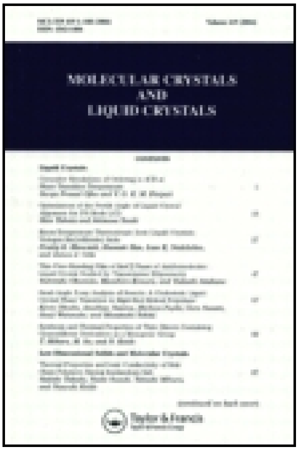

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Do the Smectic O and the Antiferroelectric Smectic C Phases Belong to the Same Phase Type?

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Do the Smectic O and the Antiferroelectric Smectic C Phases Belong to the Same Phase Type?

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Miscibility studies have been carried out between chiral 1-methylheptyl-terephthalidene-bis-amino-cinnamate (MHTAC) and chiral 4-(1-methylheptyloxycarbonyl)-phenyl-4'-octyloxybiphenyl-4-carboxylate (MHPOBC). An uninterrupted miscibility is observed between the SmO phase of MHTAC and the antiferroelectric SmC phase of MHPOBC indicating thereby that these smectic modifications belong to the same phase type. In addition, the antiferroelectric properties of MHTAC have been studied. Above a threshold electric field the SmO phase is transformed into a ferroelectric switching state which exhibits a maximum spontaneous polarization of about 380 nC/cm^2.

Keywords: antiferroelectric liquid crystals, SmO, SmC_A, miscibility studies

INTRODUCTION

In 1983 Levelut *et al.* established the existence of a new type of liquid crystalline phase which occurs in chiral as well as racemic 1-methylheptyl-terephthalidene-bis-amino-cinnamate (MHTAC).[1] X-ray investigations revealed that this phase, which they called SmO, has a tilted smectic structure without positional order within the layers. Later on, Galerne and Liebert showed that in the SmO phase of nonchiral MHTAC the tilt direction alternates from one layer to another.[2] Thereby a herringbone structure is formed which distinguishes the SmO from the SmC phase. When the SmO phase consist of chiral molecules each individual layer is equivalent to a thin ferroelectric SmC film. Due to the herringbone structure the in-plane polarization alternates from layer to layer and an antiferroelectric phase is formed.[3]

More recently, Chandani *et al.* observed a liquid crystalline phase in chiral 4-(1-methylheptyloxycarbonyl)-phenyl-4'-octyloxybiphenyl-4-carboxylate (MHPOBC), showing a double hysteresis as well as a "tristable" switching when a low frequency a.c. field is applied and a single hysteresis as well as a "bistable" switching when the frequency is increased above a certain value.[4] Conoscopic investigations on this compound indicated that the optical axis is parallel to the layer normal for the zero field state and tilted for the two other states induced by the electric field.[5] On the basis of these results an antiferroelectric arrangement of the smectic layers has been proposed and the notation SmC_A has been introduced for this phase. Since then antiferroelectric liquid crystals have received considerable interest from both fundamental as well as practical viewpoints and several new compounds exhibiting the SmC_A phase have been obtained by small structural variations of MHPOBC.[6–9]

A comparison shows that for both SmO and SmC_A the same structure has been proposed. Therefore, it seems possible that these antiferroelectric modifications are identical, but this has not been established till to date. In order to clarify the relationship between the SmO and the SmC_A phase, we have performed miscibility studies between the compounds MHTAC and MHPOBC. These studies show that the phases SmO and SmC_A are clearly miscible. We also present in this paper the

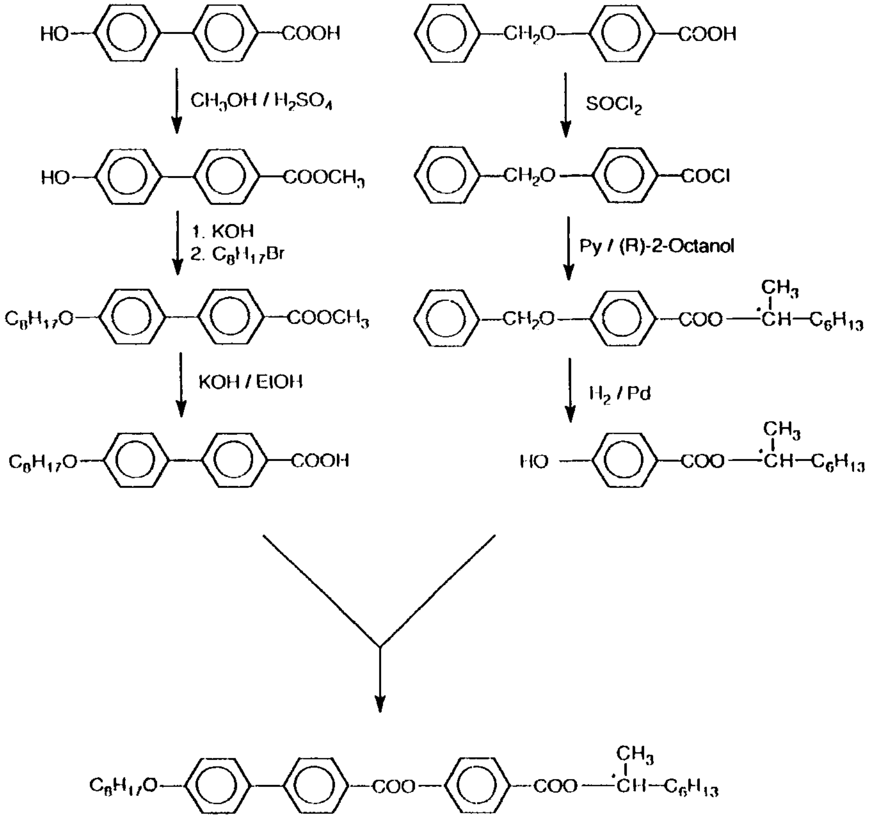

FIGURE 1 Synthetic scheme for the preparation of (*R*)-MHPOBC.

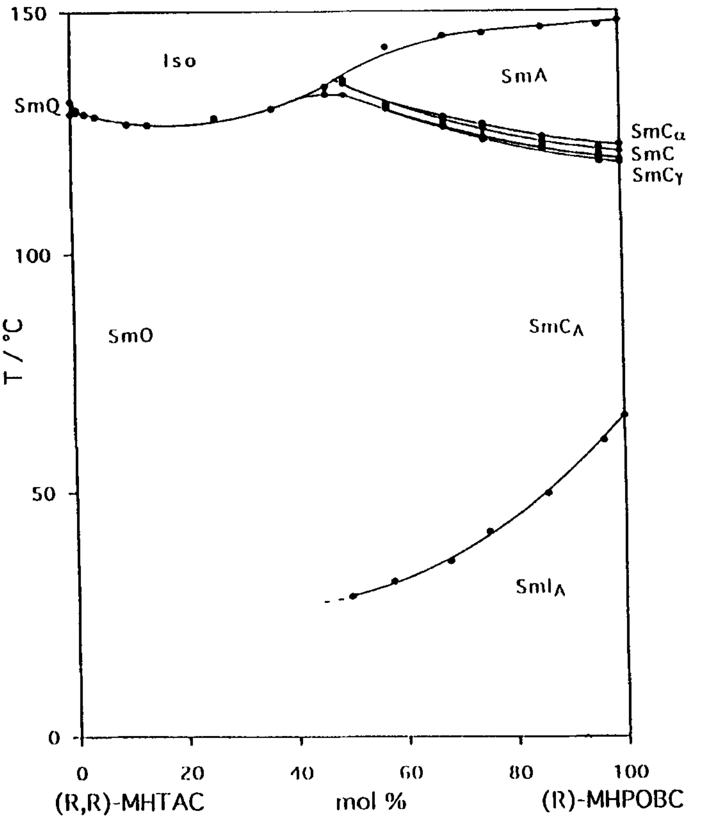

FIGURE 2 Binary diagram of state between (*R*,*R*)-MHTAC and (*R*)-MHPOBC.

results of our electro-optical investigations characterizing the antiferroelectric behaviour of the SmO phase of chiral MHTAC.

SYNTHESIS

(*R*,*R*)-1-methylheptyl-terephthalidene-bis-amino-cinnamate (MHTAC) was prepared by esterification of 4-nitro-cinnamic-acid with (*R*)-2-octanol, followed by a reduction of the nitro group to an amino group and condensation of the obtained 4-amino-cinnamate with terephthalaldehyd according to the descriptions given in Reference 10.

(*R*)-4-(1-methylheptyloxycarbonyl)-phenyl-4'-octyloxybiphenyl-4-carboxylate (MHPOBC) was synthesized as outlined in Figure 1.

RESULTS AND DISCUSSION

(*R*,*R*)-MHTAC and (*R*)-MHPOBC have been chosen to carry out miscibility studies between the antiferroelectric smectic modifications SmO and SmC_A. The re-

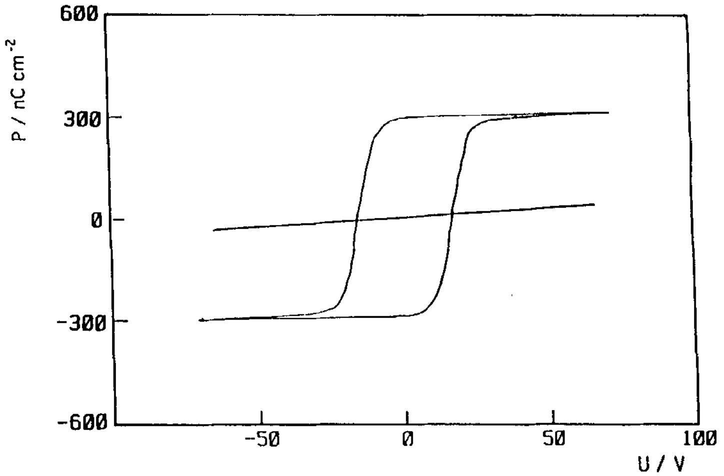

FIGURE 3 Electric response of (*R*,*R*)-MHTAC for two different amplitudes of the applied sinusoidal a.c. electric field (frequency 750 Hz, temperature 110°C).

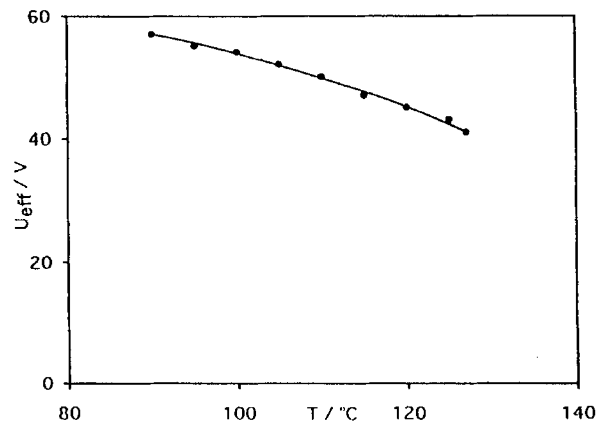

FIGURE 4 Temperature dependence of the threshold voltage where the occurrence of a ferroelectric switching behaviour of (*R*,*R*)-MHTAC is observed (cell thickness 4 μm).

sulting phase diagram, which has been obtained by the contact method and by choosing specific concentrations, is shown in Figure 2. SmO and SmC_A are uninterruptedly miscible with each other, whereas all other liquid crystalline phases (SmA, SmC, SmC_α, SmC_γ, SmI_A and SmQ) are observed only in a certain concentration range. Thus, it can be concluded that the two phases, namely the SmO phase with a herringbone structure, and the SmC_A phase exhibiting antiferroelectric switching behaviour, belong to the same phase type.

To characterize the behaviour of the SmO phase under the influence of an electric field, a glass cell (4 μm EHC) was filled with (*R*,*R*)-MHTAC, the electrodes being coated with rubbed polyimide. However, no homogeneous planar orientation could be obtained and therefore no reliable measurements of the optical response could be performed. Using a conventional Diamant bridge the electric response was

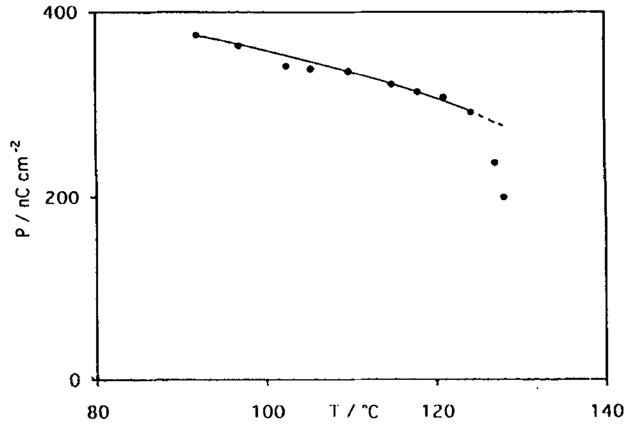

FIGURE 5 Temperature dependence of the spontaneous polarization of (*R*,*R*)-MHTAC.

studied (Figure 3). Below a certain threshold field strength the polarization depends linearly on the applied electric field, with the slope corresponding to a dielectric constant of about 3.8. At the threshold field strength, which amounts to about 50 V_{eff}/4 μm at 110°C, an abrupt textural change occurs and switching between two optically different states can be clearly observed in the still non-homogeneously oriented sample. At the same time the electric response changes to a ferroelectric hysteresis loop, with a high value of spontaneous polarization of about 350 nC/cm^2 at 110°C (Figure 3).

As shown in Figure 4, the threshold field strength slightly increases with decreasing temperature. Thus, using a.c. voltages above the threshold line the spontaneous polarization could be determined as a function of temperature (Figure 5).

In summary, we have shown here that the SmO and the SmC_A phases (of chiral compounds) are completely miscible and hence can be thermodynamically classified as being the same. However, there are some differences with regard to their electro-optic behaviour and their surface interaction. Further work to elucidate these differences on a molecular and structural basis would be of considerable interest. Experiments to resolve these questions are underway.

Acknowledgment

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