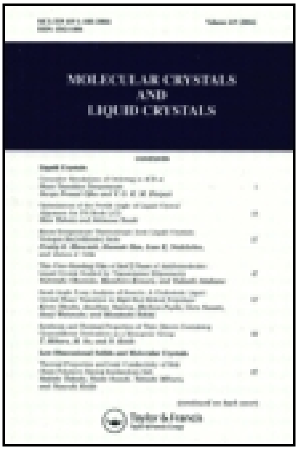

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Induced Smectic Phase in Binary Systems Containing Alkyl Cyano Phenylcyclohexane

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Induced Smectic Phase in Binary Systems Containing Alkyl Cyano Phenylcyclohexane

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The experimental investigation of the induced smectic phase (ISP) phenomenon in the binary system of the homologous series of alkyl cyano phenylcyclohexane (PCH) and 4-*n*-hexyloxyphenyl 4′-pentyl benzoate ester (5.0.$\bar{6}$) is reported. The phase transition temperatures were determined by differential scanning calorimetry and the optical textures were observed through a polarizing microscope in conjunction with a hot-stage. We found that the ISP-effect on equimole mixture of PCH and 5.0.$\bar{6}$ increased sharply with the increasing of the length of terminal alkyl chain. By comparing PCH with Cyanobiphenyl (CBP) we also found that the ISP-effect was influenced by molecular framework.

INTRODUCTION

In recent years, the phenomenon of induced smectic phase formed in mixtures of nematic liquid crystals has become one of the interesting topics as the application of liquid crystals in technology is extending. It has been found that as a nematic liquid crystal with a strong polar terminal group such as –CN, –NO_2 was mixed with terminal non-polar liquid crystals, smectic phases were produced in the investigation of a number of binary mixtures of nematic liquid crystals. In order to explain this phenomenon many models have been proposed.[1–5] As the alkyl cyano phenylcyclohexanes are quite excellent in physical and chemical properties, they are of great significance in alphabetic-numeric and graphic displays. In this paper, we intend to report the induction of smectic phase produced by the mixture of alkyl cyano phenylcyclohexanes and 4-*n*-hexyloxyphenyl-4′-*n*-pentyl benzoate (5.0.$\bar{6}$), in which each of PCH components with different alkyl chain length mixed respectively with 5.0.$\bar{6}$. Besides, a notable effect of molecular framework upon the induction was derived from the comparison with the above mixture to cyanobiphenyl.

EXPERIMENTAL

All the liquid crystal compounds used in the present experiments were provided by the Research Group of Liquid Crystal Chemistry of Tsinghua University. Their phase transition temperatures and enthalpies are listed in Table I. Blended respectively were the homologous of PCH with the carbon atom numbers C_3—, C_5—, and C_7— at their terminal alkyl chain with 5.0.$\bar{6}$ at the 50–50 mole ratio.[2,3,5–12] We put them in sample pans and measured their transition temperatures by means of differential scanning calorimetry (Du Pont 990). During scanning, each transition temperature had a good repeatability on the condition that the thermal history of samples was constant. For microscopic studies, the above mentioned mixture was poured into a

TABLE I

Transition temperature and enthalpies

Compounds	Chemical formulas	T_{K-N}(K)	T_{N-I}(K)	ΔH cal/mol
4-*n*-propyl-4′-cyano-phenylcyclohexane (PCH)	$C_3H_7C_6H_{10}C_6H_4CN$	316	319	4608
4-*n*-pentyl-4′-cyano-phenylcyclohexane (5PCH)	$C_5H_{11}C_6H_{10}C_6H_4CN$	303	328	4807
4-*n*-hexyl-4′-cyano-phenylcyclohexane (7PCH)	$C_7H_{15}C_6H_{10}C_6H_4CN$	303	330	6412
4-*n*-hexyloxyphenyl-4′-pentylbenzoate (5.0.$\bar{6}$)	$C_5H_{11}C_6H_4CO_2C_6H_4OC_6H_{13}$	308	342	3962
4-*n*-pentyl-4′-cyano-biphenyl	$C_5H_{11}C_6H_4C_6H_4CN$	295	309	
4-*n*-pentylphenyl ester of 4′-*n*-propylcyclo-hexyl benzoic acid (3CH.0.5)	$C_3H_7C_6H_{10}C_6H_4CO_2C_6H_4C_5H_{11}$	85	171	5252
4-methoxy-4′-*n*-butyl-azoxybenzene (N_4)	$CH_3OC_6H_4N_2(O)C_6H_4C_4H_9$	289	349	

cell which was made out of two pieces of glass. The interior surface of glass was treated as required and the space in the cell was adjusted by a spacer. The cell was put onto the heated stage of a polarizing microscope and we observed the various phase textures between crossed polarizers. D. Demus and L. Richter have detailed the characteristic microscopic textures of various mesophase in their works.

RESULTS AND DISCUSSION

When mixed, the liquid crystal systems always exhibited a tendency of being supercooled. To counter this effect the sample should be cooled down to about −120 °C before the DSC determination. It could be seen, from Figure 1, that the DSC curve in the system of 3PCH/5.0.$\bar{6}$ had a large endothermic peak from 5 °C to 10.5 °C. This told us that a phase change from the solid to the mesophase had occurred. At 56 °C, there was a smaller endothermic peak, it might be the clearing point as the enthalpy of transition from mesophase to isotropic was very small.

We could see fluidity occur in some local regions while observing the sample under a thermal polarizing microscope at 5 °C, it showed that the solid was starting to melt. When the sample was heated over 11 °C, it was converted into a nematic phase texture with surface inversion line as shown in Figure 2a. It was not until approaching 56 °C that such texture was converted into nematic droplets (Figure 2b), the latter existed only in a narrow temperature range. When the

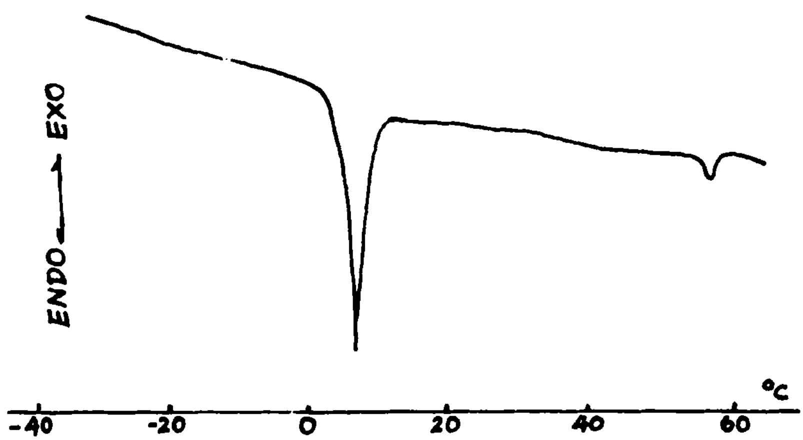
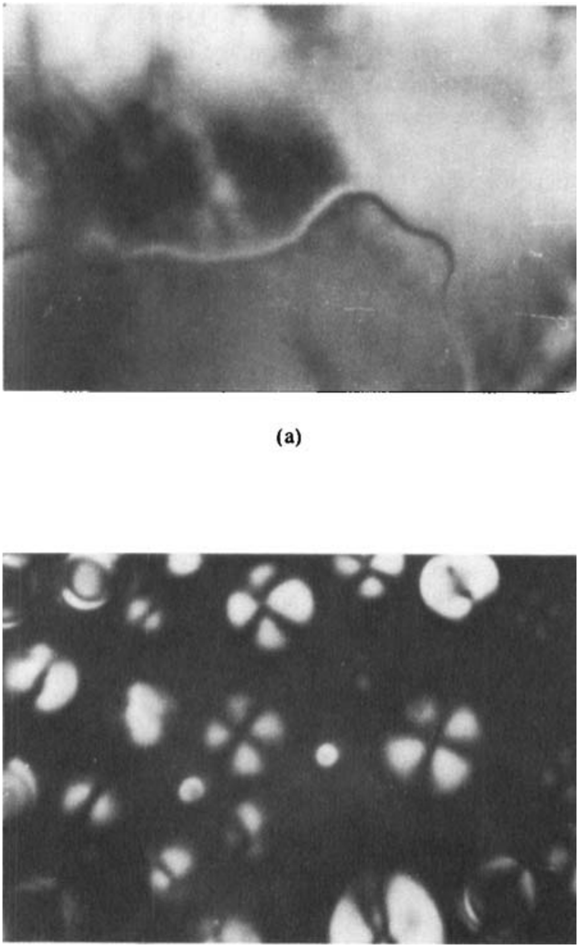


FIGURE 1 DSC thermogram for 3PCH/5.0.$\bar{6}$. Scan rate 2 °C/min.



(a)

(b)

FIGURE 2 Microscopic texture of 3PCH/5.0.$\bar{6}$. Crossed polarizers, 30 μm, 80X. (2a) Surface inversion line of nematic phase. (2b) Nematic droplets.

temperature rose to 56 °C, there appeared dark within the field of view of microscope. This showed that the sample had been converted from nematic phase to isotropic phase. During cooling the sample we could see the reversibility of the phase transition from its isotropic phase, which indicated that there was no monotropic phase in this system.

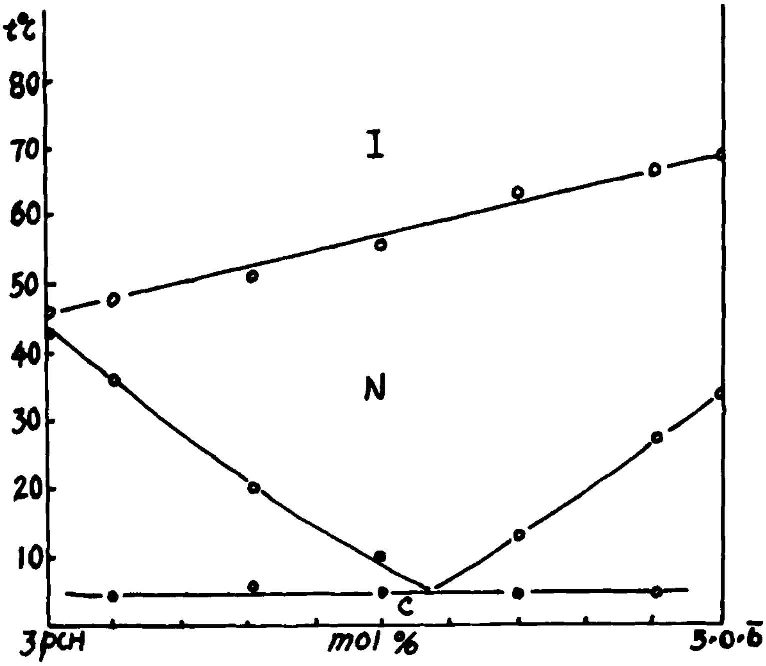


FIGURE 3 Phase diagram of 3PCH/5.0.6̄ binary system

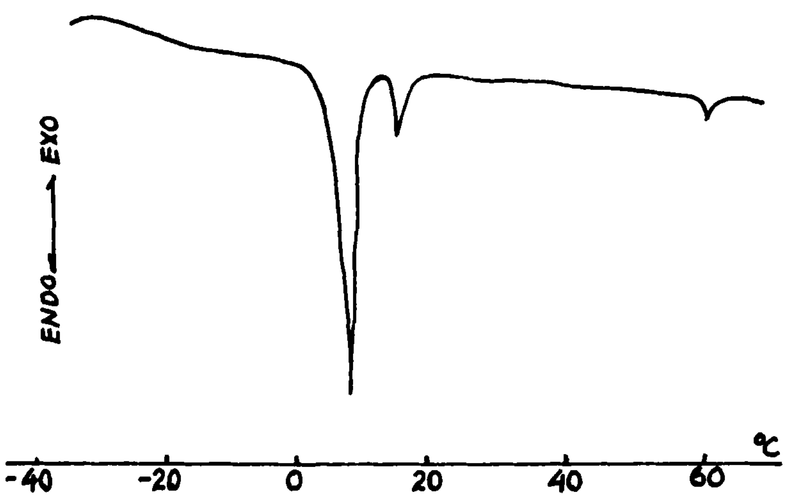
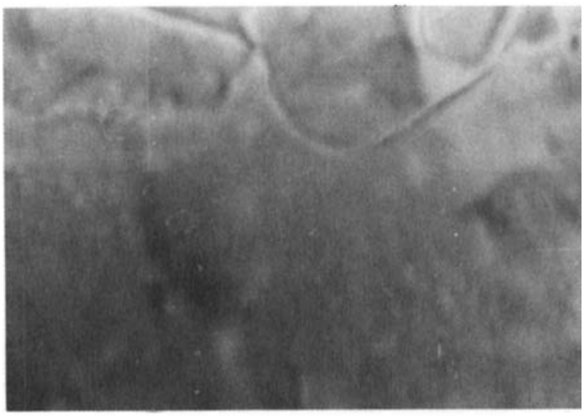
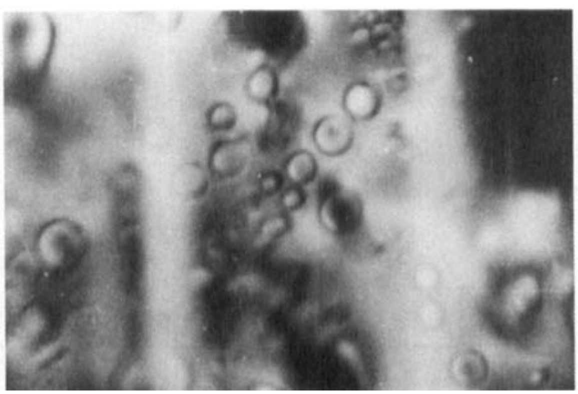


FIGURE 4 DSC thermogram for 5PCH/5.0.6̄

(a)



(b)



(c)

FIGURE 5 Microscopic texture of 5PCH/5.0.$\bar{6}$. Crossed polarizers, 70 μm, 80X. (5a) The ellipse focal conic texture of the S_A phase. (5b) The surface inverse line of nematic phase. (5c) The droplets of Nematic phase.

Based on our DSC and thermal microscopy data, the transition of the sample may be summarized by the sequence

$$K \underset{}{\overset{5\text{–}10.5\,^\circ C}{\rightleftharpoons}} N \underset{}{\overset{56\,^\circ C}{\rightleftharpoons}} I$$

The transition temperature was plotted versus the composition of the mixture of 3PCH/5.0.$\bar{6}$ in Figure 3, which exhibited a eutectic behavior in their solid–nematic transition while the nematic–isotropic transition temperature varied linearly vs composition.

The similar measurement was conducted on equimolar mixture of 5PCH/5.0.$\bar{6}$. In the DSC curve (Figure 4), during heating cycles, there was a large endothermic peak when temperature had reached 4.5 °C, and a transition from the solid to the smectic phase was taking place, as shown in Figure 5a. It exhibited a ellipse focal conic texture of the smectic A phase. When the temperature was up to 15 °C and 59 °C, there were two small endothermic peaks, respectively. The transition at 15 °C corresponded to the conversion of smectic A phase into nematic phase with surface inverse line and droplet (Figure 5b, c), while at 59 °C it converted into isotropic phase. Hence the transition

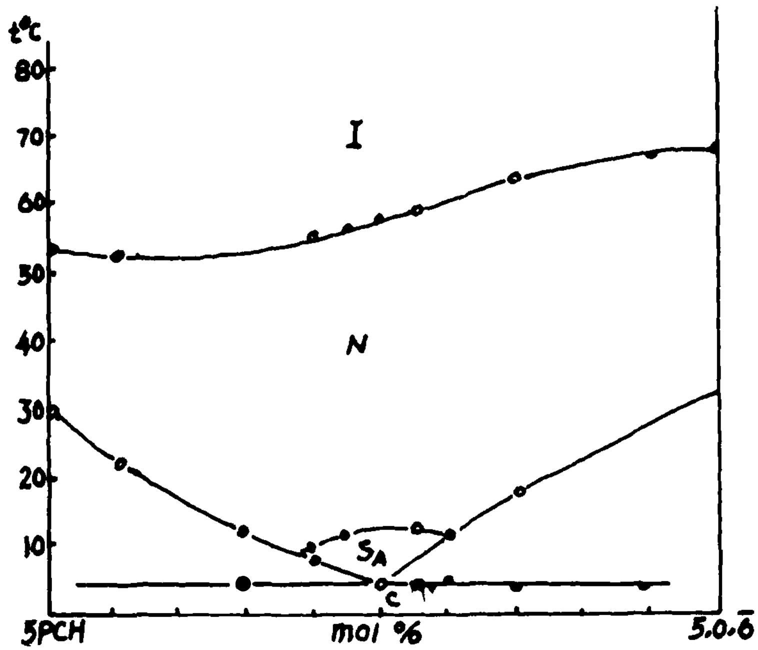


FIGURE 6 Phase diagram of 5PCH/5.0.$\bar{6}$ binary system

sequence may be summarized as follows:

$$K \underset{}{\overset{4.5\,°C}{\rightleftharpoons}} S \underset{}{\overset{15\,°C}{\rightleftharpoons}} N \underset{}{\overset{59\,°C}{\rightleftharpoons}} I$$

The phase diagram of 5PCH/5.0.$\bar{6}$ (Figure 6), showed that the S_A phase was located in the concentration range from 40–60 mol% of 5PCH, the maximum thermal stability of which occurred at the 50–50 mol% point of 5PCH-5.0.$\bar{6}$. In spite of the induced smectic phase effect, there still existed a eutectic point in the phase diagram, but the nematic–isotropic transition temperature (T_{N-I}) deviated from the linear average of the two components.

In the system of 7PCH/5.0.$\bar{6}$ (Figure 7), a series of endothermic peaks were observed during heating. There appeared the mosaic texture of S_B phase at about 6.5 °C shown in Figure 8a. At 13° C there occurred the transition from S_B phase to S_A phase (Figure 8b), which exhibited the focal conic fan texture of the S_A phase. When the temperature was above 34 °C, it exhibited the nematic thread texture and surface inverse line (Figure 8c). At near 63.5 °C, it appeared as

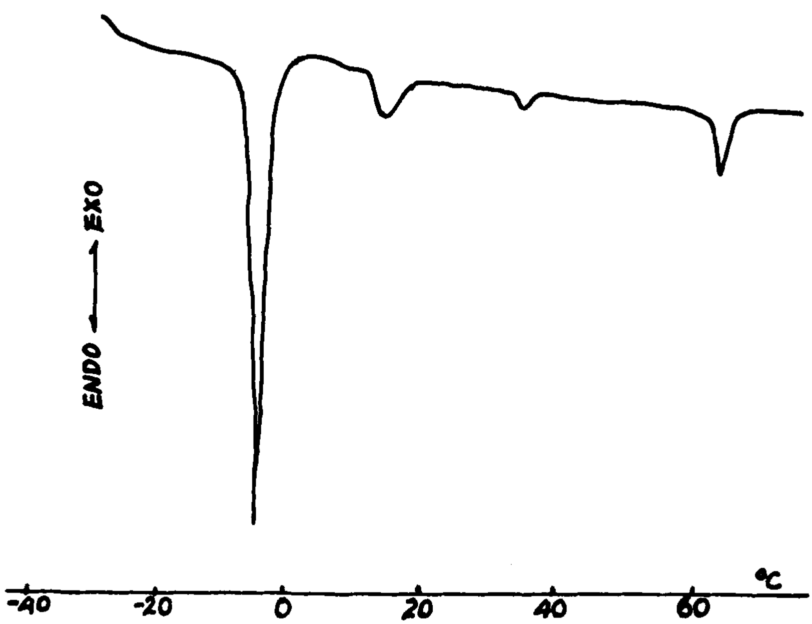
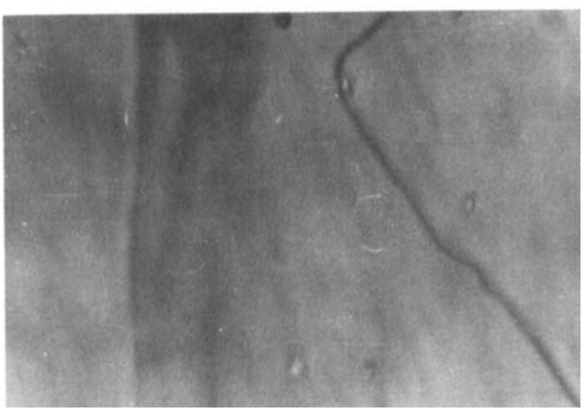


FIGURE 7 DSC thermogram for 7PCH/5.0.$\bar{6}$

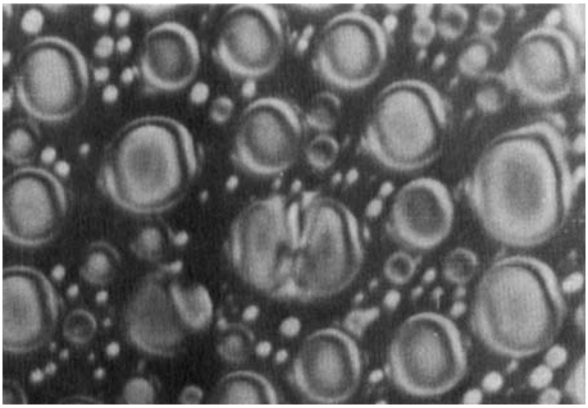
(a)

(b)



(c)

FIGURE 8 The microscopic texture of 7PCH/5.0.$\bar{6}$, crossed polarizers, 70 μm, 8X. (8a) The mosaic texture of the S_B phase; (8b) The focal conic fan texture of the S_A phase; (8c) The thread and surface inverse line texture of nematic phase. (8d) The droplets of nematic phase.



(d)

FIGURE 8 *Continued*

transient nematic droplets (Figure 8d), heating further, it transformed to isotropic phase. In cooling cycle the phase transition were performed reversibly.

The transition of this system could be represented by the scheme:

$$K \underset{}{\overset{6.5°C}{\rightleftharpoons}} S_B \underset{}{\overset{13°C}{\rightleftharpoons}} S_A \underset{}{\overset{34°C}{\rightleftharpoons}} N \underset{}{\overset{63.5°C}{\rightleftharpoons}} I$$

The diagram in Figure 9 showed that S_A phase occurred at higher temperature and S_B phase at lower temperature. The S_A phase existed in the region containing 5–55 mole% 7PCH, with the maximum thermal stability occurred at the 36 mole% point of 7PCH. The S_B phase existed in the concentration range from 35–85 mole% 7PCH and its maximum transition temperature was near 50 mole% 7PCH.

The previous experimental facts showed that when the PCH compound containing the strong polar terminal $-CN$ group was mixed with $5.0.\bar{6}$, there was to occur an induced smectic phase effect conforming to the PN rule.[2,14] However, Figure 3 showed that in the whole range of temperature the system $3PCH/5.0.\bar{6}$ did not form a smectic phase but rather a typical eutectic nematic phase. When the number of carbon in the terminal alkyl chain was increased from C_3 to C_5, a smectic A phase was formed. As the terminal alkyl chain further lengthened to C_7 both S_A and S_B phase were presented. It could be seen that in the mixture of $PCH/5.0.\bar{6}$ the alkyl chain length had apparently an influence on the induction of smectic phase. This was due to the increase of molecular polarizability caused by the lengthen-

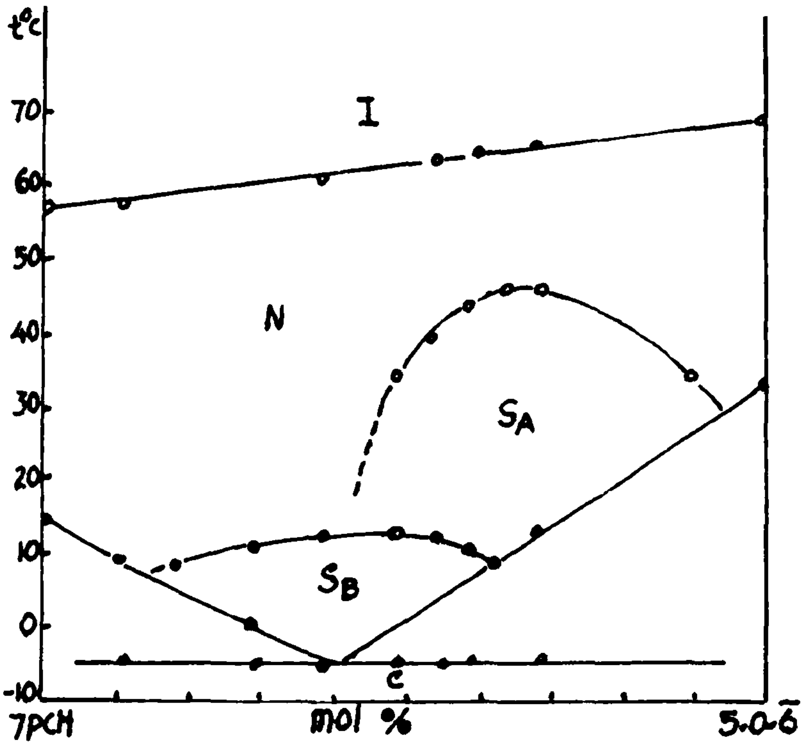


FIGURE 9 Phase diagram of 7PCH/5.0.$\bar{6}$ binary system

ing of the terminal alkyl chain and strengthing of the lateral attraction between molecules, which was favourable for the formation of smectic phase. Therefore, the ISP-effect was strengthened with the increase in the length of terminal alkyl chain of PCH. Hence the terminal chain of 3PCH was too short to form any smectic phase.

In order to illustrate the effects of small changes in molecular framework on the ISP-effect, we also compared the binary mixture consisting of 5PCH and 5CBP with 5.0.$\bar{6}$, 3CH.0.5 and N_4, respectively. It was found that a smectic A phase could be formed in all the binary system of 5CBP. Figure 10 showed the texture of the S_A phase in the system 5CBP/3CH.0.5. However the 5PCH exhibited no induced smectic phase except in the system 5PCH/5.0.$\bar{6}$. It was thus clear that the induction of smectic phase of PCH is weaker than CBP. The difference in the induction of smectic phase was considered to be caused by differences in the molecular framework. As far as we know, cyclohexane is a saturated, non-planar and non-conjugated system, it

FIGURE 10 The microscopic texture of S_A phase of system 5CBP/3CH.0.5

has a higher thermal stability, whereas the benzene ring is a planar and conjugated system, its polarizability is higher than the PCH, but its thermal stability is not as high as PCH. In general, the structural features that enhanced the thermal stability of nematic phase were considered unfavorable to the formation of smectic phase. Such effect was also applied on understanding the difference of the induction of smectic phase in the two kinds of liquid crystals.

CONCLUSIONS

The alkyl cyano phenylcyclohexane behaved like other liquid crystal compounds with polar terminal group when it was mixed with terminal non-polar liquid crystals. It was to produce the induced smectic phase and such an induced smectic phase effect was enhanced as the terminal alkyl chain was lengthened. Meanwhile different types of smectic phase appeared. The molecular framework of the polar component also had an apparent effect on the induction of smectic phase, as we had predicted that replacement of a benzene ring attached to the alkyl chain in a molecule of CBP by cyclohexane would depress the induction of smectic phase.

Acknowledgments

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