogen bonding, ionic interaction, and charge-transfer interaction can lead to the formation of liquid crystalline phases with an enhanced thermal stability and the induction of novel liquid crystalline phases. For instance, a binary mixture consisting of electron-donating and electron-accepting compounds can form induced smectic phases via the charge-transfer interaction, even though the individual components exhibit only a nematic phase or no liquid crystalline phase (Ujiie et al., 1987; 2012). It was reported that binary liquid crystalline systems consisting of a nematic main-chain polycarbonate (PC) and 4-nitroazobenzene-containing low-molecular-weight compounds (NA) with a monotropic nematic phase exhibited an induced smectic A phase (Ujiie et al., 1995a). Formation of the induced smectic A phase was driven by the interaction

between the azobenzene groups of PC and 4-nitroazobenzene groups of NA. Furthermore, binary liquid crystalline systems consisting of nematic polymers and nematic twin compounds with a polar terminal group induced smectic A and smectic C phases (Ujiie et al., 1995b; 1998). The binary liquid crystalline systems of PC and twin components with even-numbered central methylene spacers formed a smectic A phase. In the binary liquid crystalline systems having twin components with odd-numbered central methylene spacers, smectic A and smectic C phases were formed. The induction of smectic phases is related to the interactions between polar and weak polar mesogenic groups.

In this study, novel binary liquid crystalline systems consisting of a non-mesomorphic side-chain polymer and polar liquid crystals were prepared, and their thermal and orientational properties were examined. In this paper, the formation of an induced smectic A phase and smectic B phase in the binary liquid crystalline system is described.

## 2. Experimentals

### 2.1 Materials

Low-molecular-weight mesogenic compounds (LC-XR, Figure 1) were obtained by the condensation reaction of hexanoyl chloride (TCI Co., Ltd.) and 4-substituted phenol derivatives (4PHs) using the method described in the literature (Kojo et al., 2012) (Figure 1). The hexanoyl chloride was dissolved in tetrahydrofuran, and the solution was added into the tetrahydrofuran solution of 4PHs and triethylamine at 0 °C. 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 LC-XR were obtained by the recrystallization of crude products

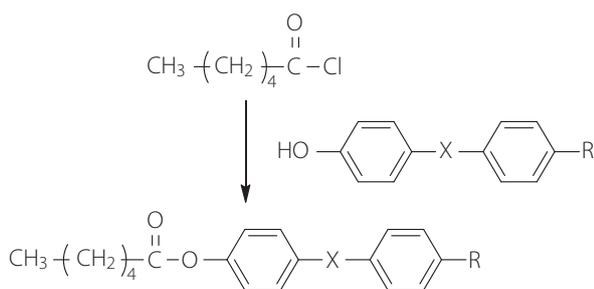


Figure 1: Synthesis of low-molecular-weight compounds (LC-XR)

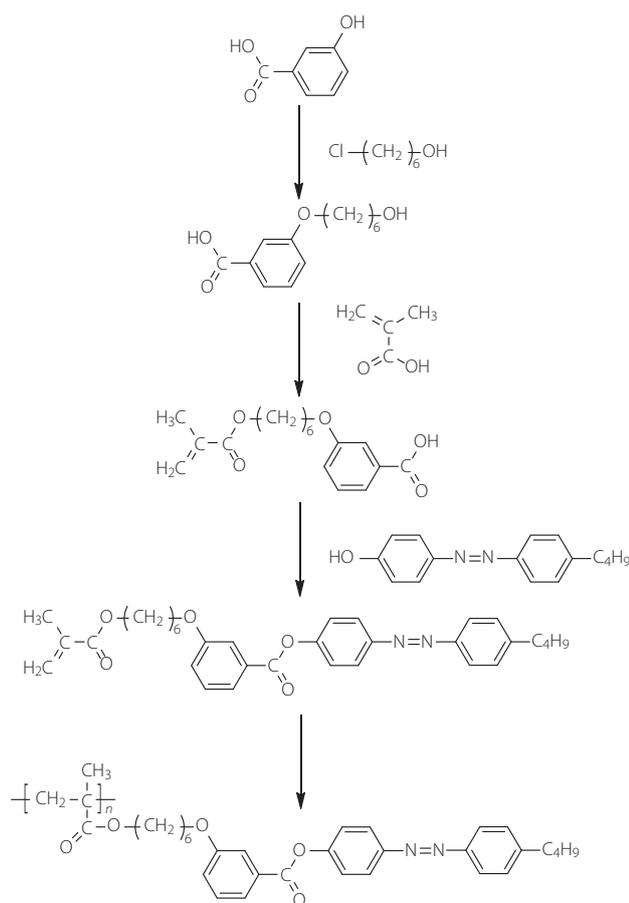


Figure 2: Synthesis of amorphous side-chain polymer (SCP) with 4-butylazobenzene group

using methanol. A side-chain polymer (SCP, Figure 2) with mesogenic side-chains was obtained by the radical polymerization of a methacrylate monomer synthesized by using the method in the literature (Ujiie et al., 1998). The binary liquid crystalline systems were prepared by mixing LC-XR and SCP.

## 2.2 Measurements

The molecular weight of SCP was measured by a GPC method (Shimadzu LC20AD-RID10A-GTO20A) in THF, calibrated against polystyrene standards. Liquid crystalline properties were examined by polarizing microscopic observation with a polarizing microscope (Nikon ECLIPSE LV100N POL) equipped

with a hot stage system (Mettler-Toledo FP90-FP82). The phase transition temperatures were determined by DSC measurement (Mettler-Toledo DSC1). The orientational structures were examined by the temperature-variable X-ray diffraction measurement (Shimadzu XRD6100, Anton Paar TTK-450).

## 3. Phase transitions

Phase transitions of LC-XR, SCP ( $M_n = 25,000$ ,  $M_w/M_n = 2.48$ ), and the binary liquid crystalline systems (SCP/LC-XR<sub>0.5</sub>, 0.5: mole fraction of LC-XR) are listed in Table 1. SCP was an amorphous polymer and exhibited glass transition at 27.2 °C. Azobenzene derivatives with polar groups such as cyano and nitro groups, revealed a monotropic nematic phase. An azobenzene derivative with a butyl group and a cyanobiphenyl derivative formed a nematic phase on heating and cooling processes. The binary liquid crystalline systems consisting of SCP and LC-XR with polar groups exhibited induced smectic phases on heating and cooling processes. However, the liquid crystalline binary system (SCP/LC-AzoBu<sub>0.5</sub>) composed of SCP and LC-AzoBu did not form a liquid crystalline phase and showed a melting point at 40.5 °C. SCP/LC-AzoCN<sub>0.5</sub> and SCP/LC-AzoN<sub>0.5</sub> induced only a smectic A phase. On

Table 1: Phase transitions of low-molecular-weight compounds (LC-XR), amorphous side-chain polymer (SCP), and binary liquid crystalline systems (SCP/LC-XR<sub>0.5</sub><sup>(1)</sup>)

Sample	X	R	Phase transition temp. <sup>(2)</sup> (°C)
LC-AzoBu	N = N	C <sub>4</sub> H <sub>9</sub>	$T_{KN} = 59.5$ $T_{NI} = 65.9$
LC-AzoCN	N = N	CN	$T_m = 108.6$ (monotropic nematic: $T_{KN} = 75.5$ , $T_{NI} = 107.9$ )
LC-AzoN	N = N	NO <sub>2</sub>	$T_m = 78.9$ I (monotropic nematic: $T_{KN} = 59.6$ , $T_{NI} = 74.1$ )
LC-BCN	none	CN	$T_{KN} = 56.7$ $T_{NI} = 70.6$
SCP	-	-	$T_g = 27.2$
SCP/LC-AzoBu <sub>0.5</sub>	N = N	C <sub>4</sub> H <sub>9</sub>	$T_g = 18.0$ $T_m = 40.5$
SCP/LC-AzoCN <sub>0.5</sub>	N = N	CN	$T_{KA} = 28.5$ $T_{AI} = 110.7$
SCP/LC-AzoN <sub>0.5</sub>	N = N	NO <sub>2</sub>	$T_{GA} = 2.3$ $T_{AI} = 104.2$
SCP/LC-BCN <sub>0.5</sub>	none	CN	$T_{GB} = 13.7$ $T_{BA} = 54.2$ $T_{AI} = 100.3$

Notes: (1) 0.5: mole fraction of LC-XR; (2)  $T_g$ : glass transition,  $T_m$ : melting,  $T_{KN}$ : solid-nematic phase transition,  $T_{NI}$ : nematic-isotropic phase transition,  $T_{KA}$ : solid-smectic A phase transition,  $T_{GA}$ : glass-smectic A phase transition,  $T_{GB}$ : glass-smectic B phase transition,  $T_{BA}$ : smectic B-smectic A phase transition,  $T_{AI}$ : smectic A-isotropic phase transition.

the other hand, SCP/LC-BCN\_0.5 with the cyanobiphenyl derivative formed a smectic B phase as well as the smectic A phase. The induction of smectic phases is due to the interaction between the mesogenic group of SCP and LC-XR with the polar derivatives.

A phase diagram was obtained for SCP/LC-BCN<sub>y</sub> (*y*: mole fraction of LC-BCN) that forms the smectic B phase (Figure 3). In SCP/LC-BCN<sub>y</sub>, the induced smectic A and smectic B phases were observed in the ranges  $y = 0.3 - 0.9$  and  $y = 0.3 - 0.6$ , respectively. The transition temperature of smectic A-isotropic phase was maximized at  $y \approx 0.55$ . On the other hand, the highest transition temperature from smectic B to smectic A phase was reached at  $y \approx 0.45$ . The orientational structure of the smectic A phase was stable when cyanobiphenyl of LC-BCN was present in excess compared with 4-butylazobenzene of SCP. When the cyanobiphenyl content was less than the 4-butylazobenzene content, the formation of smectic B phase was favored.

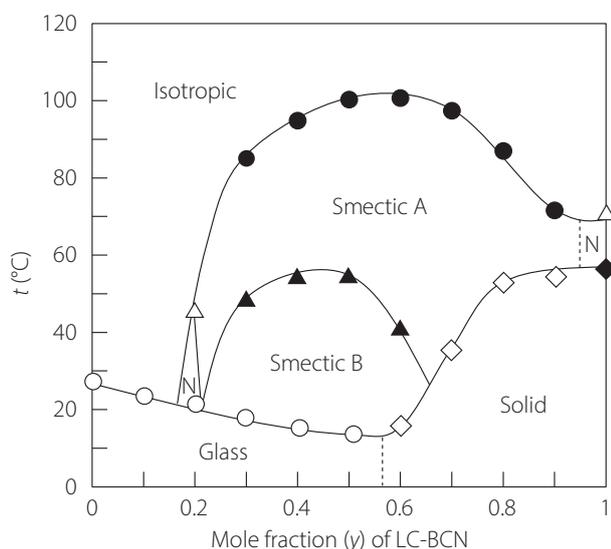
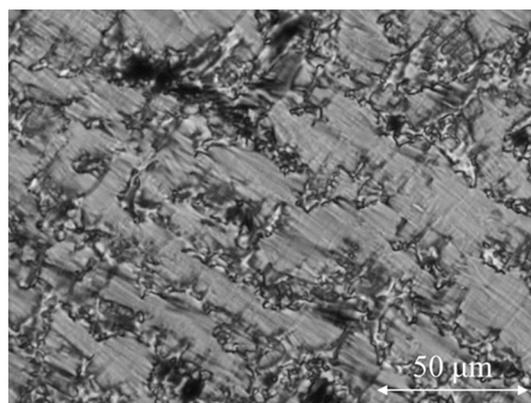


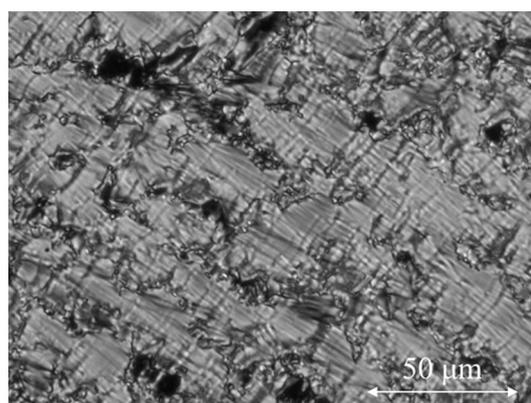
Figure 3: Phase transitions in binary liquid crystalline system SCP/LC-BCN<sub>y</sub>

Notes: ○: glass transition, ◇: solid-smectic phase transition, ◆: solid-nematic phase transition, △: nematic-isotropic phase transition, ▲: smectic B-smectic A phase transition, ●: smectic A-isotropic phase transition.

Liquid crystalline optical textures of SCP/LC-BCN\_0.5 are shown in Figure 4. Bâtonnets were formed upon the transition from the isotropic to smectic A phase. A fan texture was formed in the smectic A phase (Figure 4a). Cooling of the smectic A phase resulted in its transition to the smectic B phase, in which a striped fan texture appeared (Figure 4b). These textures were not observed for SCP and LC-BCN alone. The texture of the smectic B phase remained unaltered in the solid state. Furthermore, a perpendicular alignment, characterized by dark domains under crossed Nicol, was formed in the smectic A phase. The perpendicular alignment was



(a) Smectic A, 80 °C



(b) Smectic B, 40 °C

Figure 4: Fan texture and striped fan texture of SCP/LC-BCN\_0.5

Notes: At the isotropization temperature, bâtonnets were observed. The fan texture was formed in the smectic A phase, while the striped fan texture was formed upon cooling the smectic A phase to smectic B phase.

retained upon cooling to the smectic B phase. Conoscopic observation of the perpendicular alignment revealed the existence of an interference figure with an isogyre. This conoscopic observation also revealed the formation of optically uniaxial liquid crystalline phases such as smectic A and B phases.

#### 4. Orientational structures

The orientational behavior was studied by temperature-variable X-ray diffraction measurement. X-ray diffraction patterns of SCP/LC-BCN\_0.5 are shown in Figure 5. The X-ray diffraction pattern of the smectic A phase consists of sharp inner and broad outer reflections. The sharp inner reflections correspond to the layer spacing of the smectic A phase. The broad outer reflection denotes the existence of a short-range order between the mesogenic groups within the layer. The sharp inner reflections were also observed in the X-ray diffraction pattern of the smectic B phase. Furthermore, the sharp outer reflection, which indicates the formation of a hexatic structure within the layer, was observed.

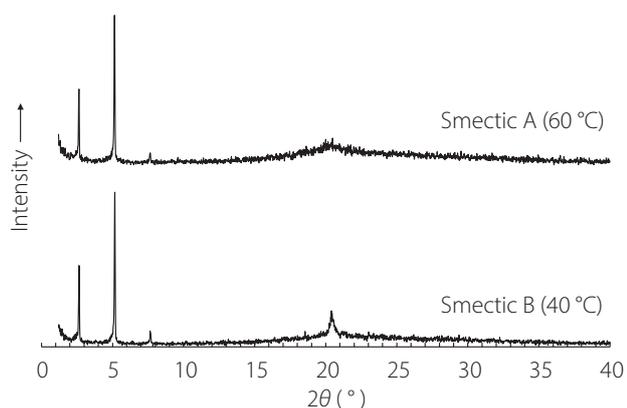


Figure 5: X-ray diffraction patterns of smectic A and smectic B phases of SCP/LC-BCN<sub>0.5</sub>

Notes: In the smectic A phase, sharp inner reflections, corresponding to the layer spacings, were observed. In the smectic B phase, sharp outer and inner reflections were observed.

The intermolecular distance within the layer of the smectic B phase was 4.4 Å. The length of the side chain of SCP was 30.2 Å, and the molecular length of LC-BCN molecule was 17.9 Å. The layer spacing of the smectic A and B phases for  $0.3 \leq y \leq 0.5$  was 34.0 Å. In this case, the formation of monolayer structures is expected in the smectic A and B phases. In contrast, the layer spacing of the smectic A and B phases for  $0.5 < y \leq 0.9$  was 51.4 Å, and therefore the formation of a bilayer structure is expected in this case. Possible packing models of the smectic phases were proposed and are shown in Figure 6. The induced smectic phases were formed be-

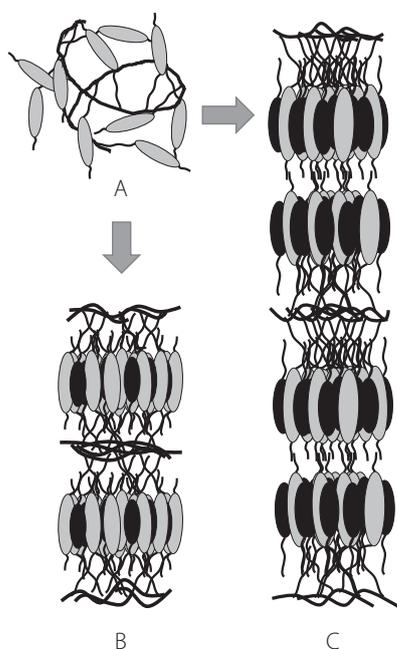


Figure 6: Possible packing models of the smectic phases of SCP/LC-BCN<sub>y</sub>

Notes: A: amorphous SCP, B: monolayer ( $0.3 \leq y \leq 0.5$ ); C: bilayer ( $0.5 < y \leq 0.9$ ). In the smectic B phase, a hexatic arrangement is formed within the layer.

cause of the interaction between the mesogenic azobenzene group of SCP and the mesogenic biphenyl group of LC-BCN.

## 5. Interaction between mesogenic groups

SCP has the weakly polar mesogenic 4-(4-(butyl)phenylazo) phenyl benzoate group in the side-chain, while LC-BCN has the mesogenic 4-cyanobiphenyl group (highly polar group). These distinct mesogenic groups form a charge-transfer complex. LC-BCN and SCP exhibited ultraviolet (UV) absorption bands at 275 and 345 nm, respectively. SCP/LC-BCN<sub>0.5</sub> showed UV absorption bands at 300 and 350 nm. Furthermore, the CN stretching vibration of LC-BCN was observed at 2229 cm<sup>-1</sup> in the infra-red (IR) spectrum. However, the CN stretching vibration of SCP/LC-BCN<sub>0.5</sub> was observed at 2226 cm<sup>-1</sup> (Figure 7). The UV and IR spectra indicate the existence of charge transfer interaction between cyanobiphenyl and butylazobenzene. As mentioned above, the charge transfer interaction between strongly polar molecules and less polar molecules drives the formation of a highly ordered liquid crystalline phase with enhanced thermal stability.

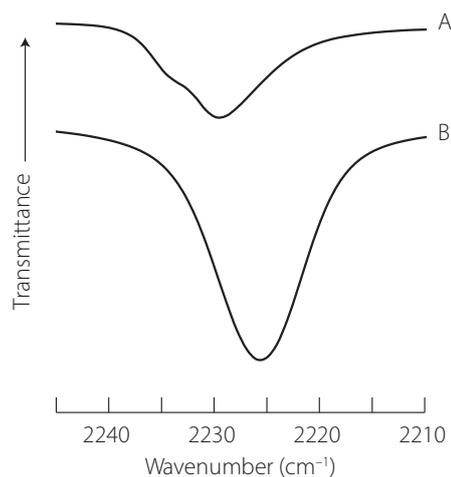


Figure 7: IR spectra denoting the CN stretching vibrations of LC-BCN (A) and SCP/LC-BCN<sub>0.5</sub> (B)

Note: The shift in the IR spectra indicates the occurrence of interaction between the cyanobiphenyl and butylazobenzene groups.

## 6. Conclusion

The novel binary liquid crystalline systems exhibited induced smectic phases, due to the charge transfer interactions between polar and weakly polar compounds. The binary liquid crystalline systems consisting of amorphous SCP and the cyanoazobenzene derivative exhibited the induced smectic A phase. However, the binary liquid crystalline systems, composed of amorphous SCP and the cyanobiphenyl derivative, induced the smectic B phase as well as the smectic A phase.

## References

- Benthack, H. and Finkelmann, H. (1985). Phase separations in binary mixtures of nematic liquid crystal side chain polymers and low-molar-mass nematic liquid crystals, 1. Influence of the chemical constitution of the low-molar-mass component. *Die Makromolekulare Chemie*, Vol. 186, No. 9, 1895-1903.
- Demus, D., Pelzl, G., Sharma, N. K., and Weissflog, W. (1981). EDA complexes in liquid crystalline mixed phases. *Molecular Crystals and Liquid Crystals*, Vol. 76, Nos. 3-4, 241-251.
- George, E. R. and Porter, R. S. (1986). Novel approach for the processing of thermotropic liquid-crystal polymers. 1. Thermodynamics and solid-state transesterification. *Macromolecules*, Vol. 19, No. 1, 97-105.
- Huh, W., Weiss, R. A., and Nicolais, L. (1983). Thermal and rheological properties of blends of polystyrene and thermotropic liquid crystals. *Polymer Engineering and Science*, Vol. 23, No.14, 779-783.
- Imrie, C. T. (1995). Supramolecular chemistry and liquid crystal polymers. *Trends Polymer Science*, Vol. 3, No. 1, 22-29.
- Kiss, G. (1987). In situ composites: Blends of isotropic polymers and thermotropic liquid crystalline polymers. *Polymer Engineering and Science*, Vol. 27, No. 6, 410-423.
- Kojo, T., Nata, M., and Ujiie, S. (2012). Liquid-crystalline binary systems with nonmesomorphic comb-shaped polymer component. *Molecular Crystals and Liquid Crystals*, Vol. 563, No. 1, 75-82.
- Park, J. W., Bak, C. S., and Labes, M. M. (1975). Effects of molecular complexing on the properties of binary nematic liquid crystal mixtures. *Journal of American Chemical Society*, Vol. 97, No. 15, 4398-4400.
- Pelzl, G., Bottger, U., Diele, S., and Demus, D. (1987). Induced SA phases in binary systems with EDA complexing. *Crystal Research and Technology*, Vol. 22, No. 10, 1321-1331.
- Ujiie, S., Uchino, H., Iimura, K., and Sato, M. (1999). Relationship between liquid crystal formation and conformations of twin components in liquid crystalline binary systems. *Kobunshi Ronbunshu*, Vol. 56, No. 6, 341-349.
- Ujiie, S., Uchino, H., and Iimura, K. (1995). Induced smectic phase formed by new liquid crystalline binary systems consisting of main chain polymer and twin compound. *Chemistry Letters*, Vol. 24, No. 3, 195-196.
- Ujiie, S., Uchino, H., and Iimura, K. (1995). Induced smectic A and C phases formed by liquid-crystalline binary systems consisting of nematic twin compounds. *Journal of Materials Chemistry*, Vol. 5, No. 12, 2229-2232.
- Ujiie, S., Sato, M., Uchino, H., and Iimura, K. (1998). Induced smectic A and C phases formed by binary systems of main-chain polymeric and twin nematics. *Molecular Crystals and Liquid Crystals*, Vol. 309, No. 1, 283-289.

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