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Influence of Polar Endgroups on Mesomorphic Behavior of Symmetric Smectogens

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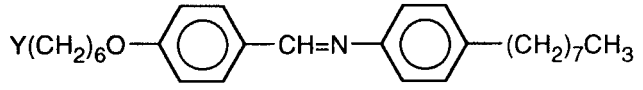
This paper describes the thermotropic polymorphic behavior of a set of new compounds carrying a variety of Y endgroups:



with Y = HOOC—, CH_3OCO—, CH_3CH_2CO—, and CH_3NHCO—. Of these compounds only the ester derivative proved capable of producing liquid crystals in the pure state. The absence of mesomorphic behavior in the other derivatives is due to the high thermal stability of the crystalline phases, as shown by a systematic study of their binary mixtures with the previously reported Y=NC—compound.

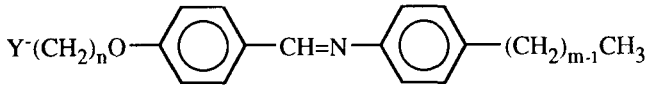
Keywords: polar mesogens, mixtures, polymorphism

INTRODUCTION

In a recent series of papers,[1–3] attention was focused on polar symmetric smectogens whose molecules are formed of a central elongated aromatic core, of two terminal aliphatic chains, and of one cyano polar endgroup. The particular series considered was that of 4-cyanoalkoxybenzylidene-4-alkylanilines. Despite their symmetric overall molecular architecture, these compounds were found to display single-layered as well as double-layered smectic A and B phases. In each sublayer, the molecules are arranged side by side and oriented normal to the smectic planes. The difference between the two types of layering is due to the presence of the polar cyano endgroups. Showing a strong tendency to associate head to head and to differentiate

themselves from the nonpolar methyl endgroups by their electronic density, the cyano endgroups affect the intensity distribution of the Bragg reflections in the X-ray patterns, depending upon their exact location in the layers. The occurrence of single- or double-layered structures relies on the length of the alkyl chains as well as on the temperature. In the particular case of the 4-cyanohexyloxybenzylidene-4-octylaniline, the double-layered structure detected at low temperature turns into a single-layered one upon heating at high temperature, through a second order phase transition.

To analyze the influence of the chemical nature of the polar endgroups on the mesomorphic behavior of symmetric smectogens, a set of new compounds carrying a variety of Y endgroups (abbreviated as Y-nO.m) were considered:



$n = 6, m = 8$

$Y = HOOC\text{-}, CH_3OCO\text{-}, CH_3CH_2CO\text{-}, CH_3NHCO\text{-}$

The experimental techniques used were: differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction.

MATERIALS

The compounds studied in this work were all synthesized following the same general method of Schiff base condensation described in the literature,[4,5] consisting in our case in condensing 4-octylaniline, $CH_3—(CH_2)_7—Ph—NH_2$, with the Y-substituted 4-hexyloxybenzaldehyde, $Y—(CH_2)_6—O—Ph—CH{=}O$. The reaction was conducted under reflux at boiling temperature, in absolute ethanol used as a solvent and in the presence of acetic acid. The resulting products were carefully purified by successive recrystallizations from ethanol solutions.

The benzaldehyde intermediate derivatives used were synthesized by simple reaction of 4-hydroxybenzaldehyde with the corresponding $Y—(CH_2)_6—Br$,[6,7] except for the $HOOC—(CH_2)_6—O—Ph—CH{=}O$ derivative which was obtained by hydrolysis from $CH_3OCO—(CH_2)_6O—Ph—CH{=}O$ after the $—CH{=}O$ group had been suitably protected.[8,9]

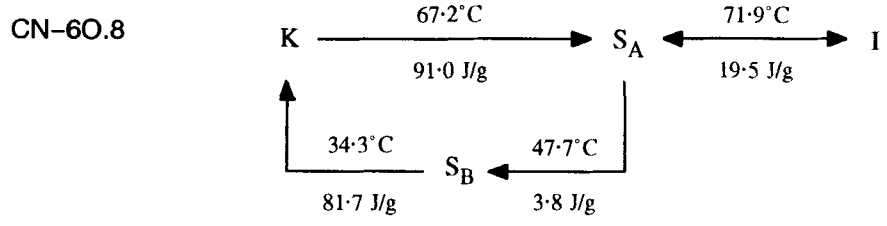
As for the $Y—(CH_2)_6—Br$ intermediate compounds, they were all prepared starting from $N{\equiv}C—(CH_2)_6—Br$ (obtained from Aldrich) first hydrolyzed into the carboxylic acid form,[10,11] and then transformed into the corresponding chloride: $ClCO—(CH_2)_6Br$.[12] The $Y{=}CH_3OCO—$derivative was obtained by methanolysis,[13] while the $Y{=}CH_3NHCO—$derivative was prepared by a method described by d'Alelio and Freid[14] and the $Y{=}CH_3CH_2CO—$derivative by a method described by Normant and Jones.[15,16]

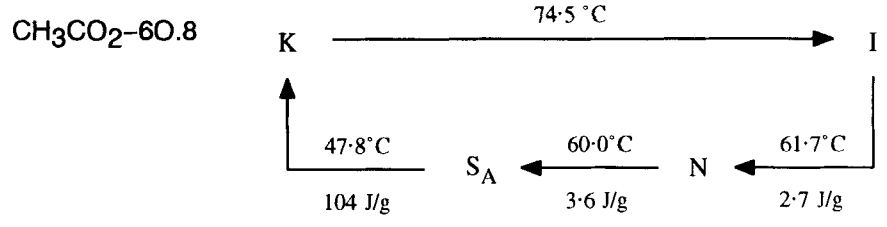
The purity of the final compounds, along with that of all the intermediate reac-

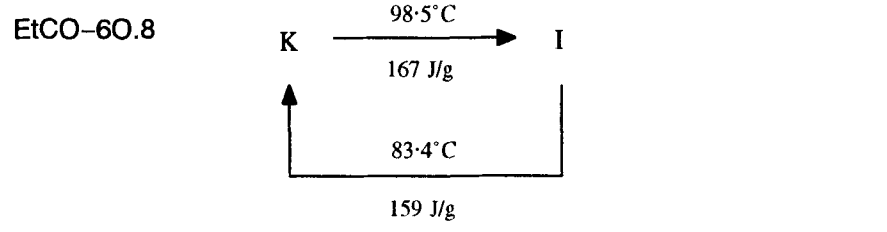
tants, was controlled by nuclear magnetic resonance and elemental analysis. Purity was also controlled by checking that the phase transition temperatures do not change in the course of successive recrystallizations.

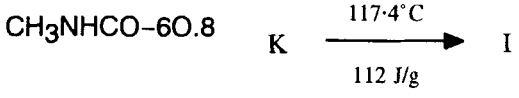
THERMOTROPIC POLYMORPHISM OF PURE COMPOUNDS

A systematic study of all these compounds using differential scanning calorimetry (Perkin-Elmer DSC-VII, heating and cooling rates of 5 K/min) and polarizing optical microscopy (Leitz-Orthoplan, Mettler FP82 hot stage) made it possible to establish the following polymorphic schemes:









The polymorphic behavior of CN-60.8, already reported in the literature,[2] was included in the above list in order to show the behavior differences of the Y-60.8 compounds more clearly. The obvious conclusion from these observations is that the Y=CH_3OCO—derivative is the unique one found to display mesomorphic phases, which are in addition monotropic in character.

The absence of liquid crystalline phases in the Y-60.8 derivatives with Y=HOOC—, CH_3CH_2CO—, CH_3NHCO— is at first sight very surprising, because the chemical architecture of these compounds is very similar to that of the actually mesogenic CN-60.8 and CH_3OCO-60.8 derivatives. This is, however, simply due to the higher thermal stability of their crystalline phases as compared to that of the mesophases expected. The higher stability of the crystal is no doubt related to the specific interactions introduced by the particular endgroups involved. The HOOC-endgroups strongly interact with each other through hydrogen bonds, reducing considerably the flexibility of the aliphatic chains and the entropic propencity of the crystal to melt; the CH_3CH_2CO-endgroups participate in lateral dipolar interactions with the azomethine bridges of the aromatic cores, as clearly shown by the crystallographic study of CH_3CH_2CO-60.8[17]; finally, the CH_3NHCO-endgroups are well known to establish strong intermolecular hydrogen bonding, leading to supramolecular "polymer" structures.

The nematic and smectic A structures (Figures 1 and 2) of the mesophases encountered were fully confirmed by X-ray diffraction. In addition, the smectic period (30.2 Å) was found to correspond to one molecular length, indicative of single-layered smectic structure. Such a layering is not very surprising as the ester polar endgroups, contrary to the cyano ones, cannot lead efficiently to dimerization through head to head association.

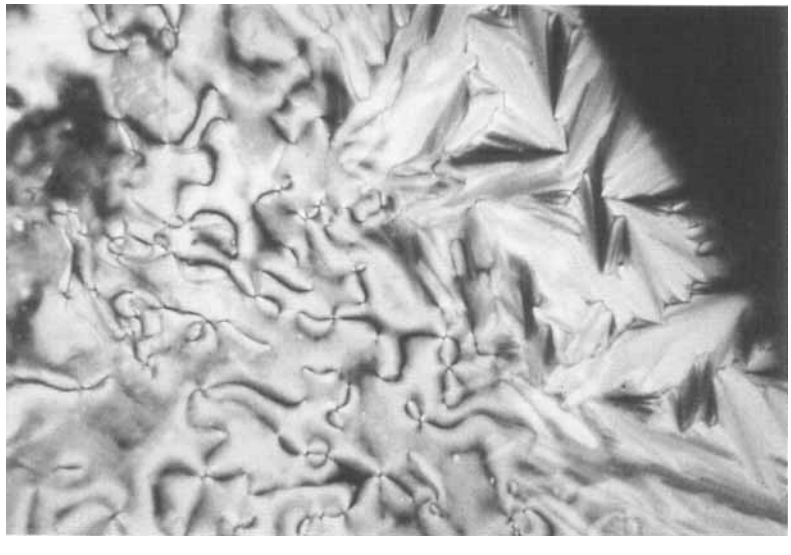


FIGURE 1 Schlieren texture of the nematic phase at 61°C, obtained with CH_3OCO-60.8 upon cooling from the melt.

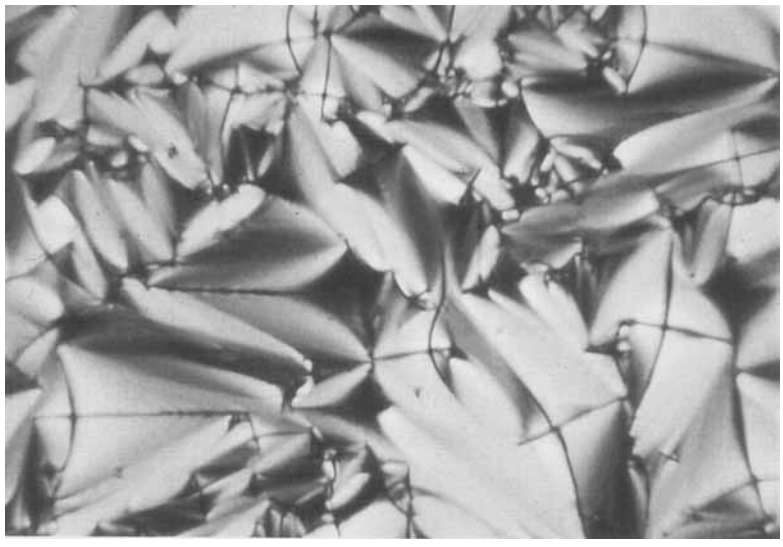


FIGURE 2 Focal conic texture of the smectic A phase at 55°C, obtained with CH_3OCO-60.8 upon cooling from the nematic phase.

MESOMORPHIC BEHAVIOR OF BINARY MIXTURES

The mesomorphic behavior of Y-60.8 in binary mixtures was then studied, for two main reasons. It seemed useful, first, to evaluate the intrinsic tendency for the nonmesogenic compounds to nevertheless participate in the formation of mesophases, and second, to analyze the composition dependence of the monolayer to bilayer phase transition (in mixtures with CN-60.8 which undergoes this transition[3]). The binary phase diagrams of these compounds were established using differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The results obtained are shown in Figures 3 to 6.

In the case of the CN-60.8/CH_3OCO-60.8 binary mixtures (Figure 3), formed of two compounds both able to effectively produce liquid crystals, the smectic A phase is obtained in the whole range of concentration of the two components. The existence domain of the smectic B phase extends over a very wide range of concentration suggesting that CH_3OCO-60.8 in the pure state is indeed very near to presenting this phase. It is of interest to note that both components of the mixture have rather low melting temperatures and exhibit rather strong hysteresis in the crystallization process; this is why the monotropic mesophases observed can really occur in such a large temperature range extending from about 20 up to 70°C.

On the contrary, in the case of the CH_3NHCO-60.8/CH_3OCO-60.8 and CN-60.8/CH_3NHCO-60.8 binary mixtures (Figures 4 and 5), the smectic A phase displayed by the pure CH_3OCO-60.8 and CN-60.8 components continue to exist in the mixture, but in a very narrow range of concentrations. This is obviously due to the high (120°C) melting temperature of CH_3NHCO-60.8, well above the temperature range of thermal stability of the mesophases, and also to its very weak supercooling.

The case of the CN-60.8/CH_3CH_2CO-60.8 binary mixtures (Figure 6) is inter-

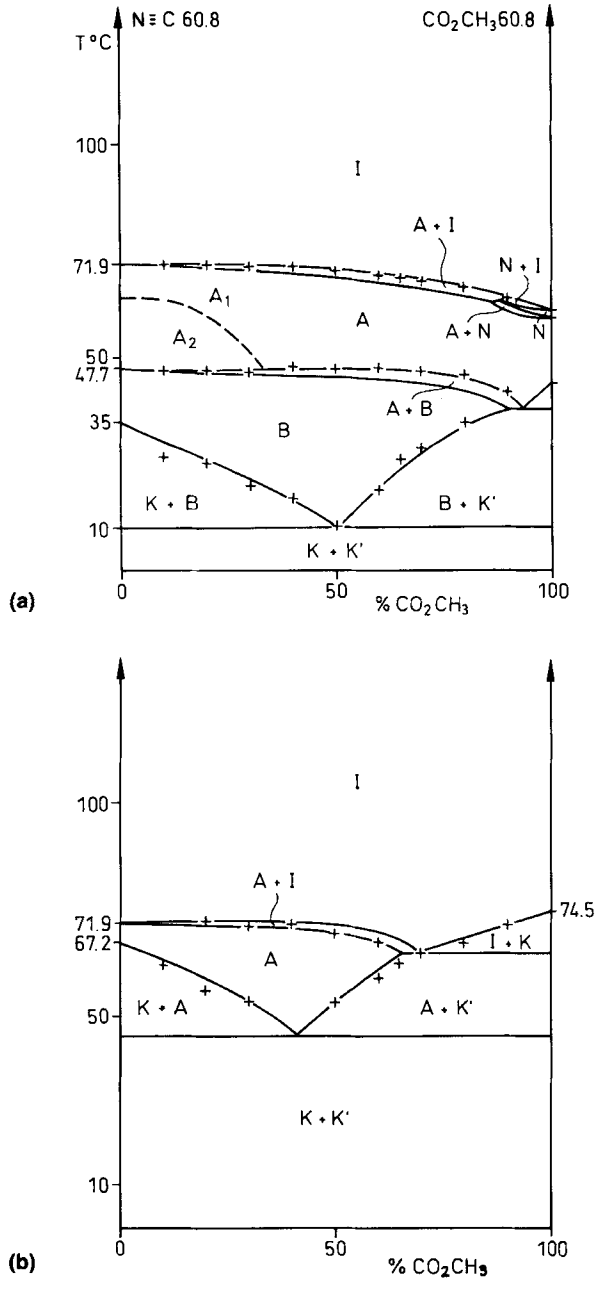


FIGURE 3 Phase diagrams of the binary mixture CN-60.8/CH_3OCO-60.8 obtained upon cooling from the melt (a) and upon heating from the crystal (b). I, N, A_1, A_2, B, and K stand for the isotropic, nematic, single-layered smectic A, double-layered smectic A, smectic B, and crystal phases.

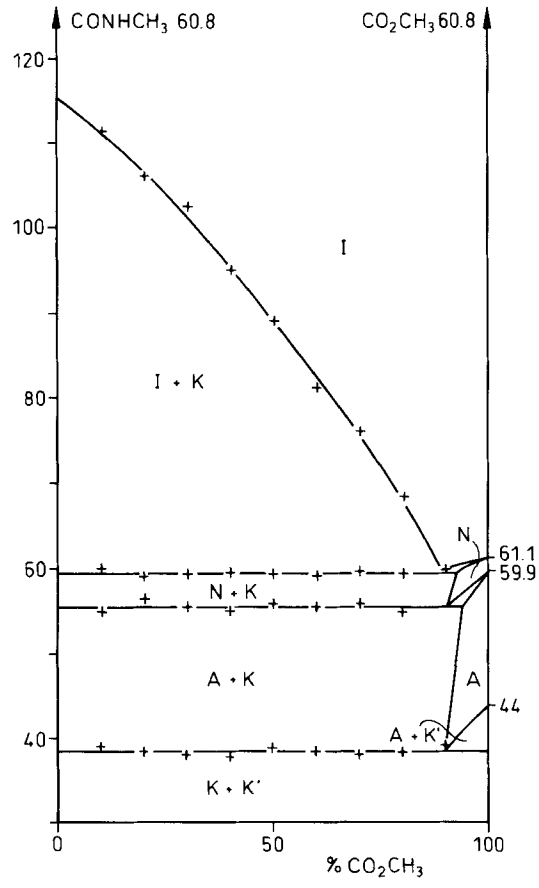


FIGURE 4 Phase diagram of the binary mixture CH_3NHCO-60.8/CH_3OCO-60.8 obtained upon cooling from the melt. I, N, A, and K stand for the isotropic, nematic A, and crystal phases.

mediate. Although the pure CH_3CH_2CO-60.8 component still presents a high (100°C) melting temperature, its strong hysteresis in the crystallization process makes the occurrence of the mesophases immediately possible on the slightest addition of the smectogenic CN-60.8 compound.

Finally, X-ray diffraction was used to ascertain the single- or double-layered nature of the smectic phases observed. As far as the smectic A phase is concerned, which is double-layered for the pure cyano component at low temperature, the addition of small quantities of the single-layered CH_3OCO-60.8 compound immediately transforms the double-layered phase into a single-layered one over nearly the whole range of compositions. This very fact prevents of course any systematic study of the concentration dependence of the A_2/A_1 phase transition. Returning now to the smectic B phase exhibited by the pure cyano compound, its ephemeral monotropic character makes it extremely difficult to determine its single- or double-layered nature by X-ray diffraction. Its appearance upon cooling from a double-layered smectic A phase might be taken for continuity reasons to suggest that its

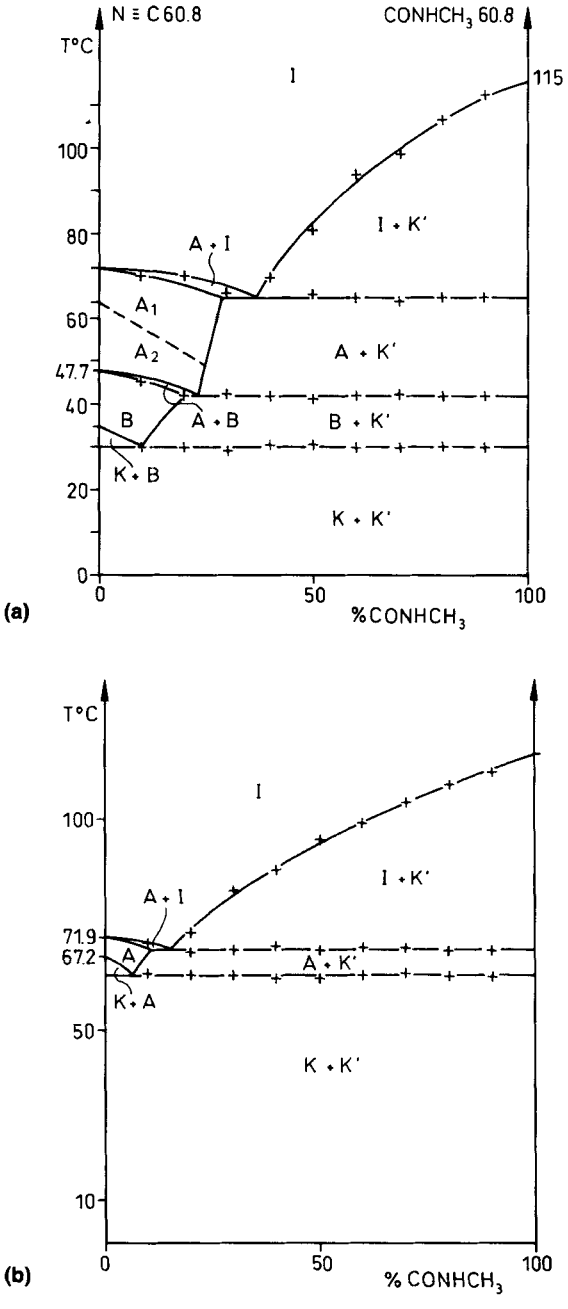


FIGURE 5 Phase diagrams of the binary mixture CN-60.8/CH_3NHCO-60.8 obtained upon cooling from the melt (a) and upon heating from the crystal (b). I, A_1, A_2, B, and K stand for the isotropic, single-layered smectic A, double-layered smectic A, smectic B, and crystal phases.

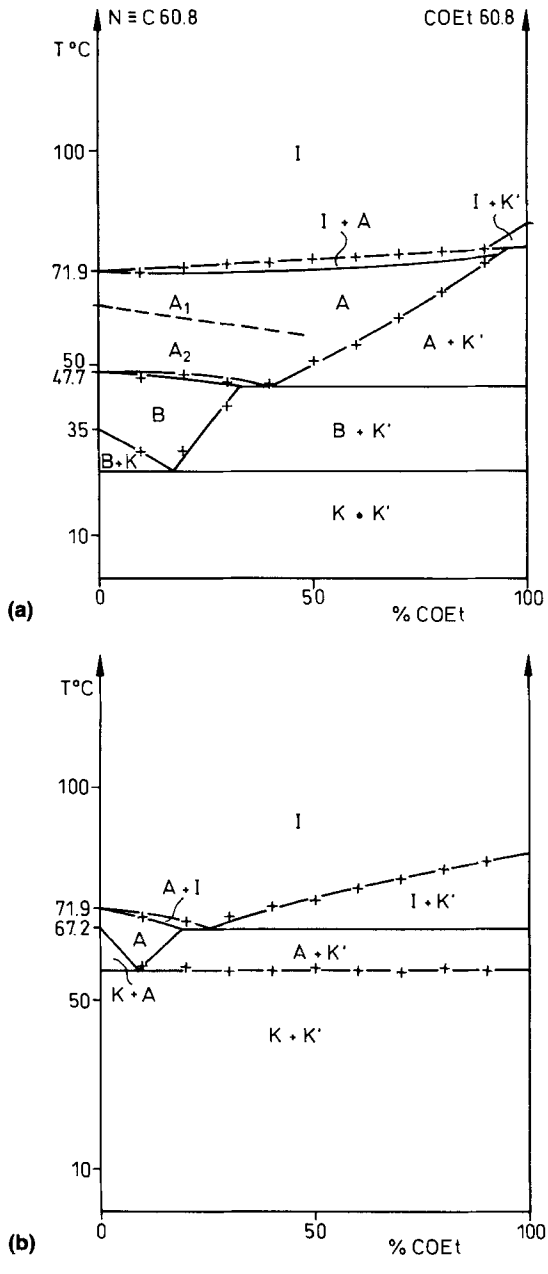


FIGURE 6 Phase diagrams of the binary mixture CN-60.8/CH_3CH_2CO-60.8 obtained upon cooling from the melt (a) and upon heating from the crystal (b). I, A_1, A_2, B, and K stand for the isotropic, single-layered smectic A, double-layered smectic A, smectic B, and crystal phases.

nature is also double-layered.[2] However, an X-ray diffraction study of binary mixtures (Figure 3), which are stable over long enough periods of time, clearly proved that the smectic B phase encountered is in fact single-layered.

CONCLUSION

The present study shows that the chemical nature of the polar endgroup carried by smectogens of symmetric overall architecture plays an important part in the occurrence of mesophases. While preserved with NC- and CH_3OCO-endgroups, the smectic structures generally observed in the absence of polar endgroups[18] are totally nonexistent with HOOC-, CH_3CH_2CO-, and CH_3NHCO-endgroups. The reason is not related to the stability of the mesophases, which seems independent of the endgroup (as shown by the negligible concentration dependence of the clearing temperature of the binary mixtures), but more specifically to the stability of the crystalline phases themselves, which depends upon the specific interactions imported by the endgroups.

References

1. F. Barbarin, M. Dugay, D. Guillon and A. Skoulios, *J. Phys. France*, **47**, 931 (1986).
2. F. Barbarin, M. Dugay, A. Piovesan, H. Fadel, D. Guillon and A. Skoulios, *Liq. Cryst.*, **2**, 815 (1987).
3. H. Fadel, D. Guillon, A. Skoulios, F. Barbarin and M. Dugay, *J. Phys. France*, **50**, 375 (1989).
4. D. Vorländer, *Ber.*, **71**, 501 (1938).
5. D. Coates, K. J. Harrison and G. W. Gray, *Mol. Cryst. Liq. Cryst.*, **22**, 99 (1973).
6. G. W. Gray and B. Jones, *J. Chem. Soc.*, 1467 (1954).
7. J. W. Emsley, G. R. Luckhurst and C. P. Stockley, *Mol. Cryst. Liq. Cryst.*, **44**, 565 (1981).
8. T. H. Chan, M. A. Brook and T. Chaly, *Synthesis*, 203 (1983).
9. R. E. Ireland and D. M. Walba, *Org. Synth.*, **56**, 44 (1977).
10. E. C. Kendall and P. McKenzie, *Org. Synth.*, **3**, 25 (1923).
11. H. W. Heine, E. Becker and J. F. Lane, *J. Am. Chem. Soc.*, **75**, 4514 (1953).
12. R. C. Elderfield, *Croat. Chem. Acta*, **35**, 85 (1963).
13. R. Merchant, J. N. Wickert and C. S. Marvel, *J. Am. Chem. Soc.*, **49**, 1828 (1927).
14. G. F. d'Alelio and E. E. Freid, *J. Am. Chem. Soc.*, **59**, 109 (1937).
15. H. Normant, *Compt. Rend. Acad. Sci., Paris*, **231**, 909 (1950).
16. R. G. Jones, *J. Am. Chem. Soc.*, 1467 (1954).
17. H. Fadel and F. Enkelmann, to be published.
18. A. J. Leadbetter, M. A. Mazid and R. M. Richardson, in *Liquid Crystals*, edited by S. Chandrasekhar (Heyden), p. 65 (1980).