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Liquid Crystalline and Ferroelectric Properties of Tartrate with Two Chiral Centers

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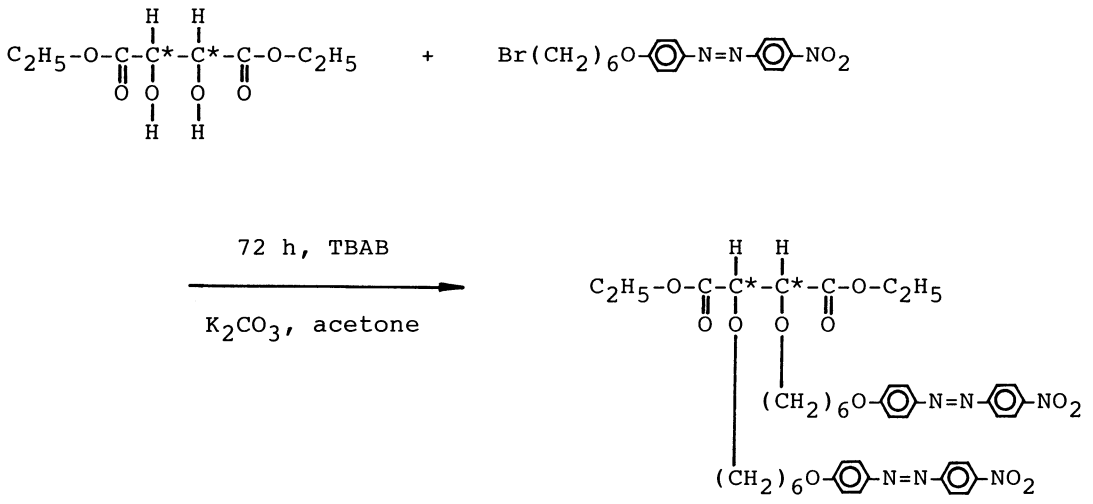
A liquid crystalline chiral tartrate with p'-nitoazobenzene mesogenic moiety was found to show cholesteric and chiral smectic phases. In the chiral smectic phase, the tartrate exhibited the ferroelectric properties. The mode value of spontaneous polarization was 5 mC/m^2 at 90°C.

We have synthesized a polymerizable liquid crystalline tartrate with two chiral centers in order to obtain a new ferroelectric liquid crystalline side-chain polyester with chiral skeletal main-chain. In this papar we report the preliminary result on the liquid crystalline and ferroelectric properties of the chiral tartrate.

The chiral tartrate was prepared by etherification of p-bromohexyloxy-p'-nitroazobenzene with chiral diethyltartrate[2R,3R-(+)] as shown below:



chiral tartrate [2R,3R]
(C* : chiral center)

A solution of optically active diethyltartrate(1.15 ml, 6.7 mmol) in acetone(50 ml) was added dropwise to a mixture of p-bromohexyloxy-p'-nitroazobenzene(5.5 g, 13.5 mmol), tetra-n-butylammonium bromide(TBAB)(4.4 g, 13.6 mmol),

potassium carbonate(1.9 g, 13.8 mmol) and acetone(100 ml), and the mixture was refluxed for 72 h. The reaction mixture was filtered, and evapolated. The pure chiral tartrate(3.8 g, 66.3 %) was obtained by the recrystallization from a mixed solution of chloroform and hexane: $[\alpha]_D^{25}$ +4.8° (c 1, $CHCl_3$); IR (KBr) 1740 ν(C=O), 1522 $\nu(NO_2)a$, 1343 $\nu(NO_2)s$, 860, 841 cm^{-1} (benzene ring out of plane vibration); ^1H NMR(60 MHz, $CDCl_3$); δ 1.20-2.40(m, 22H), 3.10-4.60(m, 14H), 6.96 (d, J=8.0 Hz, 4H), 7.95(d, J=8.0 Hz, 8H), 8.34(d, J=8.0 Hz, 4H).

The chiral tartrate exhibited chiral smectic and cholesteric phases. A finger print texture was observed in the cholesteric phase. Fan and schlieren textures were found in the chiral smectic phase. The schlieren texture in the chiral smectic phase is characteristic of a tilted smectic phase.

The transition temperatures are shown as follows:

K (52.5 °C) Sm* (103.7 °C) Ch (118.2 °C) I

where, K is the solid phase, Sm* the chiral smectic phase, Ch the cholesteric phase, and I the isotropic phase.

A hysteresis loop was obtained by using the Sawyer-Tower circuit in the chiral smectic phase(Fig. 1). An electric reversal of polarization was measured by applying a triangular wave voltage in the chiral smectic phase. These results demonstrate that the chiral tartrate exhibits the ferroelectricity.

In the chiral smectic phase, the magnitude of the spontaneous polarization(Ps) changed depending on the preorientation. The mode value of Ps at 90 °C was determined to be 5 mC/m^2. In general the value of Ps becomes small when a chiral center is located in a nonpolar group, and is far apart from a mesogenic core. The chiral centers in the tartrate are separated with the hexamethylene spacer from the mesogenic core. However, the strong polar carbonyl group is directly attached to the chiral center in the chiral tartrate. In this case, the value of Ps is independent of the position of the chiral center because a stereopolar coupling takes place.[1] From this reason, the chiral tartrate has much larger Ps even if the chiral center is separated from the mesogenic core.

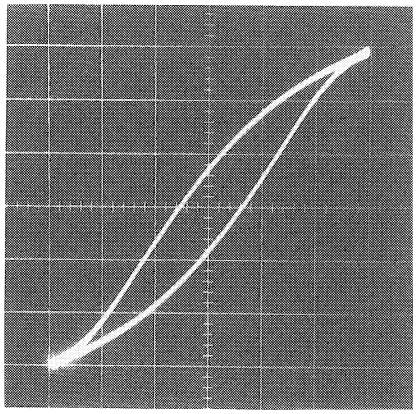


Fig. 1. Hysteresis loop at 90 °C (chiral smectic phase): X-axis ; 500 kV/m/div: Y-axis ; 3.6 mC/m^2/div.

In the cholesteric phase, the chiral tartrate exhibited the same electric reversal of polarization observed for the chiral smectic phase. This indicates that the cholesteric phase has a pseudo-ferroelectricity. Detailed study is in progress.

Reference

1) B. Otterholm, M. Nilsson, S. Lagerwall, and K. Skarp, Liq. Cryst., 2, 757 (1987).

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