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Novel phase behaviour in two (smectic/cholesteric) liquid crystal mixtures

JENN CHIU HWANG*, SHI CHANG LIANG, KUNG HENG LIANG and JENN RONG CHANG

Department of Chemical Engineering, Yuan-Ze University, Neili, Taoyuan, Taiwan 32026, ROC

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The phase behaviours of mixed liquid crystal systems having either Sm/N or Sm/Ch properties have been studied. The (smectic/nematic) binary system formed smectic phases over a wide and much enhanced range of temperature (42°C) and a broad concentration range (0–90 wt %). The ternary smectic/cholesteric system, in appropriate concentration ranges, exhibited the smectic A phase, a TGBA-like twist grain boundary A phase, the cholesteric phase and blue phases. The TGBA-like phase appeared in the cholesteric–smectic phase transition range. Three textures (chiral pitch, fan-shaped and scale-like) for the cholesteric phase of the ternary smectic/cholesteric mixtures were observed in the ranges 0–7, 7–43 and > 43 wt % respectively, of cholesteric CB15, in a binary Sm/N mixture.

1. Introduction

Recently, functional characteristics of low molecular mass liquid crystals (LCs) have been studied in many fields because of their unique orientational behaviour and hydrodynamic properties. The orientation of nematic LCs is easily controlled by applying an electric or magnetic field.

It is known that binary mixtures of a mesogen with a strongly polar cyano or nitro terminal group and a weakly polar mesogen can give induced smectic phases [1–4]. Indeed, a binary mixture of a nematic LC material with a weakly polar end group and a nematic LC material with a strongly polar end group can also yield an induced smectic phase [5–7]. Such induced smectic phases may form over a wide range of concentrations (20–80 wt %) and temperatures (70–100°C). A reversible opaque (light scattering)–transparent change has been observed upon application of a.c. electric fields with low and high frequencies, respectively, to such induced Sm phases. Therefore, a LC/LC mixture in an induced smectic phase can behave as a novel type of 'light valve' with a memory effect and exhibiting bistable light switching characteristics. Recently, the electro-optical effects of nematic/cholesteric mixtures have been reported [8–10], and the cholesteric phase of a nematic and cholesteric LC mixture has been shown to exhibit opaque and transparent states [8, 9]. The induced smectic phase formed by mixing two nematics and a cholesteric to form ternary mixtures could also exhibit a highly transparent state and an opaque state [10].

In this paper, we add a cholesteric LC material to a pure LC material (Sm and N) and to the Sm/N system formed by mixing a nematic and a Sm/N LC material. The phase behaviours of the resulting mixtures are reported.

2. Experimental

2.1. *Materials*

The structures of the liquid crystal materials used in this study are shown in figure 1. 4′-Octyloxy-4-cyanobiphenyl (8OCB) has a strongly polar cyano terminal

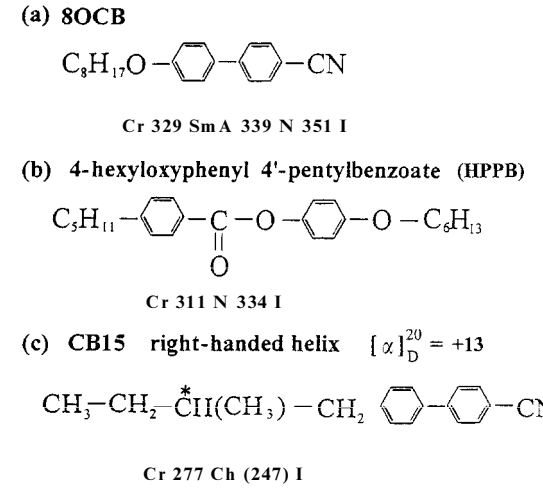

Figure 1. The structures of the mesogens 8OCB, HPPB and CB15.

*Author for correspondence; e-mail: cejhwang@saturn.yzu.edu.tw

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group, while 4-hexyloxyphenyl 4-pentylbenzoate (HPPB) has no such polar group. 8OCB shows a smectic and a nematic phase, and HPPB exhibits only a nematic phase. The cholesteric material used in this study is CB15. The mixtures of mesogens were first dissolved in acetone and the LC mixtures were prepared by solvent casting.

2.2. *Characterization*

The phase transition behaviour and the phase characterization of the mixtures were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The heating/cooling rates for the DSC and POM studies were 1 and 0.1°C min^{-1}, respectively. The accuracy of temperature control was ±0.1°C. A Perkin Elmer DSC-7 instrument was used to determine the thermal transitions. A Nikon POM-FXA equipped with a Mettler FP82 hot stage was used to observe thermal transitions and to analyse the anisotropic textures.

3. Results and discussion

3.1. *8OCB/HPPB mixture*

DSC curves of the 8OCB/HPPB mixture are shown in figure 2. In order to obtain reliable DSC data, the second heating scans were used. Three endothermic peaks were observed, corresponding to the crystalline–smectic, smectic–nematic and nematic–isotropic phase transitions of the 8OCB/HPPB binary mixture above 10 wt % fraction of 8OCB. For the 8OCB/HPPB (10/90 wt %) mixture, the endothermic transitions correspond to the crystalline–nematic and nematic–isotropic phase transitions. No endothermic peak for smectic–nematic phase transition was observed in the 8OCB/HPPB (10/90 wt %) mixture. A large endothermic peak was observed for the crystalline–smectic phase transition for pure 8OCB. The corresponding peaks for the 8OCB/HPPB mixtures decreased in size due to the added HPPB. The temperature of the crystalline–smectic phase transition of the 8OCB/HPPB mixtures decreased from 55°C to below 20°C with increasing weight fraction of HPPB, and the mixed smectic phase ranges increased correspondingly with increasing weight fraction of HPPB from 0% to 50%. The binary mixtures formed a homogeneous mixed mesophase above the crystalline–mesophase transition temperature, and HPPB was miscible with 8OCB over the entire concentration range. The homogeneity of the phase was confirmed by POM, indicating that the smectic/nematic binary mixture could be used as a miscible blend sample.

DSC cooling curves of the 8OCB/HPPB binary mixtures are shown in figure 3. Three exothermic peaks were observed for the 8OCB/HPPB binary mixtures with 0–80 wt % of HPPB; these correspond to the I–N, N–Sm and Sm–Cr phase transitions. For the 8OCB/HPPB (10/90 wt %) mixture, the exothermic transitions correspond to the I–N and N–Cr phase transitions. Figure 4 shows the phase diagram for the 8OCB/HPPB binary system. The mixed smectic phase gave a well defined fan texture, as observed by POM. The mixed smectic phase existed over a wide composition range (0–90 wt % of HPPB) and a wide temperature range (42°C). The temperature range of the smectic phase is broader than that of pure 8OCB (about 10°C), but the thermal stability is never greater than that of pure 8OCB.

3.2. *8OCB/HPPB/CB15 ternary mixture*

The 8OCB/HPPB (55/45 wt %) mixture was selected for studying the effects of adding CB15 on the phase behaviour and optical properties. DSC heating curves

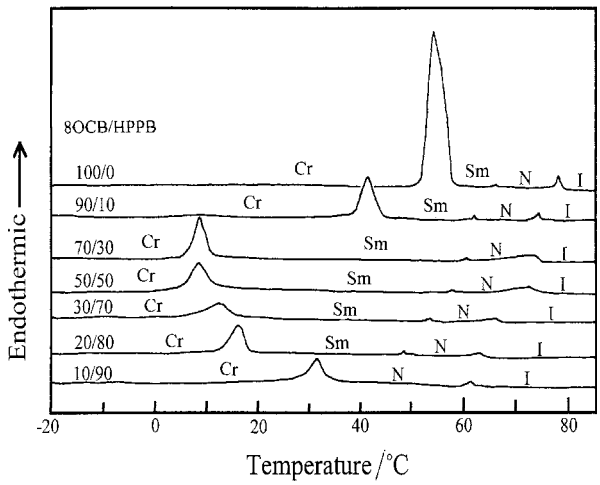


Figure 2. DSC heating curves for the 8OCB/HPPB binary system.

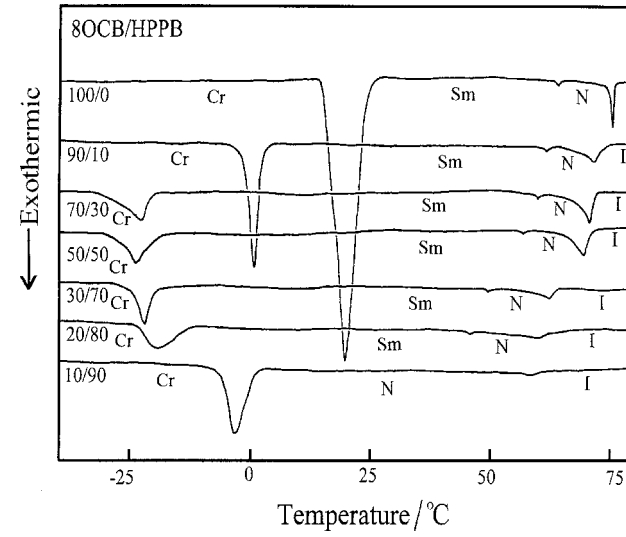


Figure 3. DSC cooling curves for the 8OCB/HPPB binary system.

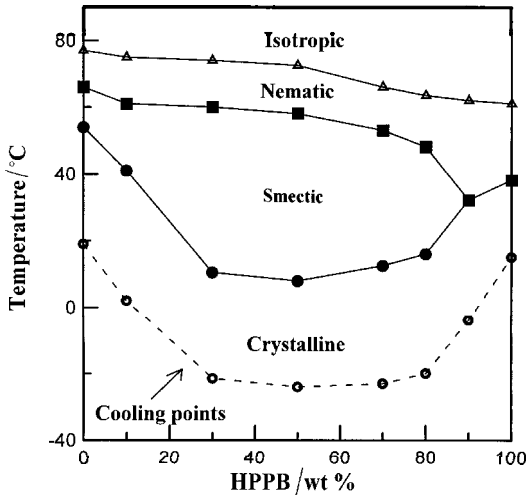


Figure 4. Phase diagram of the 8OBC/HPPB binary system.

of the HPPB/8OCB/B15 mixtures are shown in figure 5. In order to obtain reliable DSC data, the second heating scans were again used. Three endothermic peaks were observed, corresponding to the crystalline–smectic, smectic–cholesteric and cholesteric–isotropic phase transitions of the 8OCB/HPPB/CB15 ternary mixture. The Cr–Sm phase transition of the ternary mixtures decreased from 8 to −23°C with increasing weight fraction of CB15 from 0% to 60%. Also the smectic phase range decreased and the cholesteric phase range increased with increasing weight fraction of CB15. Consequently, CB15 is miscible with the 8OCB/HPPB mixture and the ternary mixture exhibited a mesophase over the entire concentration range. The homogeneity of the phase was confirmed by POM observations, and the ternary mixture can therefore be used as a miscible blend sample.

DSC cooling curves of the HPPB/8OCB/CB15 ternary mixture are shown in figure 6. Two exothermic peaks were observed for the 8OCB/HPPB binary mixture, corresponding to the I–N and N–Sm phase transitions. A simple exothermic peak at the N–Sm phase transition was observed for the 8OCB/HPPB mixture, but it was interesting that a significant peak was observed as a shoulder on the exothermic peak for the smectic–cholesteric phase transition for each ternary mixture. The associated phase is denoted the 'M phase' as shown in figure 6.

In order to study the texture of this M phase, POM observations were made. Figure 7 shows the polarizing microscope textures of the 8OCB/HPPB/CB15 (45/55/5 wt %) ternary mixture upon cooling from the isotropic to the smectic phase. The ternary mixture first displays a helical structure with a pitch which is characteristic for a cholesteric phase, figure 7 (*a*). At low temperatures, it displays the fan texture which is characteristic of a smectic phase. It is interesting, however, that a unique piled circular texture is observed in the cholesteric–smectic phase transition range where the M phase appears, figure 7 (*b*). This texture of the M phase exhibits this spiral texture in a narrow 2°C temperature range. The texture of the M phase is similar to that of the twist grain boundary TGBA phase. The TGBA-like phase is therefore formed between the smectic phase and cholesteric phase for the ternary mixtures. This novel phase was not found in the N–Sm phase transition range of the 8OCB/HPPB binary mixture.

Figure 8 shows the phase diagram of the 8OCB/HPPB/CB15 ternary mixture, which was obtained by DSC and POM. The 8OCB/HPPB mixture and CB15

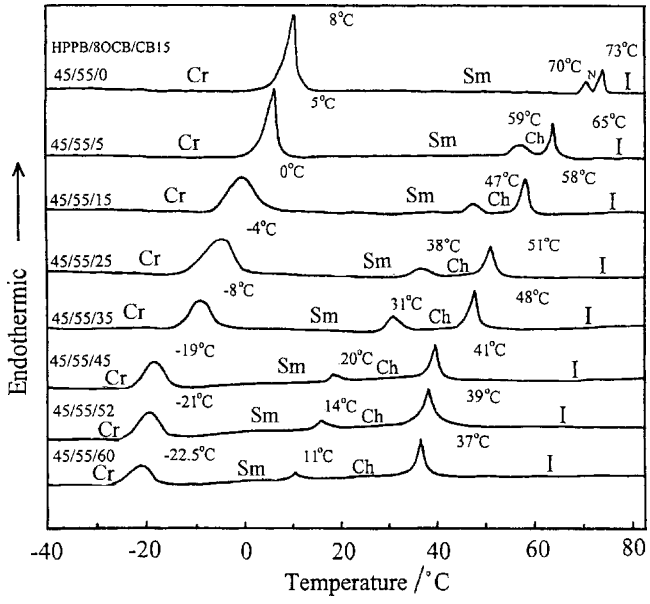


Figure 5. DSC heating curves for the 8OCB/HPPB/CB15 ternary system.

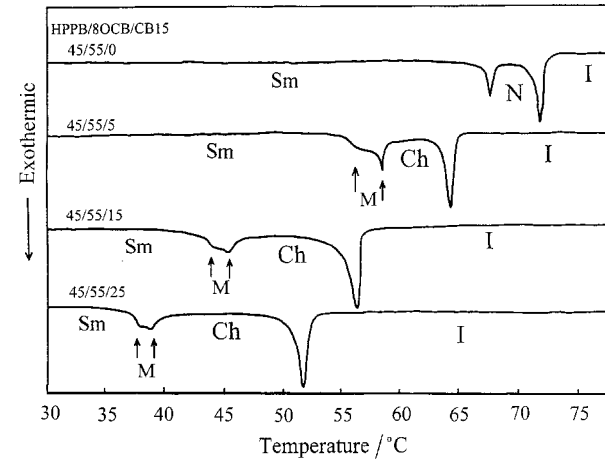
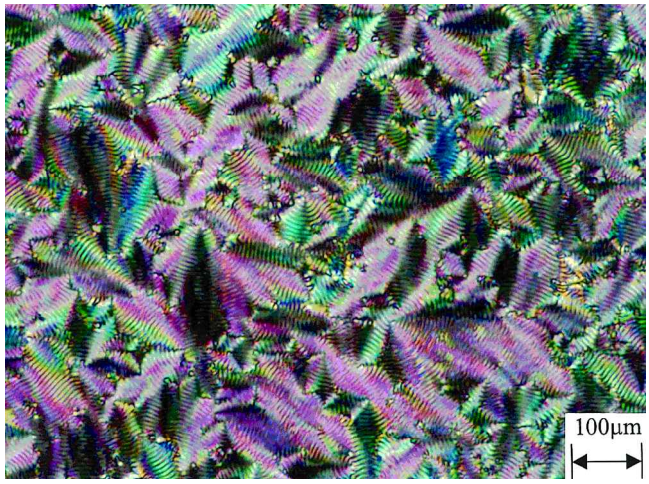
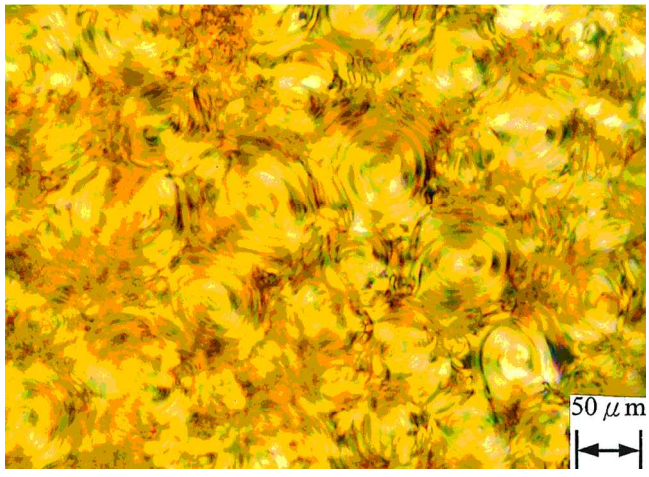


Figure 6. DSC cooling curves for the 8OCB/HPPB/CB15 ternary system.



(*a*)



(*b*)

Figure 7. Optical microscopic texture of the 8OBC/HPPB/CB15 (55/45/5 wt %) ternary mixture: (*a*) cholesteric phase at 61°C, (*b*) M phase at 57°C.

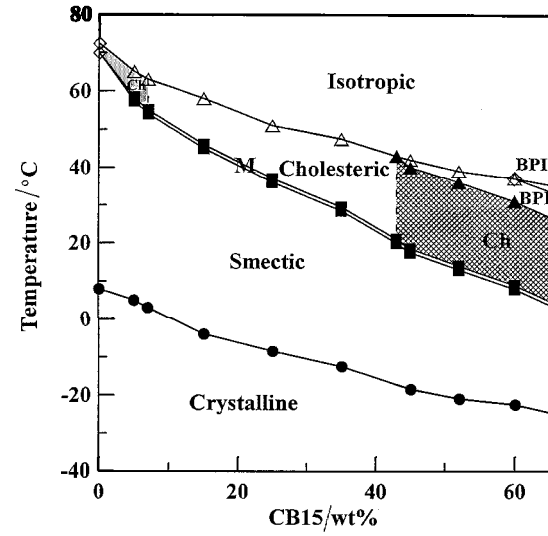


Figure 8. Phase diagram of the 8OCB/HPPB/CB15 ternary system.

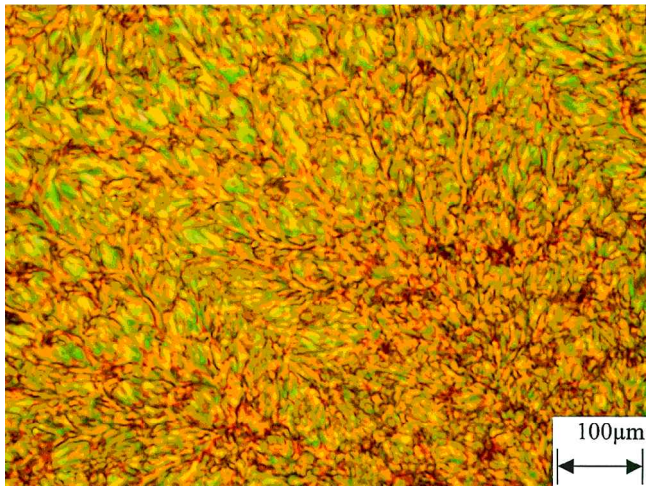
were completely miscible over the whole composition range. The existence of the smectic phase was confirmed by the fan texture observed by POM, showing that after adding cholesteric CB15, the smectic phase was maintained over the entire composition range and a wide range of temperature below T_{SmCh}. The novel M phase was observed within a narrow temperature range at the cholesteric–smectic phase transition. This M phase was observed during cooling cycles, but not during heating cycles. The texture of the M phase, shown in figure 7 (*b*), is similar to that of the twist grain boundary A (TGBA) phase. The TGBA phase occurs at the phase transition from a cholesteric to a smectic A phase when the molecules try to form a helical structure with the cholesteric helical axis perpendicular to the long axis of the molecules and also try to form a layered smectic A structure [11–15]. It is reasonable therefore to consider that the M phase is similar to the TGBA phase.

The ternary system therefore exhibited the isotropic phase, the cholesteric phase, blue phases, a TGBA-like phase, the smectic phase and the crystalline state. No chiral smectic C phase was observed. Three textures (chiral pitch, fan-shaped and scale-like) for the cholesteric phase of the 8OCB/HPPB/CB15 ternary mixture were indentified at 0 ~ 7, 7 ~ 43 and > 43 wt % of CB15, respectively. Figures 7 (*a*) and 9 display these POM textures which differ from normal cholesteric textures. The optical texture of one blue phase is displayed in figure 10. It shows a geometric platelet texture with many colours and resembles a stained glass window. Blue phases I and II appeared at > 43 wt % and > 60 wt %, respectively, of added CB15.

3.3. *8OCB/CB15 binary mixture*

Figure 11 shows the DSC heating curves for the 8OCB/CB15 binary system. Three endothermic peaks were observed for the 8OCB/CB15 binary mixtures below 20% weight fraction of CB15; these correspond to the crystalline–smectic, smectic–cholesteric and cholesteric–isotropic phase transitions. For the compositions above 40 wt % of CB15, three endothermic transitions occur and correspond to the crystalline–cholesteric, cholesteric–blue phase and blue phase–isotropic liquid transitions. The smectic phase range dropped and the cholesteric phase range increased with increasing weight fraction of CB15. The smectic phase was not observed above 30 wt % of CB15. Figure 12 shows the DSC cooling curves for the 8OCB/CB15 binary mixtures. It was interesting that a significant peak was again observed as a shoulder on

(*a*)



(*b*)

Figure 9. Two kinds of texture of the cholesteric phase for the 8OCB/HPPB/CB15 mixture: (*a*) fan-shaped (25 wt % for CB15) at 42°C, (*b*) scale-like (60 wt %) at 25°C.

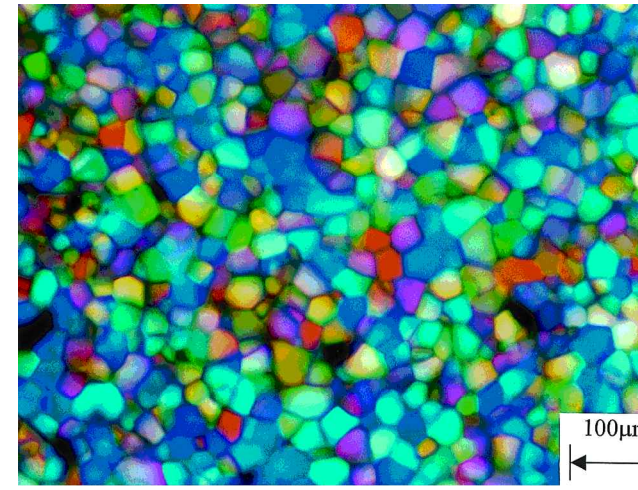


Figure 10. Optical microscopic texture of the Blue phase I for 8OCB/HPPB/CB15 (55/45/60 wt %) mixture at 34°C.

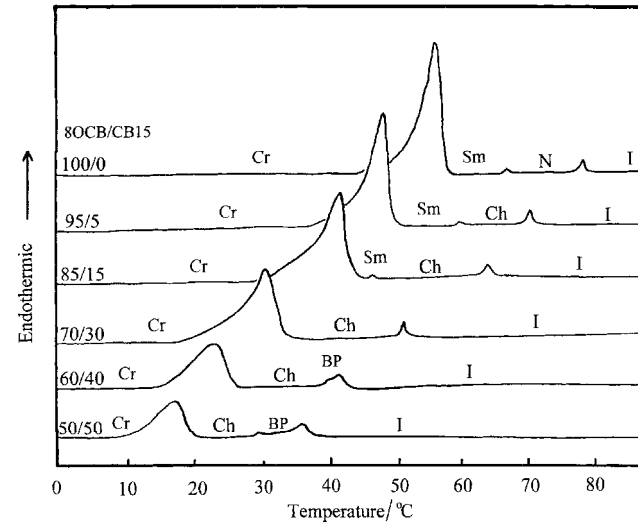


Figure 11. DSC heating curves for the 8OCB/CB15 binary system.

the exothermic smectic–cholesteric phase transition peak for three of these binary mixtures. The M phase was also observed by POM. The unique piled circular texture of the M phase of the 8OCB/CB15 binary mixtures is the same as that of the M phase of the 8OCB/HPPB/CB15 ternary mixtures. The spiral texture of the TGBA phase has been mostly observed for materials giving ferroelectric liquid crystals (FLCs). We have found a unique piled circular texture for the first time in a non-FLC system.

Figure 13 shows the phase diagram of the 8OCB/CB15 binary mixture obtained by DSC and POM. The 8OCB LC was completely miscible with the cholesteric LC over the whole composition range, and the system exhibited isotropic, cholesteric, blue, M (TGBA-like) and smectic A phases. The smectic phase was not observed above 25 wt % of CB15. The chiral smectic C phase did not appear. The binary mixture again gave three cholesteric textures which are chiral pitch (0–7 wt % of CB15), fan-shaped (7–43 wt %) and scale-like (> 43 wt %). The Blue phases I and II were observed between the isotropic and cholesteric phases above 42 and 60 wt % of CB15, respectively.

4. Conclusions

Binary mixtures of a Sm/N mesogen with a strongly polar end group and a nematogen with a weakly polar end group retained the smectic phase over a wide range of temperature (42°C) and concentration (0–90 wt %). The mixed smectic phase range is broader in range than that of pure 8OCB smectic (10°C), but has lower Sm–N transition temperatures.

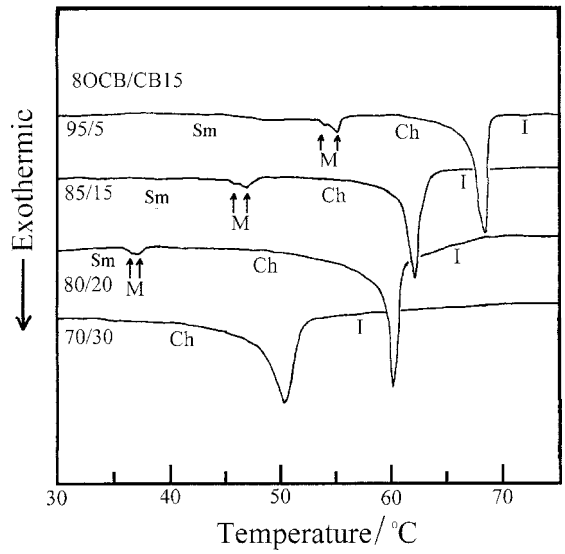


Figure 12. DSC cooling curves for the 8OCB/CB15 binary system.

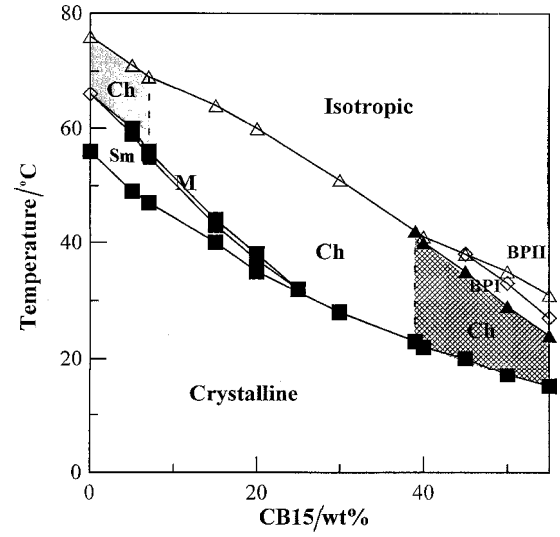


Figure 13. Phase diagram for the 8OCB/CB15 binary system.

One such binary mixture formed miscible blends with a homogeneous phase over the whole concentration range of CB15 studied. The smectic phase was maintained for the (8OCB/HPPB/CB15) ternary mixture while the smectic phase composition range was only 0–25 wt % of CB15 for the (8OCB/CB15) binary mixture. These mixtures exhibited the cholesteric phase, blue phases, the M phase and the smectic phase. The novel M phase appeared at the cholesteric–smectic phase transition, and is similar to the twist grain boundary A (TGBA) phase. It was interesting that for both the boundary and ternary systems, the three textures (chiral pitch, fan-shaped and scale-like) for the cholesteric phase were observed at 0–7, 7–43 and >43 wt % of cholesteric CB15, respectively. The smectic/cholesteric mixtures will be examined to see if they behave as a novel type of 'light valve' with light switching effects.

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