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Effect of core structures and swallow-tailed groups on the mesomorphic properties of chiral liquid crystals derived from (L)-lactic acid

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Effect of core structures and swallow-tailed groups on the mesomorphic properties of chiral liquid crystals derived from (L)-lactic acid

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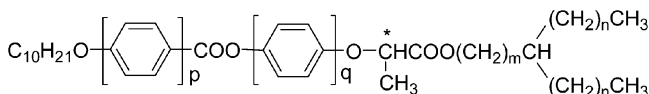
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A homologous series of chiral swallow-tailed materials, $I(p,q,m,n)$, derived from (L)-lactic acid was synthesized for investigation of the effects of variation of the molecular core structure and the terminal swallow-tailed group on the formation of mesophases. The mesophases and their corresponding transition temperatures were identified by polarizing optical microscopy and differential scanning calorimetry. The results indicate that the variations of the core structure and of the methylene group between the chiral centre and the swallow-tailed group, have a remarkable effect on the appearance of mesophases; change in length of the swallow-tail group has less effect. The spontaneous polarization and dielectric constant in the ferroelectric SmC^* phase were also measured.

1. Introduction

Optically active lactic acid is commonly used as a chiral precursor for the preparation of chiral liquid crystals [1–8]. Our previous results from a series of chiral materials derived from (L)-lactic acid with 3-pentanol as swallow-tailed group, and with an ether linkage to the core structure of the molecules, showed a phase sequence of BP, N^* , TGB_A^* , SmA^* and SmC^* phases [9]. However another series, with the same chiral tail but connected to the core structure by an ester linking group, exhibited a different phase sequence— SmA^* , SmC^* and unidentified SmX^* phases [10]. These results indicated that the variation of linking group for chiral swallow-tailed materials could change the nature of mesophases. In this study, therefore, more materials were prepared with variation in the core structures and in the length of the chiral swallow-tail groups, in order to investigate further the structural effect on mesophases. The general structural formula of the target chiral swallow-tailed materials is shown below.



$$I(p, q, m, n; p=1,2; q=1,2; m=0,1; n=1,2)$$

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2. Experimental

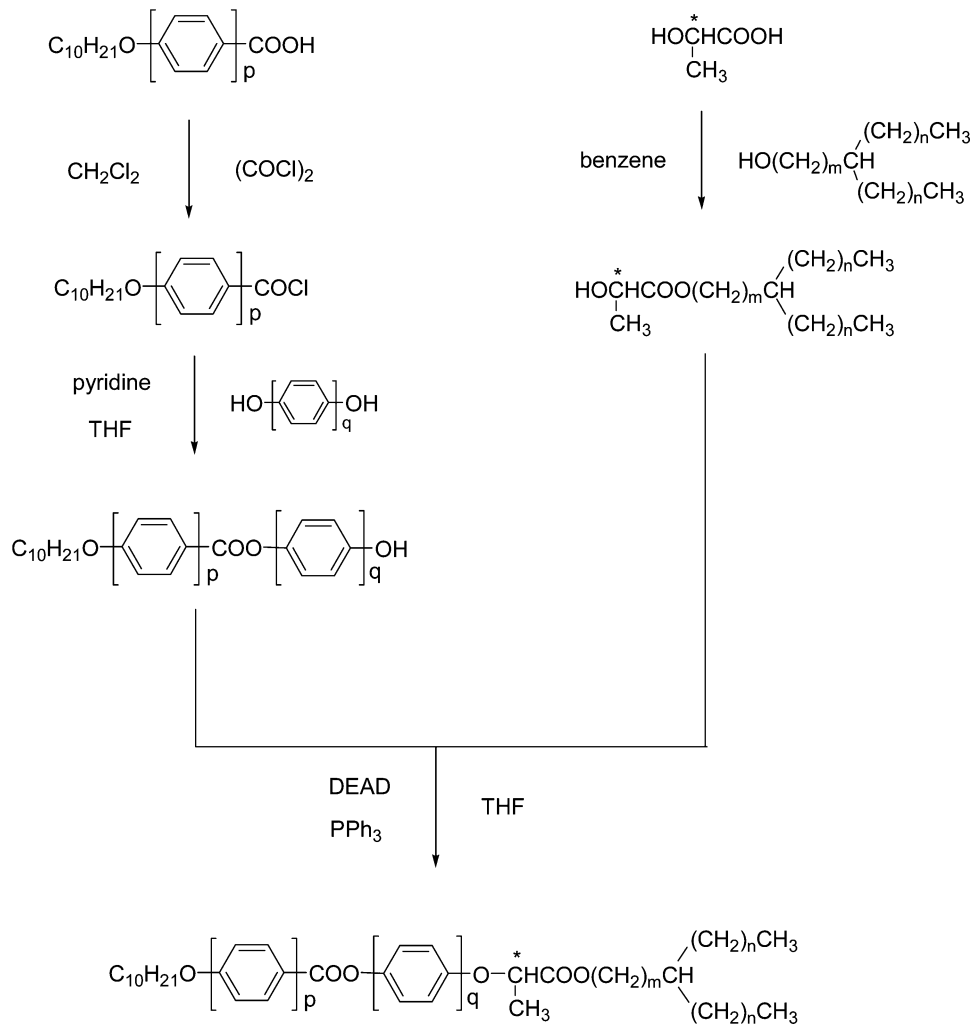
2.1. Characterization of the materials

The purity of the intermediates and final products was checked by thin layer chromatography using dichloromethane as solvent, and further confirmed by elemental analysis using a Perkin-Elmer 2400 spectrometer. The phase transition temperatures and corresponding enthalpies of the compounds under study were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 calorimeter. Mesophases were principally identified by polarizing optical microscopy (Nikon Microphot-FXA) in conjunction with a hot stage (Mettler FP82-HT) using clean, untreated microscope slides and cover slips. All transition sequences were recorded on cooling from the isotropic liquid at a rate of 5°C min^{-1} .

The physical properties of the ferroelectric phase of these materials were measured in anti-parallel aligned cells purchased from E.H.C. Co., Japan. The spontaneous polarization (P_s) was measured by a triangular wave method [11].

2.2. Preparation of the materials

The synthetic procedures for the chiral materials are outlined in the scheme. General synthetic procedures for examples of compounds $I(p,q,m,n; p=2, q=1, m=0,1, n=1,2)$ are described in the following.



Scheme. Synthetic procedures for the target compounds.

2.2.1. Synthesis of alkyl (*L*)-2-hydroxypropionates

A mixture of (*L*)-lactic acid (12 g, 0.13 mol) and the appropriate alcohol (0.15 mol) in dry benzene (30 ml) was heated under reflux with a Dean and Stark strap for 10 h. The benzene was evaporated and the alkyl (*L*)-lactates were collected as colourless liquids by vacuum distillation. The boiling points and yields for lactates are shown in table 1.

Table 1. Boiling points and yields for lactates (m, n ; $m = 0, 1$, $n = 1, 2$).

| Compound (m, n) | Boiling point/ $^{\circ}\text{C}$ | Yield % |
|---------------------|-----------------------------------|---------|
| (0,1) | 83 $^{\circ}\text{C}$ /40 torr | 21 |
| (0,2) | 90 $^{\circ}\text{C}$ /50 torr | 16 |
| (1,1) | 92 $^{\circ}\text{C}$ /36 torr | 33 |
| (1,2) | 95 $^{\circ}\text{C}$ /41 torr | 31 |

2.2.2. Synthesis of 4'-decyloxybiphenyl-4-carboxylic acid chloride

A mixture of 4'-decyloxybiphenyl-4-carboxylic acid (5 mmol) and oxalyl chloride (12.6 mmol) in dry dichloromethane (15 ml) was heated under reflux for 2 h. The reaction mixture was then distilled under reduced pressure to remove excess oxalyl chloride. The residues obtained were used immediately for the subsequent reaction.

2.2.3. Synthesis of 4-hydroxyphenyl 4'-decyloxybiphenyl-4-carboxylate

The acid chloride (from § 2.2.2.) (5 mmol) dissolved in dry dichloromethane was added dropwise to a mixture of hydroquinone (25 mmol), dry pyridine (5 ml) and anhydrous tetrahydrofuran (THF, 30 ml). The reaction mixture was cooled in a refrigerator for 2 days. Silica gel was then added, and the mixture was dried and

powdered. The product was purified by column chromatography over silica gel (70–230 mesh ASTM) using dichloromethane as eluent. After recrystallization from ethanol, a 68% yield of white powder was obtained.

2.2.4. Synthesis of alkyl (L)-2-[4-(4'-decyloxybiphenyl-carbonyloxy)phenoxy]propionates

A solution of diethyl azodicarboxylate (DEAD, 1.6 mmol) and the alkyl (L)-2-hydroxypropionate (1.08 mmol) in anhydrous THF (7 ml) was added dropwise to a solution of triphenyl phosphine (Ph_3P , 1.6 mmol) and 4-hydroxyphenyl 4'-decyloxybiphenyl-4-carboxylate (1.6 mmol) in anhydrous THF (7 ml) at room temperature with vigorous stirring. After standing the mixture overnight at room temperature, triphenyl phosphine oxide was filtered off and THF removed under vacuum. After the work-up procedure, the products were isolated by column chromatography over silica gel (70–230 mesh ASTM) using ethyl acetate/hexane ($V/V=1/9$) as eluent. After purification by recrystallization from absolute ethanol, 56–60% yields of the final products were obtained.

2.2.5. Synthesis of 4'-decyloxyphenyl-4-carboxylic acid chloride

A mixture of 4-decyloxybenzoic acid (5 mmol), oxalyl chloride (12.6 mmol) and dry dichloromethane (15 ml) was heated under reflux for 2 h. The reaction mixture was then distilled under reduced pressure to remove excess oxalyl chloride. The remaining solid was used immediately for the subsequent reaction.

2.2.6. Synthesis of 4-hydroxybiphenyl 4'-decyloxyphenyl-4-carboxylate

The acid chloride (from §2.2.5.) (5 mmol) dissolved in dry dichloromethane was added dropwise to a mixture of hydroquinone (25 mmol), dry pyridine (5 ml) and THF (30 ml). The reaction mixture was cooled in a refrigerator for 2 days. Silica gel was then added, and the mixture was dried and powdered. The product was purified by column chromatography over silica gel (70–230 mesh) using dichloromethane as eluent. After recrystallization from ethanol, a 65% yield of white solid was obtained.

2.2.7. Synthesis of alkyl (L)-2-[4-(4'-decyloxyphenyl-carbonyloxy)biphenyloxy]propionates

A solution of DEAD (1.6 mmol) and the alkyl (L)-2-hydroxypropionate (1.08 mmol) in anhydrous THF (7 ml) was added dropwise to a solution of triphenyl phosphine (Ph_3P , 1.6 mmol) and

4-hydroxybiphenyl 4'-decyloxyphenyl-4-carboxylate (1.6 mmol) in anhydrous THF (7 ml) at room temperature with vigorous stirring. After standing the mixture overnight at room temperature, triphenyl phosphine oxide was filtered off and THF was removed under vacuum. After the work-up procedure, the products were isolated by column chromatography over silica gel (70–230 mesh ASTM) using ethyl acetate/hexane ($V/V=1/9$) as eluent. After recrystallization from absolute ethanol, 50–56% yields of the final products were obtained.

3. Results and discussion

3.1. Mesomorphic phases

The mesophases were identified mainly by observing microscopic textures. The BP phase displayed a blue fog texture, while the N^* phase showed a paramorphic defective scale-like texture. The TGB_A^* phase was identified by the existence of filament texture. The SmA^* phase was confirmed by the formation of focal-conic texture and the SmC^* phase by the formation of a broken focal-conic texture. The temperatures of the phase transitions and their associated enthalpies were determined by DSC and are listed in table 2.

The effect of changes in molecular structure on the appearance of liquid crystal phases was studied. In general, an increase of swallow-tailed length n has no significant change on the formation of liquid crystal phases. For example, both chiral compounds $\text{I}(2,1,0,1)$ and $\text{I}(2,1,0,2)$ have the same phase sequence: BP, N^* , TGB_A^* , SmA^* and SmC^* . However, with an increase of methylene group length m between the lactic acid and swallow-tailed group, for example moving from compound $\text{I}(2,1,0,1)$ to compound $\text{I}(2,1,1,1)$, the BP, N^* and TGB_A^* phases were suppressed, while SmA^* and SmC^* phases remain unaltered. It was found that a change of core structure of the molecules from compound $\text{I}(2,1,0,1)$ to compound $\text{I}(1,2,0,1)$, dramatically suppressed most of the mesophases, leaving only the N^* phase. However, on adding a methylene group to compound $\text{I}(1,2,0,1)$, to give compound $\text{I}(1,2,1,1)$, the N^* phase was augmented to BP, N^* , TGB_A^* , SmA^* and SmC^* phases. It was also interesting to find that the two different core structures of the molecules PhPhCOOPh and PhCOOPhPh provided opposite results in the formation of mesophases as m was changed. Although, the cause of the change in mesophases with structural change is too complicated to clarify here, our results strongly indicate that the variation of core structure and length of methylene group m has a remarkable effect on the formation of liquid crystal phases.

Table 2. Transition temperatures ($^{\circ}\text{C}$) and associated enthalpy data (J g^{-1} , in square brackets) for the compounds $\text{I}(p,q,m,n; p=1,2, q=1,2, m=0,1, n=1,2)$: recorded by DSC thermograms at a cooling rate of $5^{\circ}\text{C min}^{-1}$.

| (p,q,m,n) | I | BP | N^* | TGB_{A}^* | SmA^* | SmC^* | Cr | m.p. ^d |
|-------------|--------------------------------|--------------|-------------------|---------------------------|------------------|--------------------|--------------------|-------------------|
| (2,1,0,1) | • 114.2 [0.75] ^c | • 113.3 a | • 109.6 a | • 107.8 [0.85] | • 61.0 b | • 27.47 [37.42] | • 59.45 [51.77] | |
| (2,1,0,2) | • 119.2 [8.68] | • 118.5 a | • 107.3 a | • 106.7 [1.46] | • 46.4 b | • 31.4 [30.04] | • 73.4 [54.92] | |
| (2,1,1,1) | • 95.9 [17.46] | — | — | — | • 77.8 [0.75] | • 39.3 [30.57] | • 69.2 [58.70] | |
| (2,1,1,2) | • 83.8 [4.03] | — | — | — | • 66.0 [0.47] | • 28.4 [30.42] | • 51.4 [42.50] | |
| (1,2,0,1) | • 112.0 [9.80] | — | • 30.0 [31.04] | — | — | — | • 75.9 [61.70] | |
| (1,2,0,2) | • 117.3 [9.50] | — | • 31.5 [29.40] | — | — | — | • 73.3 [59.06] | |
| (1,2,1,1) | • 76.2 [7.66] | • 71.3 c | • 61.5 c | • 59.4 [0.33] | • 51.0 [0.51] | • 42.6 [27.16] | • 74.9 [53.29] | |
| (1,2,1,2) | • 73.5 [8.88] | • 64.3 c | • 47.5 c | • 46.9 c | • 46.1 [0.56] | • 32.8 [29.04] | • 44.1 [54.22] | |

^aThe enthalpies of BP– N^* and N^* – TGB_{A}^* transitions were added together with that of the I–BP and TGB_{A}^* – SmA^* transitions, respectively.

^bThe enthalpy was too small to be measured.

^cThe enthalpies of BP– N^* , N^* – TGB_{A}^* and TGB_{A}^* – SmA^* transitions were added to that of the I–BP transition.

^dm.p. refers to the melting point taken from DSC thermograms recorded at a heating rate of $5^{\circ}\text{C min}^{-1}$.

3.2. Dielectric properties

Figure 1 illustrates the temperature dependence of the real part of the dielectric constant ϵ' for the compound $\text{I}(2,1,1,1)$ at 100 Hz during heating and cooling. The dielectric constants ϵ' in the SmA^* phase are small. On decreasing the temperature to the SmC^* phase, at approximately 74°C the dielectric constants increasing rapidly due to the contribution of the Goldston mode, providing more evidence for the

existence of the ferroelectric SmC^* phase. A continuous decrease of dielectric permittivity in the SmC^* phase can be observed as the temperature decrease; there is no clear explanation for this at the moment.

3.3. Spontaneous polarization (\mathbf{P}_s)

The magnitudes of spontaneous polarization \mathbf{P}_s as a function of temperature for the compounds $\text{I}(p,q,m,n; p=1,2, q=1,2, m=0,1, n=1,2)$ were determined in LC cells made of ITO-coated glass whose surface had been treated with a parallel alignment of polyimide. The \mathbf{P}_s values were observed after slow cooling to the SmC^* temperature range, with results illustrated in figure 2. The \mathbf{P}_s values are temperature-dependent and exhibit a maximum at the lower temperature range of the SmC^* phase. Maximum \mathbf{P}_s values were in the range $55\text{--}78 \text{ nC cm}^{-2}$.

4. Conclusion

A homologous series of chiral swallow-tailed materials, $\text{I}(p,q,m,n)$, derived from (L)-lactic acid was synthesized for investigating structure mesophase relationships. The results demonstrated that, variation of the core structure and length of methylene group m have a remarkable effect on the nature of mesophase formation; but change in length of the swallow-tail terminal group has little effect. However, the correlation between molecular structure mesophase formation is not yet clearly rationalized in this series of chiral materials.

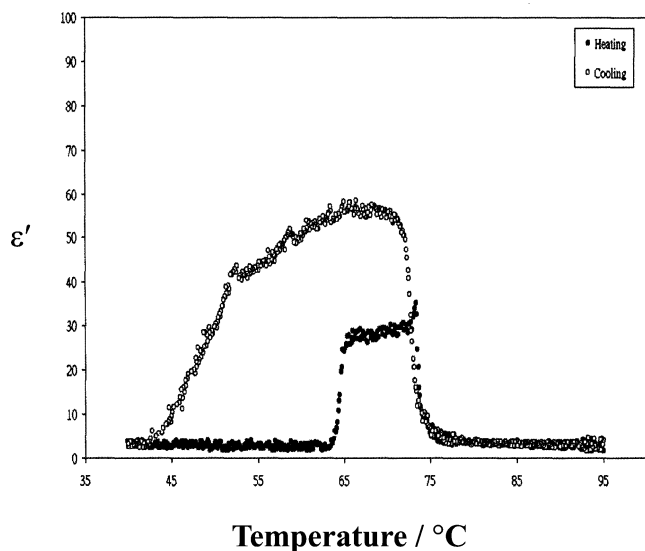


Figure 1. Temperature dependence of the real part of the dielectric constant for compound $\text{I}(2,1,1,1)$ at 100 Hz.

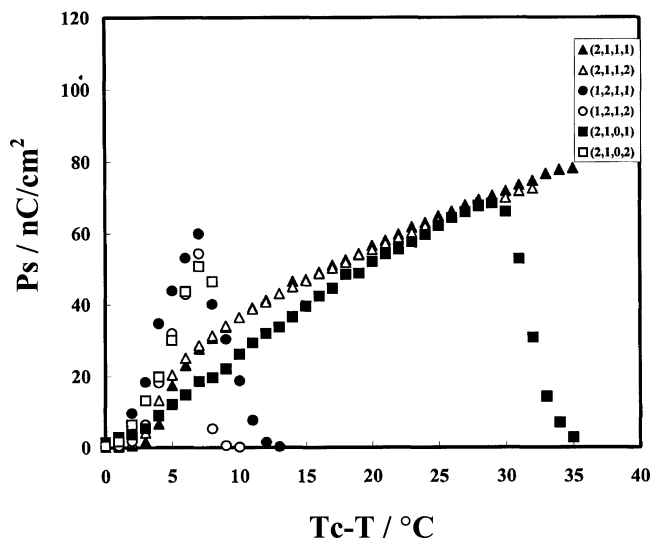


Figure 2. Spontaneous polarization plotted as a function of temperature for compounds I(p,q,m,n ; $p=1,2$, $q=1,2$, $m=0,1$, $n=1,2$). The T_c is the temperature of SmA*–SmC* transition.

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