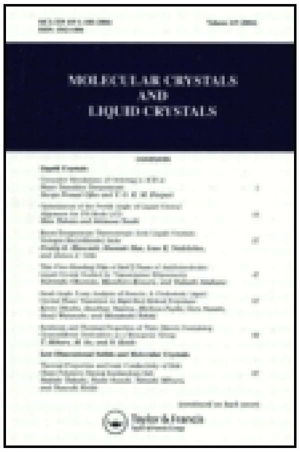

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Exploratory Studies on Novel Liquid Crystal Acrylates

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EXPLORATORY STUDIES ON NOVEL LIQUID CRYSTAL ACRYLATES

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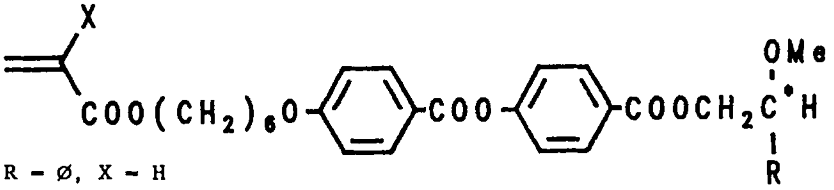
Abstract Three new liquid crystalline monomers were synthesized and polymerized. The backbone was either acrylate or methacrylate, and polar groups with a chiral center were incorporated into the mesogens. Two monomers displayed a smectic C* phase below room temperature, while the third one was a plastic lc. The homopolymers and copolymers had lc phases, smectic C* or smectic A, between 40 and 80°C.

INTRODUCTION

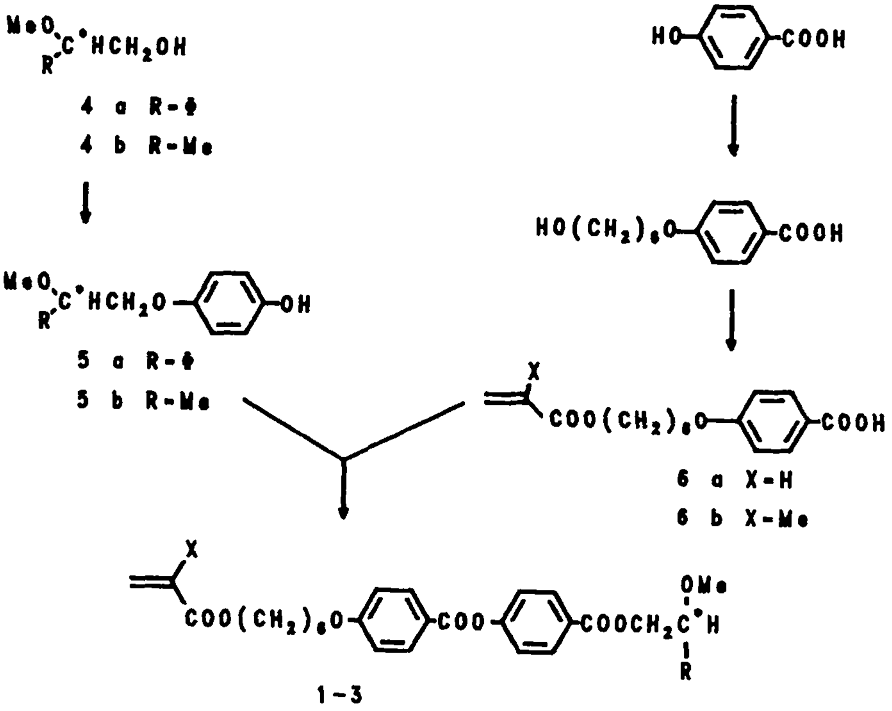
In the past 10 years, much attention has been focused on the design and synthesis of new liquid crystalline materials, both monomers and polymers.[1-4] Chiral side chain liquid crystals have been of particular interest because they can frequently exhibit cholesteric or smectic C* phases.[5] We will describe the synthesis and polymerization of the following monomers with potential smectic C* properties. The l.c. properties of all the novel materials will be examined.



1 R = Ø, X = H
2 R = Ø, X = CH_3
3 R = CH_3, X = CH_3

SYNTHESIS

Using some of the synthetic tools from Weinshenk,[6] Decobert[4] and Ringsdorf,[7,8] the following synthetic scheme was employed:



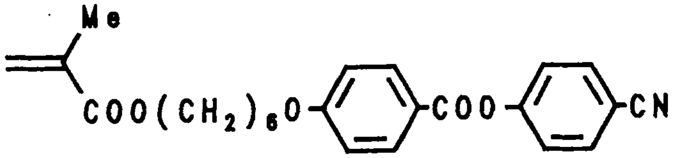
For monomer 1 and 2, the commercially available R-2-methoxy-2-phenylethanol 4a was used as starting material. For monomer 3, the optically active S-2-methoxypropanol 4b had to be synthesized. The one step transesterification of phenyl p-hydroxybenzoate with the optically active alcohols with DMAP (dimethylamino pyridine) as catalyst yields 5 in 70-90% yields.

The two moieties of the l.c. monomers were linked via an acid chloride reaction of the (meth)acrylates 7 with the optically active hydroxyphenyl derivatives 5a and 5b. The yields for the coupling were in the 30-50% range. All spectral data are in agreement with the proposed structures.

POLYMERIZATIONS

The thermal AIBN-initiated polymerization in toluene of 1 led to a polymer in 61.5% yield, which had an inherent viscosity of 2.46 dL/g. Homopolymers of 2 was obtained in trace yields from solution polymerization. (Inherent viscosity 0.5 dL/g), while the homopolymer of 3 was obtained in 20% yield. (Inherent viscosity 0.4 dL/g).

A commonly used comonomer for monomers with chiral l.c. side chains is the p-cyanophenyl terminated methacrylate 4:



Monomer 4 was copolymerized with methacrylate 3 using two different monomer feeds. Copolymers with almost the same composition as the monomer feed were obtained: copolymer 5 was obtained from a monomer feed ratio 4/3 of 70/30, while copolymer 6 had a feed ratio of 80/20. The molecular weights of these polymers were 21,000 and 15,400, respectively.

L.C. BEHAVIOR OF THE MONOMERS

Monomer 1 showed two reversible phase transitions at 14 and 52° in the DSC. Using optical microscopy through crossed polarizers, a cholesteric phase appears at 5°C but only after shearing. This behavior possibly depicts a plastic crystal phase.

For monomer 2 reversible phases were observed near 14°C and between 39.8 and 23.8°C by DSC. Under the microscope, a cholesteric or chiral nematic phase was observed from 0-5°C with or without shearing.

For monomer 3, again reversible phase transitions were observed by DSC. A very typical cholesteric phase is observed from -4 to 0°C. The color is blue-grey and darkens at lower temperature.

Thus, we can conclude that monomer 2 and 3 definitely exhibit cholesteric phases below room temperature. In contrast monomer 1 behaves as a plastic crystal.

LC BEHAVIOR OF THE POLYMERS

All three homopolymers displayed two reversible phase transitions between 13 and 35°C by DSC.

Using optical microscopy, poly-1 and poly-3 only displayed lc behavior after several days in the refrigerator, while poly-2 formed the lc phase spontaneously at room temperature after 1 week. Poly-1 and poly-2 display lc character, but the specific phase is not defined. Poly-3 forms a smectic A phase at room temperature as shown by the focal conics.

The copolymers both displayed a reversible phase transition in the DSC at a higher temperature than the homopolymers, namely at 95°C. Using optical microscopy, we could detect a classical cholesteric phase for both of these copolymers. Copolymer 5 had a very sharp clearing temperature at 95.2°, while copolymer 6 cleared between 98.4 and 99.4°.

REFERENCES

1. H. Finkelmann, H. Ringsdorf, H., J. Wendorff, Makromol. Chem., 179, 273 (1978).
2. V.P. Shibaev, N.P. Plate, Y.S. Freidzon, J. Polym. Sci. Polym. Chem. Ed., 17, 1655 (1979).
3. C.B. McArdle, in "Side Chain Liquid Crystal Polymers," edited by C.B. McArdle (Blackie, London 1989), pp. 4-6.
4. G. Decobert, F. Soyer, J.C. Dubois, Polym. Bull., 14, 179 (1985).
5. J.W. Goodby, T.M. Leslie, Mol. Cryst. Liq. Cryst., 110, 175 (1984).
6. J.I. Weinschenk, III, Ph.D. Thesis, University of Arizona, 1988.
7. M. Portugall, H. Ringsdorf, H., R. Zentel, Makromol. Chem., 183, 2311 (1982).
8. H. Finkelmann, M. Happ, M. Portugall, H. Ringsdorf, Makromol. Chem., 179, 2541 (1978).