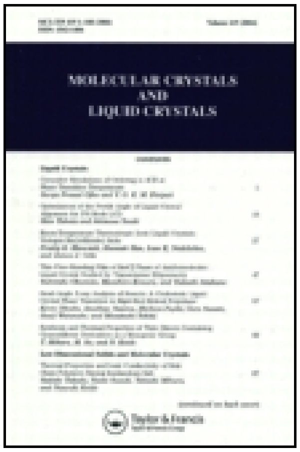

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Induced Smectic A and C Phases Formed by Binary Systems of Main-Chain Polymeric and Twin Nematics

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The thermal and liquid crystalline properties of the new binary systems, consisting of a polycarbonate type of a main-chain liquid crystal polymer (PC) and a twin liquid crystal (TN-*n*: *n* = number of central methylene units) with a nitro terminal unit, were examined. The binary systems having PC and TN-*n* with even-numbered central methylene units ($n = 6, 8$) showed an induced smectic A phase with batonnets and a fan texture. However, the binary systems consisting of PC and TN-*n* with odd-numbered central methylene units ($n = 5, 7$) formed an induced smectic C phase in addition to an induced smectic A phase. In the induced smectic C phase, the schlieren with two and four brushes was observed.

Keywords: Liquid crystalline binary system; main-chain LCP; Twin LC; induced smectic phase; X-ray; phase transitions

INTRODUCTION

The noncovalent interactions between distinct mesogenic groups can lead to the modification and enhancement of the liquid crystallinity and the creation of new liquid crystalline systems that are of considerable interest

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from both fundamental and technological viewpoints. In general, the mixing of two or more liquid crystals allows one to improve the thermal properties of the liquid crystalline systems [1–8]. For example, liquid crystalline mixtures have wider temperature ranges for the mesophase than either of the components. Furthermore, it is known that the binary mixtures of terminal polar and nonpolar nematic compounds can induce smectic orientational orderings, such as a smectic A state. In many cases, the creation of the induced smectic orientational orderings is due to intermolecular interactions.

In this work, new binary systems were prepared by mixing a nematic polycarbonate and nematic twin compounds with nitro terminal units. This present paper reports the novel findings that the orientational orderings in induced smectic phases formed by the new binary systems depend on the conformation of the twin components.

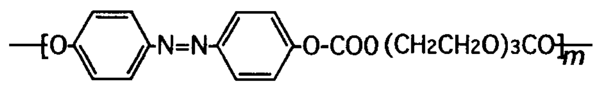
EXPERIMENTS

The polycarbonate (PC: $Mn = 5,400$) and twin compounds (TN-n) with penta-, hexa-, hepta-, or octamethylene units were synthesized by the previous methods [1–2]. The binary systems are a mixture with 2:1 molar ratio of PC and TN-n, maintaining the 1:1 stoichiometry of dioxyazobenzene (PC) and nitroazobenzene (TN-n). The thermal properties were examined with a Mettler TA 3000 system, a Shimadzu DSC-50Q and a Nikon polarizing microscope with a Linkam hot stage system.

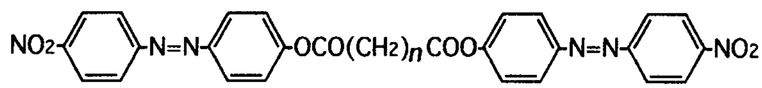
The orientational behaviour of the induced smectic A phase was examined at variable temperatures by X-ray diffraction measurements. The X-ray diffraction pattern was measured with a Rigaku Rint 2100 using Ni-filtered Cu-Kα radiation and the measuring temperature was controlled with a Linkam hot stage system.

RESULTS AND DISCUSSION

PC and all of TN-n showed only a nematic phase with a schlieren texture (Fig. 1, Tab. I). PC/TN-6 and PC/TN-8, which have the twin component with an even-numbered central methylene chain, showed an induced smectic A Phase (Fig. 2). In PC/TN-6 and PC/TN-8, 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



PC



TN-*n*

FIGURE 1 Structures of PC and TN-*n*.

TABLE I Phase transition temperatures of PC and TN-*n*

Sample	*Phase transition temp*/°C*				
PC	K	76.4	N	111.7	I
TN-5	K	152.2	N	188.6	I
TN-6	K	163.8	N	222.4	I
TN-7	K	120.1	N	181.3	I
TN-8	K	139.6	N	203.9	I

*K: solid phase, N: nematic phase, I: isotropic phase.

smectic layer spacings (PC/TN-6: 19.5 Å, PC/TN-8: 20.5 Å) correspond to the distance between the mesogenic cores in the extended twin molecules. The noncovalent interactions between the twin and polymeric molecules, such as donor–acceptor effects, allow the binary systems to produce the smectic A orientational ordering. In this case, the mesogenic cores in both the twin liquid crystal and the liquid crystalline polycarbonate overlap each other and the distance between the mesogenic cores along the director corresponds to the smectic A layer spacing (Fig. 3).

PC/TN-7 and PC/TN-5, having the odd-numbered twin component, exhibited induced smectic A and C phases (Fig. 2). A fan texture formed in the induced smectic A phase of PC/TN-7 and PC/TN-5. A broken fan texture on cooling from the induced smectic A to C phases formed. In DSC measurements, PC/TN-7 and PC/TN-5 clearly showed the solid-smectic C and smectic A-isotropic phase transitions. A smectic A–C phase transition was characterized by a very weak transition peak, which shows a weak

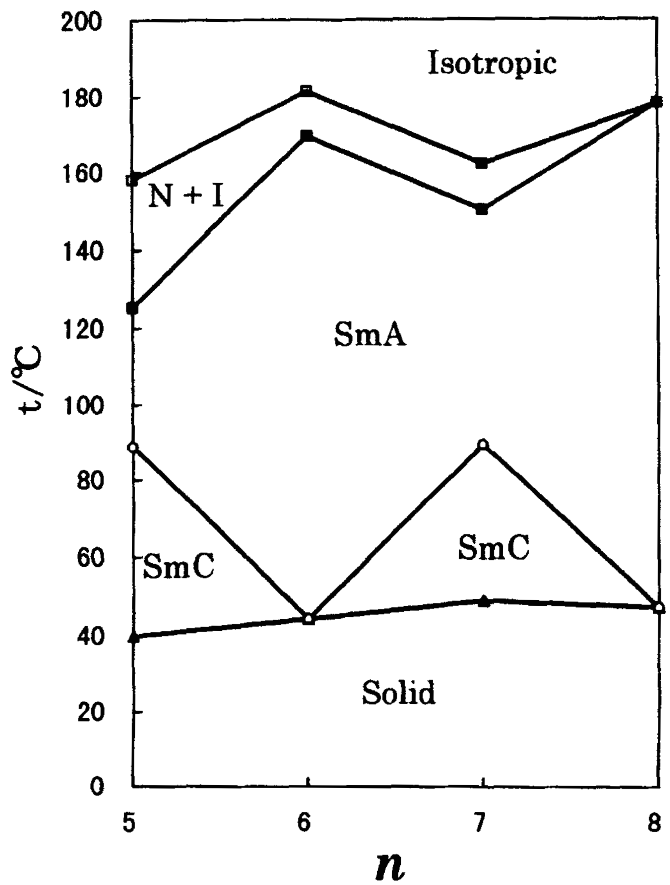


FIGURE 2 Phase transitions of liquid crystalline binary systems (PC/TN-*n*) consisting of main-chain polymer and twin compound; N + I, biphase of nematic and isotropic domains; SmA, induced smectic A phase; SmC, induced smectic C phase.

first-order or a second-order change. In general, the smectic A – ordinary smectic C phase transition is the second-order change in nature. However, the smectic C phases in PC/TN-7 and PC/TN-5 have a zigzag layer structure and are different from an ordinary smectic C phase, as described below. For a low-molecular-weight liquid crystal with a smectic C zigzag layer structure, it was found that the smectic A–C phase transition appears as the first-order change with a small amount of enthalpy change [10]. This shows that the smectic A–C phase transition in PC/TN-7 and PC/TN-5 may be in keeping with the first-order change.

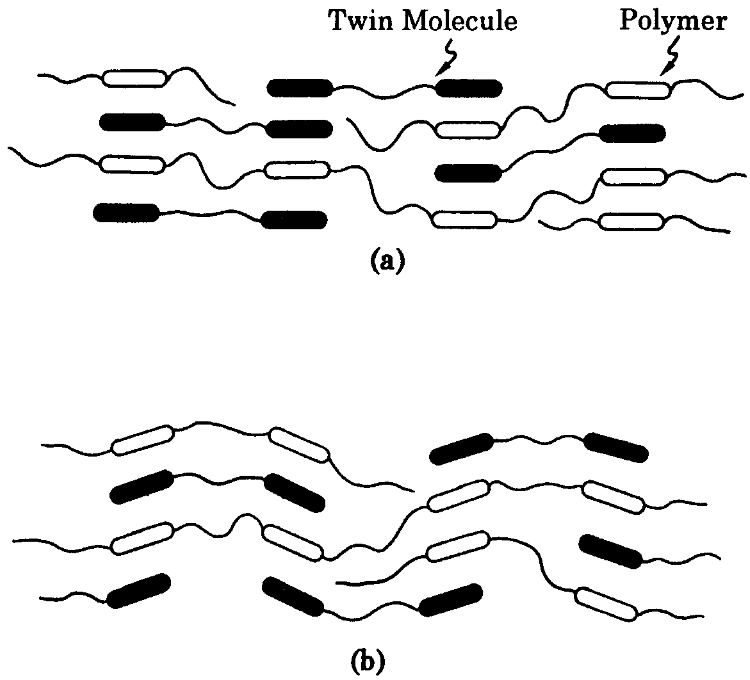


FIGURE 3 Possible packing models of induced smectic A and C phases: (a), induced smectic A phase; (b), induced smectic C phase with zigzag orientational ordering.

In X-ray measurements of PC/TN-7 and PC/TN-5, the first and the second layer reflections were observed. The smectic layer spacings elucidated from the first layer reflections are shown in Figure 4. The smectic C layer spacing was shorter than the smectic A layer spacing because the mesogenic cores tilted for the smectic C layer normal. The changes in the layer spacings shown in Figure 4 corresponded to the transition from the fan to the broken-fan textures. A broad scattering peak in the smectic A and C phases was located on the X-ray wide angle region, corresponding to the absence in a long-range orientational order such as a hexagonal packing.

The induced smectic C phase, which PC/TN-7 and PC/TN-5 showed, was not produced in both PC/TN-8 and PC/TN-6 containing the even-numbered central methylene units. Moreover, it was found that the binary systems of PC and TN-8 did not show the induced smectic C phase, independent of a molar ratio of TN-8 [1]. This difference is related to the conformation of the central methylene chain in the twin molecules [2, 3, 9]. The twin liquid crystals, having the even-numbered central methylene units,

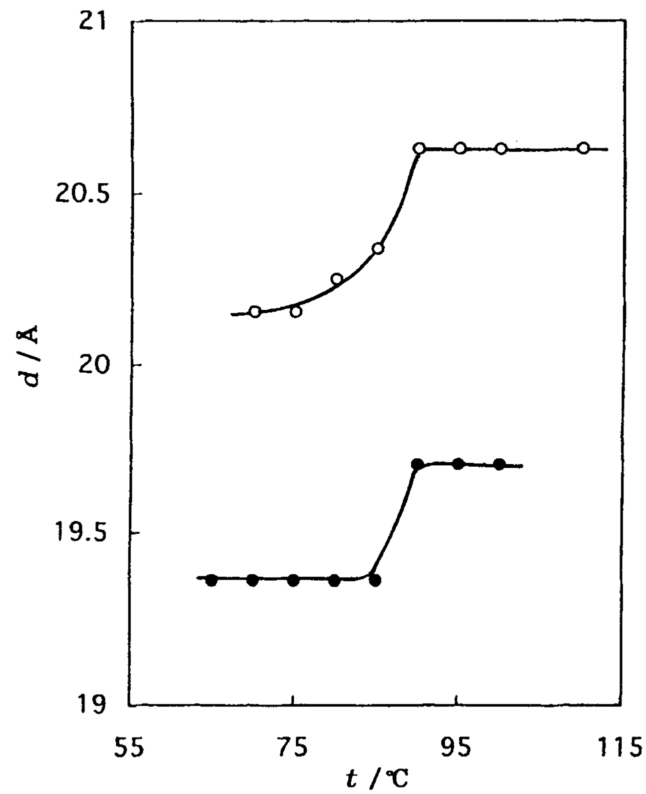


FIGURE 4 Layer spacings of induced smectic A and C phases in PC/TN-7 (○) and PC/TN-5(●).

such as TN-8 and TN-6, form a linear molecular shape in which the mesogenic cores are aligned parallel. On the other hand, TN-7 and TN-5, involving the odd-numbered central methylene units, have a nonlinear molecular shape (a bend structure), in which one mesogenic core is tilted towards the other mesogenic core. In the induced smectic C phases of PC/TN-7 and PC/TN-5, the mesogenic units are tilted to the layer normal and the direction of the twin molecules lies parallel to it. The mesogenic cores are tilted in opposite directions between the layers of the nearest neighbours and the direction is invariable in each second-nearest neighbouring layer (Fig. 3). This zigzag ordering in the induced smectic C phase was supported by the schlieren with two brushes (Fig. 5), in addition to the schlieren with four brushes that are found in ordinary smectic C liquid crystals [2, 3, 10, 11].

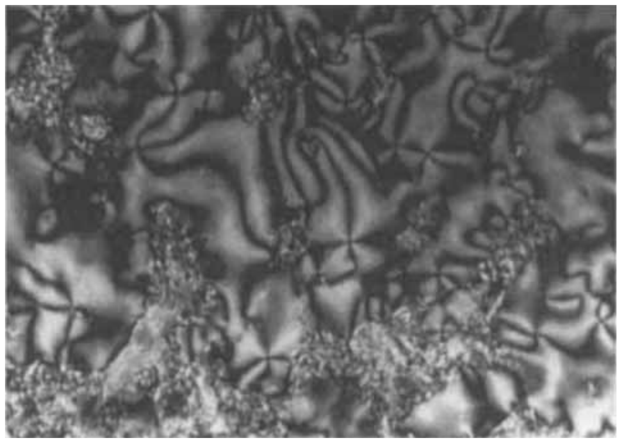


FIGURE 5 Schlieren texture of smectic C phase with zigzag orientational ordering.

References

[1] S. Ujiie, H. Uchino and K. Iimura, *Chem. Lett.*, 195 (1995).
[2] S. Ujiie, H. Uchino and K. Iimura, *J. Mater. Chem.*, **5**, 2229 (1995).
[3] S. Ujiie, S. Tanimoto and M. Sato, *Transactions of Materials Research Society of Japan*, **20**, 323 (1996).
[4] C. T. Imrie, *Trends Polym. Sci.*, **3**, 22 (1995).
[5] C. T. Imrie, F. E. Karasz and G. S. Attard, *Liq. Cryst.*, **9**, 47 (1991).
[6] T. Schleeh, C. T. Imrie, D. M. Rice, F. E. Karasz and G. S. Attard, *J. Polym. Sci. Polym. Chem. Ed.*, **31**, 1859 (1993).
[7] D. Demus, G. Pelzl, N. K. Sharma and W. Weissflog, *Mol. Cryst. Liq. Cryst.*, **76**, 241 (1981).
[8] Y. Matsunaga, N. Kamiyama and Y. Nakayasu, *Mol. Cryst. Liq. Cryst.*, **147**, 85 (1987).
[9] J. Watanabe and M. Hayashi, *Macromolecules*, **22**, 4083 (1989).
[10] I. Nishiyama and J. W. Goodby, *J. Mater. Chem.*, **2**, 1015 (1992).
[11] Y. Takanishi, H. Takezoe, A. Fukuda, H. Komura and J. Watanabe, *J. Mater. Chem.*, **2**, 71 (1992).