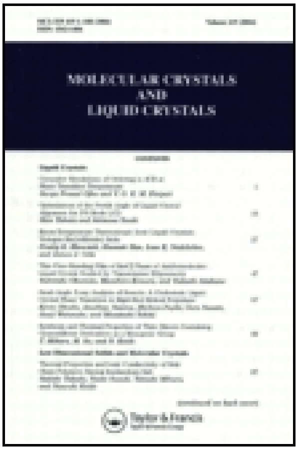

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Synthesis and Physical Properties of Thioester Liquid Crystals that Exhibit an Anti-Ferro-Anti Phase Sequencing

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The thioester unit has been commonly used to enhance the mesophase thermal stability and phase range in numerous liquid crystal materials. In this paper we report the synthesis of a homologous series of thioesters with similar structures to AS620 {(*S*)-(+)-1-methylheptyl 4-[5-(4-dodecyloxyphenyl)thien-2-ylcarbonyloxy]benzoate, **10d** in this paper}. A complex phase morphology is observed that indicates an anti-ferro-anti phase sequencing [for the octyloxy derivative (**9a** in this paper)] based on electrooptic evaluation and especially the observation of polarization threshold on either side of the ferroelectric phase.

Keywords: ferroelectric; antiferroelectric; thioester; electrooptics

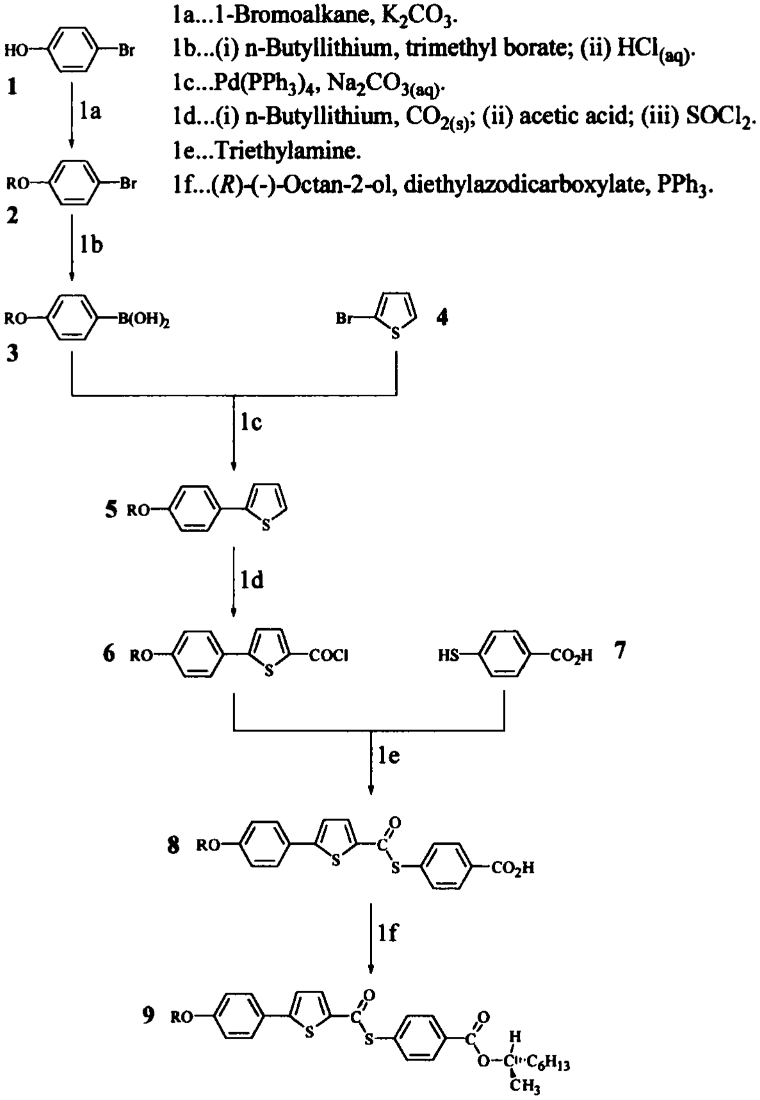
INTRODUCTION

In an ongoing program concerned with the synthesis of ferroelectric liquid crystals with high dielectric biaxiality, we have synthesized a homologous series of thioester-containing materials with the thiophene unit as a principal core substituent. The heterocycle imparts a large lateral dipole without the extra molecular breadth that so severely reduces mesophase thermal stability and phase range in materials that contain for example, lateral cyano, nitro and trifluoromethyl substituents. A 2,5-disubstitution pattern of the heterocycle was chosen in order to give the highest linearity of the molecular structure and hence the widest mesophase range and stability[1].

The incorporation of the thioester unit was expected to give rise to enhanced phase ranges and mesophase thermal stabilities when compared to the analogous carboxylates synthesized by Byron[2, 3] and Seed[4]. These trends were indeed observed and are attributed to a combination of both the enhanced molecular polarizability and the increase in the aspect ratio of the thioester materials.

SYNTHESIS

A typical synthetic pathway used in obtaining the desired thioester materials is given in SCHEME 1. Alkoxybromobenzenes (**2**) were synthesized using Williamson's etherification[5] in near-quantitative yields. Boronic acids (**3**) were obtained through halogen metal exchange, reaction with trimethyl borate and subsequent hydrolysis of the borate ester (quantitative yields)[1, 6]. Palladium-catalyzed cross-coupling[7] of **3** and **4** gave compounds **5** in yields of between 39 and 65%. Subsequent carboxylation and conversion into the acid chlorides under standard conditions gave compounds **6**. **6** and **7** were esterified in the presence of triethylamine to give compounds **8**[8]. The Mitsunobu reaction[9] was finally used to effect clean esterification of the carboxylic acids (**8**) with *(R)*-(-)-octan-2-ol.



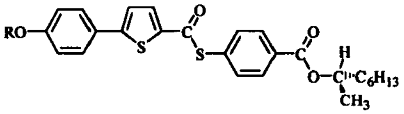
1a...1-Bromoalkane, K_2CO_3.
1b...(i) n-Butyllithium, trimethyl borate; (ii) $HCl_{(aq)}$.
1c...$Pd(PPh_3)_4$, $Na_2CO_{3(aq)}$.
1d...(i) n-Butyllithium, $CO_{2(s)}$; (ii) acetic acid; (iii) $SOCl_2$.
1e...Triethylamine.
1f...(*R*)-(-)-Octan-2-ol, diethylazodicarboxylate, PPh_3.

SCHEME 1 The synthesis of the (*S*)-(+)-1-Methylheptyl 4-[2-(4-alkoxyphenyl)thiophene-5-carbonylthiooxy]benzoates

RESULTS AND DISCUSSION

Optical Microscopy

The transition temperatures for the final products are given in TABLE 1. All of the reported transition temperatures were obtained using polarized optical microscopy (plain slide and cover slip) and confirmed by DSC.



9a...R = C_8H_{17}...Cryst 67.8 $S_C{}^{*}{}_{\mathrm{ANTI}}$ 103.4 $S_C{}^{*}{}_{\mathrm{FERRI}}$ 105.9 $S_C{}^{*}{}_{\mathrm{FERRO}}$ 111.6 S_A 128.5 I

9b...R = C_9H_{19}...Cryst 67.1 $S_C{}^{*}{}_{\mathrm{ANTI}}$ 80.4 $S_C{}^{*}{}_{\mathrm{FERRI}}$ 87.5 $S_C{}^{*}{}_{\mathrm{FERRO}}$ 114.0 S_A 123.9 I

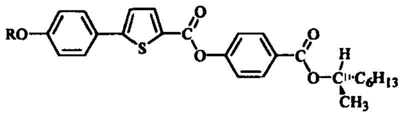
9c...R = $C_{10}H_{21}$...Cryst 60.6 $S_C{}^{*}{}_{\mathrm{ANTI}}$ 97.8 $S_C{}^{*}{}_{\mathrm{FERRI}}$ 100.5 $S_C{}^{*}{}_{\mathrm{FERRO}}$ 112.5 S_A 121.7 I

9d...R = $C_{11}H_{23}$...Cryst 66.4 ($S_C{}^{*}{}_{\mathrm{ANTI}}$ 62.8) $S_C{}^{*}{}_{\mathrm{FERRO}}$ 112.2 S_A 119.0 I

9e...R = $C_{12}H_{25}$...Cryst 64.5 $S_C{}^{*}{}_{\mathrm{ANTI}}$ 77.5 $S_C{}^{*}{}_{\mathrm{FERRI}}$ 83.2 $S_C{}^{*}{}_{\mathrm{FERRO}}$ 110.3 S_A 116.9 I

TABLE 1 Transition temperatures (°C) of the (*S*)-(+)-1-methylheptyl 4-[2-(4-alkoxyphenyl)thiophene-5-carbonylthiooxy]benzoates

The transition temperatures for the analogous carboxylate derivatives are given in TABLE 2.



10a...R = C_8H_{17}...Cryst 87.5 ($S_C{}^*{}_{ANTI}$ 83.0 $S_C{}^*{}_{FERRI}$ 85.4 $S_C{}^*{}_{FERRO}$ 87.2) S_A 107.3 I

10b...R = C_9H_{19}...Cryst 76.8 ($S_C{}^*{}_{ANTI}$ 65.7 $S_C{}^*{}_{FERRI}$ 69.2) $S_C{}^*{}_{FERRO}$ 90.1 S_A 103.9 I

10c...R = $C_{10}H_{21}$...Cryst 65.5 $S_C{}^*{}_{ANTI}$ 78.6 $S_C{}^*{}_{FERRI}$ 81.4 $S_C{}^*{}_{FERRO}$ 92.2 S_A 97.4 I

10d...R = $C_{12}H_{25}$...Cryst 64.2 $S_C{}^*{}_{ANTI}$ 80.2 $S_C{}^*{}_{FERRI}$ 82.8 $S_C{}^*{}_{FERRO}$ 92.6 S_A 97.9 I

TABLE 2 Transition temperatures (°C) of the (*S*)-(+)-1-methylheptyl 4-[2-(4-alkoxyphenyl)thiophene-5-carbonyloxy]benzoates

In looking at tables 1 and 2 it is clear that there are a number of trends in the mesomorphic behavior. The thioesters exhibit smectic A, smectic $C^*{}_{FERRO}$ and $C^*{}_{ANTI}$ phases; the $C^*{}_{FERRI}$ phase is observed in all compounds except **9d**. The clearing points decrease regularly with increasing chain length. In comparing the thioester compounds to the carboxylate series it is seen that the thioester link has resulted in a decrease in the melting points for **9a**, **9b**, and **9c** by 19.7 °C, 9.7 °C, and 4.9 °C respectively, but has raised it 0.3 °C in compound **9e**. The clearing points for **9a**, **9b**, **9c**, and **9e** have increased by 21.2 °C, 20.0 °C, 24.3 °C and 19.0 °C respectively. The $S_C{}^*{}_{FERRO}$-S_A transition temperatures have also increased by 24.4 °C, 23.9 °C, 20.3 °C, and 17.7 °C for compounds **9a**, **9b**, **9c**, and **9e** respectively. The ferroelectric phase range has increased by 3.9 °C, 5.6 °C, 1.2 °C, and 17.3 °C for **9a**, **9b**, **9c**, and **9e** respectively. In comparing the $S_C{}^*{}_{ANTI}$-$S_C{}^*{}_{FERRI}$ transitions, we see an increase in thermal stability for **9a**, **9b**, and **9c** of 20.4 °C, 14.7 °C, and 19.2 °C respectively, and a decrease of 2.7 °C for **9e**. The $S_C{}^*{}_{FERRI}$- $S_C{}^*{}_{FERRO}$ phase stabilities show increases of 20.5 °C, 18.3 °C, 19.1 °C and 0.4 °C for **9a**, **9b**, **9c**, and **9e** respectively.

Physical measurements of 9a

Optical microscopy indicated that we had a single antiferroelectric phase. However, textures of frustrated phases such as those exhibited by our compounds are often difficult to assign and electrooptic evaluation is an excellent supplementary tool. In addition, the synthesis of the racemic mixtures can also shed light on the existence of the antiferroelectric phase through the observation of two-brush dispirations[10] which confirm the antiferroelectric structure.

9a was subjected to a number of physical tests in a 15μm cell. Our initial studies concentrated on optical scanning spectroscopy with the results being shown in FIGURE 1. These observations show characteristic textural changes at 103 °C, 110 °C and 116 °C. In addition there is a slightly less pronounced changed at ~113 °C.

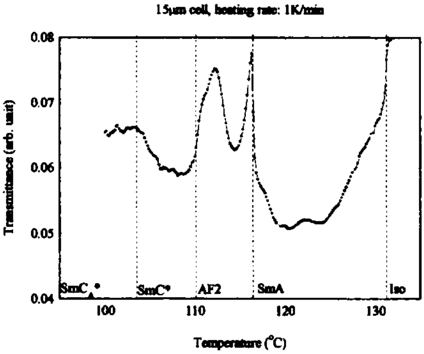


FIGURE 1 Textural variations of **9a** with temperature

The threshold for switching polarization was subsequently examined and an unexpected threshold voltage was observed between 110 °C and 116 °C (see FIGURE 2).

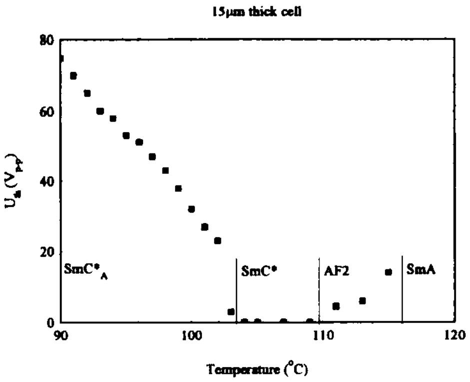


FIGURE 2 Temperature dependence of the threshold voltage of **9a**

The temperature dependence of the threshold voltage indicates that the material is antiferroelectric below ~103 °C and above 110 °C, contrary to our microscopy evaluation.

The value of the polarization was measured as a function of voltage and the saturated values were taken for the spontaneous polarization. The voltage dependence of the polarization also confirms that two different regimes of antiferroelectric phases exist: one below and one above the ferroelectric state.

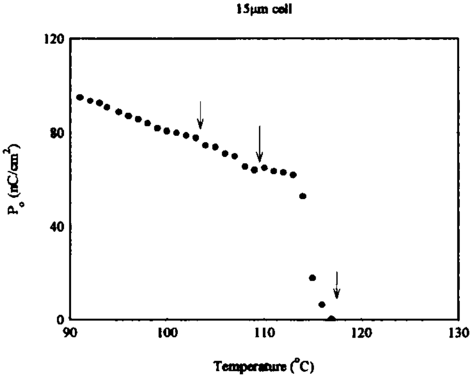


FIGURE 3 Temperature dependence of the spontaneous polarization (saturated) for **9a**.

The temperature dependence of the spontaneous polarization (see FIGURE 3) also shows pronounced changes at 103°C, 110°C and 116°C, corresponding to the SmC^*_A - SmC^*-AF2-SmA phase sequences suggested by Figures 1 and 2. The drastic decrease of the polarization at 113°C coincides with the pronounced textural change observed in FIGURE 1.

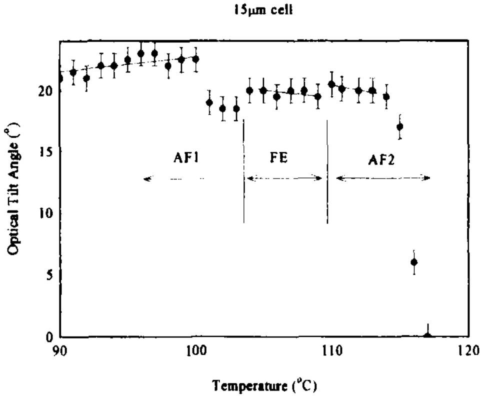


FIGURE 4 Temperature variation of the optical tilt angle for **11a**

The temperature dependence of the tilt-angle (see FIGURE 4) also reflects the transition to the SmA phase above 116°C, and the ferroelectric range between 103 °C and 110 °C. Here the low-temperature antiferroelectric to ferroelectric transition seems to be preceded by another transition. Considering the measurement errors and the fluctuation effects, we think that it is only pre-transitional effect.

CONCLUSIONS

We have synthesized a series of thioester derivatives. Standard microscopic evaluation indicated that all of the materials (except **9d**) had an anti-ferri-ferro phase sequencing. The octyloxy derivative has undergone extensive electrooptical evaluation and appears to have a anti-ferro-anti phase morphology when confined within a 15μm cell. In thinner films the antiferroelectric character of AF2 replaces the ferrielectric-type behavior, probably due to the surface forces imposed by the thin cell. Confirmation of the high temperature antiferroelectric phase may be additionally sought by synthesis of the enantiomerically pure racemic mixture, and the observation of a two-brush dispiration. This phase sequence is the first example of a ferroelectric phase flanked by two antiferroelectric phases.

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