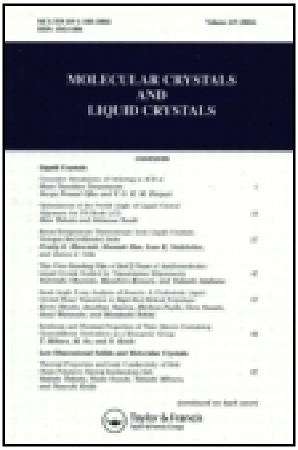

Molecular Crystals and Liquid Crystals

Molecular Design Controlling Smectic Stability and Clinicity

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Molecular Design Controlling Smectic Stability and Clinicity

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Both peripheral ends of some straight-shaped mesogenic compounds, possessing a biphenyl or azobenzene as a central rigid core, have been systematically modified, and the effect on the liquid-crystalline properties investigated. A fluorinated moiety introduced into the peripheral alkyl chains stabilized the smectic phase, whereas that into the terminally positioned phenyl rings resulted in the appearance of the nematic phase. Introduction of phenyl rings into the middle of the flexible chains produced a well-defined smectic layered structure. Further introduction of another phenyl ring at each terminal end was found to show a significant effect on the determination of the clinicity.

Keywords: anticlinic; fluorine; liquid crystal; peripheral end; phenyl, Smectic

1. INTRODUCTION

The interlayer interactions play an important role in determining a style of molecular assembly in the smectic liquid crystal phases. For example, in order to form a helical macrostructure in the tilted chiral smectic phases [1], the twist structure should be propagated from one layer to another by means of the interlayer permeation of the tails of

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mesogenic molecules [2]. Another important and interesting example can be seen when the clinicity in the smectic phase, i.e., *synclinic* or *anticlinic*, is determined. The essential difference between the synclinic and anticlinic orderings is the tilting direction between adjacent smectic layers, and therefore, the interlayer interaction should have a dominant role in determining the clinicity. The anticlinic ordering has first been observed in the antiferroelectric smectic phase, and lots of models have so far been proposed for the emergence of the anticlinic structure, in which a number of different steric and electricinteractions have been considered [3]. From the molecular-designing point of view, the modification of the terminal ends of the molecular structure is important, because the peripheral parts exist near to the interfaces between the smectic layers so that they have a significant effect on the interlayer interaction. In this study, both peripheral ends of some straight-shaped mesogenic compounds, possessing a biphenyl or azobenzene moiety as a central rigid core, have been systematically modified, and the effects of replacing terminal alkyl tails by phenyl rings, introducing fluorinated moieties, and substituting a *para*-position of the terminal phenyl ring, on the liquid-crystalline properties investigated (Fig. 1).

2. EXPERIMENTAL

Final compounds were prepared by the esterification according to the reported procedure [4]. The structural analyses and the physical property measurements were performed as reported earlier [4]. The structures of the final compounds were elucidated by elemental analyses, IR, ^{1}H NMR, and FD/MS spectrometric methods. An example of the preparation and characterization of the compound is shown below.

Preparation of 4,4′-bis-(7-phenoxycarbonylheptyloxy)biphenyl (1c)

4,4′-bis-(7-carboxyheptyloxy)biphenyl (0.47 g, 1.0 mmol), phenol (0.19 g, 2.0 mmol), DMAP (0.02 g, 0.2 mmol) were added in dry dichloromethane (15 mL). DCC (0.62 g, 3.0 mmol) was then added and the resulting mixture was stirred at room temperature overnight. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography using a dichrolomethane/hexane (7:2) mixture as the eluent, and recrystallized from an ethanol

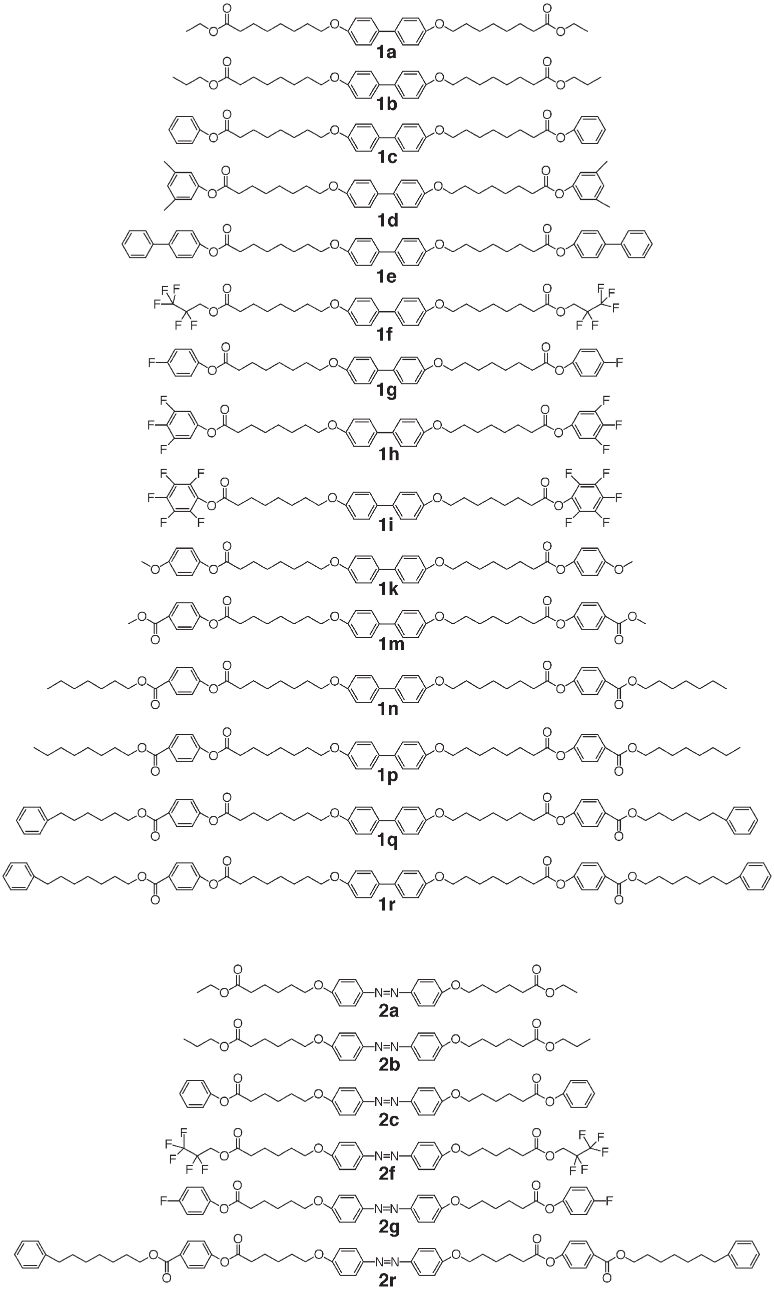

FIGURE 1 Structures of the terminally modified biphenyl and azobenzene compounds.

(17 mL), giving a colourless solid. Yield = 0.88 g, (51%). Elemental analysis; found: C% 77.0, H% 7.4, calculated for $C_{40}H_{46}O_6$ C% 77.2, H% 7.4. δH (400 MHz, CDCl3, TMS); 7.45 (m, 4H, Ar–**H**), 7.39 (m, 4H, Ar–**H**), 7.23 (m, 2H, Ar–**H**), 7.09 (m, 4H, Ar–**H**), 6.94 (m, 4H, Ar–**H**), 3.99 (t, 4H, $-Ar-O-C\mathbf{H_2}-CH_2-$, $^3J = 6.6$ Hz), 2.57 (t, 4H, $-CH_2-C\mathbf{H_2}-COO-$, $^3J = 7.6$ Hz), 1.80–1.45 (m, 20H, aliphatic–H). ν/cm^{-1} (KBr); 2934, 2855 (C–H str.), 1757 (C=O str.), 1607 (C–C str.), 839 (1,4-disub. C–H o.o.p.d). m/z; 622 (M^+).

3. RESULTS AND DISCUSSION

3.1. Phase Transition Behaviour

Phase transition temperatures (°C), phase sequences, and transition enthalpies (kJ mol^{-1} in square brackets) for Series **1** and **2** were found to be as follows (brackets indicate the monotropic phase transition).

1a: **Cr** 92.6 [62.29] **Iso**
1b: **Cr** 84.1 [66.60] **Iso**
1c: **Cr** 104.2 [76.62] (**S_Y** 85.9 [4.06] **S_A** 90.9 [10.87]) **Iso**
1d: **Cr** 91.2[55.63] **Iso**
1e: **Cr** 167.7 [82.01] **Iso**
1f: **Cr** 85.6 [32.74] **S_C** 91.2 [9.36] **Iso**
1g: **Cr** 116.4 [72.17] (**N** 109.8 [6.30]) **Iso**
1h: **Cr** 94.5 [63.96] (**N** 83.4 [3.36]) **Iso**
1i: **Cr** 83.6 [60.17] (**N** 75.0 [3.25]) **Iso**
1k: **Cr** 134.8 [79.34] (**S_Y** 109.9 [5.79] **S_A** 122.4 [1.37] **N** 129.2 [11.17]) **Iso**
1m: **Cr** 133.4 [69.69] **N** 137.2 [11.54] **Iso**
1n: **Cr** 106.1 [53.25] (**S_X** 103.2 [3.94]) **S_C** 112.5 [23.71] **Iso**
1p: **Cr** 104.6 [54.62] (**S_X** 101.4 [3.81]) **S_C** 112.3 [24.36] **Iso**
1q: **Cr** 105.7 [88.56] (**S_X** 84.0 [3.45]) **S_C** 100.3 [22.56] **Iso**
1r: **Cr** 90.0 [85.75] (**$S_C$anti** 89.9 [21.18]) **Iso**

2a: **Cr** 95.1 [61.74] **Iso**
2b: **Cr** 104.7 [81.26] **Iso**
2c: **Cr** 137.9 [66.94] (**S_A** 111.2 [8.00]) **Iso**
2f: **Cr** 95.5 [60.26] **S_C** 111.0 [10.33] **Iso**
2g: **Cr** 138.7 [73.21] (**S_A** 128.7 [0.83] **N** 141.2 [4.98]) **Iso**
2r: **Cr** 97.3 [57.48] **$S_C$anti** 115.8 [20.02] **Iso**

In the following sections, the effects of the modification of the peripheral ends of the molecular structure are presented and discussed.

3.2. Introduction of Phenyl Rings at Both Ends of the Molecular Structure

Compounds **1a**, **1b**, **2a**, and **2b** that possess ethyl or propyl terminal chains, did not show the liquid crystal phases, however, a smectic C (S_C) phase was induced by mixing **1b** and **2b**. Replacing each terminal ethyl or propyl group by a phenyl ring showed a significant effect on the phase transition behaviour. Both of **1c** and **2c**, which possess terminal phenyl rings, exhibited the smectic (S_A) phase instead of the S_C phase, suggesting that the permeation of the alkyl tails between the smectic layers contributes to produce the tilted molecular organization. The introduction of the phenyl ring at the peripheral ends surely stabilizes the liquid-crystalline nature. The clearing temperature (T_C) of the mixture between **1b** and **2b**, which possess the propyl terminal chains, was ca. 68°C, however, when propyl was replaced by phenyl, T_C increased to 90.9°C for **1c** and to 111.2°C for **2c**. Further increase in the bulkiness of the terminal moieties showed a significant effect on the liquid crystal stability, i.e., introduction of dimethyl-substituted phenyl (**1d**) or biphenyl (**1e**), instead of phenyl, destroyed the mesogenic properties of the compounds.

Compound **2c** exhibited typical focal conic fan-shaped and homeotropic textures in the S_A phase. The x-ray diffraction pattern of **2c** showed one sharp peak in the small angle region corresponding to the smectic layer spacing of 37.3 Å which is well agree to the molecular length of 37.7 Å calculated by the MM2 method. The corresponding biphenyl compound, **1c**, also showed the homeotropic texture, and its homogeneously aligned texture obtained in a polyimide-coated and buffed cell is quite similar to that for the common S_A phase. However, at the transition from the isotropic liquid to the smectic phase, a typical "batonnet" texture was not observed for the sample placed between two untreated clean glass plates. Instead of the appearance of the batonnet texture, a round-shaped or tube-shaped texture appeared from the isotropic liquid phase on cooling (Fig. 2(a)), where a dark region indicates an isotropic liquid phase. The round-shaped domains often produced a characteristic deformed shape as shown in figure 2 (b). The appearance of the tube-shaped and round-shaped domains at the transition is not typical for the usual S_A phase, however, similar textures have been reported to appear at the isotropic liquid-S_A phase transition of the other liquid crystal compounds [4,5] or of binary mixtures between octyloxycyanobiphenyl and dodecyl alcohol [6,7]. The X-ray scattering intensity of the peak corresponding to the S_A layer spacing of **1c** was found to be relatively low as shown in Figure 3, indicating that the smectic layer is weakly formed. Another

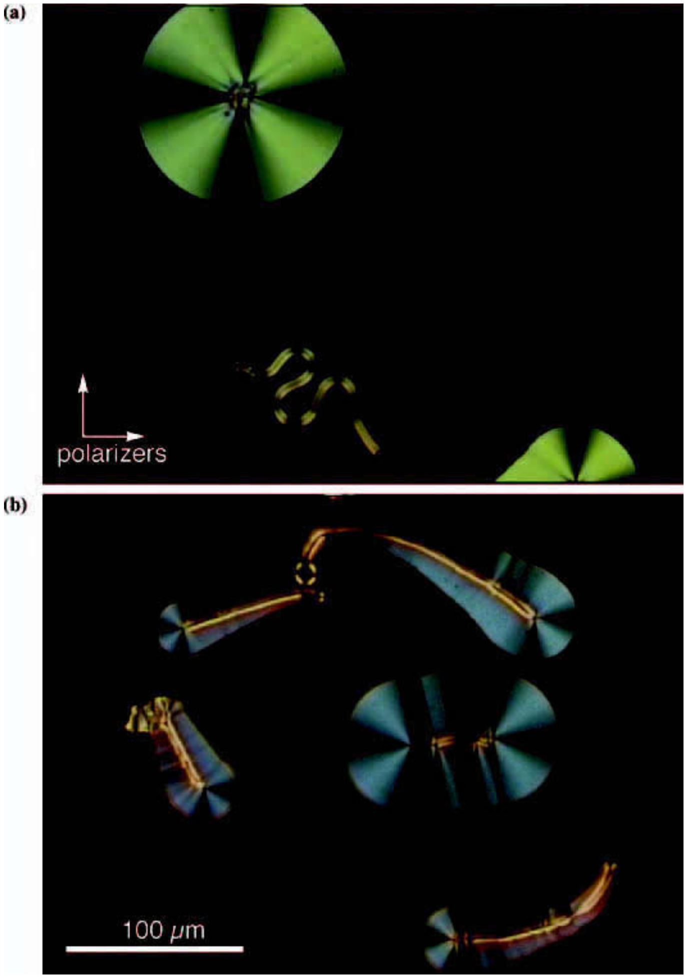

FIGURE 2 Optical texture observed at the transition from the isotropic liquid to smectic phase (90.8°C) of **1c**. A dark region shows isotropic liquid phase, where the liquid crystal phase appeared as round- or tube-shaped domains.

possibility for the emergence of such a weak peak is that this peak is not the first order peak but the second one, however, detailed small angle measurements showed no sign of the appearance of another peak at the angle corresponding to the twice longer spacing. The layer spacing derived from the position of the small angle scattering peak is 39.5 Å in the S_A phase of **1c**, which well corresponds to the expected

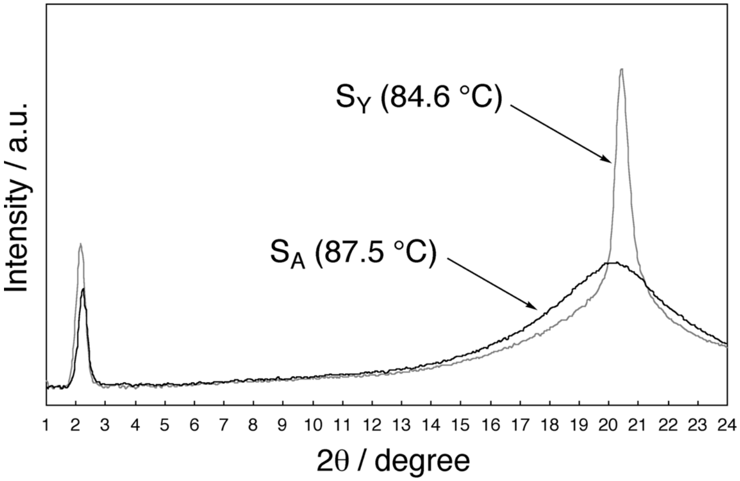

FIGURE 3 Wide angle X-ray diffraction patterns obtained in the S_A and S_Y phases of **1c**.

molecular length of 40.7 Å calculated by the MM2 method. These results strongly suggest that the S_A phase of **1c** is the monolayered S_A phase in nature, however, possesses a relatively weak layered structure. At the transition from the S_A to the lower-temperature unidentified smectic Y (S_Y) phase, many stripes appeared and the resulting S_Y phase also showed the homeotropic textures, which suggests that the S_Y phase is in fact the smectic B (S_B) phase. The X-ray profile obtained in the S_Y phase (Fig. 3) shows clear peaks both in the small and wide angle regions which indicates that the S_Y phase is a higher ordered smectic phase. The layer spacing of the S_Y phase was found to be 41.0 Å by X-ray diffraction measurements, suggesting the S_Y phase is a non-tilted phase. These results are consistent with the phase assignment of the S_B phase.

3.3. Effect of Introducing Fluorinated Moieties

Introduction of the highly fluorinated moieties, such as perfluoro and semiperfluoro alkyl chains, into the liquid-crystalline molecular structure has widely been investigated [8,9], and unconventional liquid crystalline phases have sometimes been found [9]. Both of the peripheral propyl chains of **1b** and **2b** were replaced by the 2,2,3,3,3-pentafluoro propyl chains, producing compounds **1f** and **2f**, respectively. Fluorinated compounds **1f** and **2f** showed the S_C phase, which is the same phase as obtained for the mixtures between **1b** and **2b**, however, the stability of the liquid crystal phase was significantly increased (Fig. 4). Similarly, fluoro modification was performed on the terminal phenyl rings of compounds **1c** and **2c**. Totally different effect was this time observed. Compound **1c** showed the S_A phase, however, the fluorinated analogues, **1g**, **1h** and **1i**, showed the nematic (N) phase. Usually the introduction of fluorinated moieties are considered to stabilize the smectic layered organization, because of the micro-segregation produced by the strong incompatibility between hydrocarbon and highly fluorinated moieties [9]. Thus the appearance of the N phase observed in this study is a unique effect of introducing fluoro moieties. The different effects of fluoro-substitution between alkyl and phenyl suggest that the permeation of the semiperfluoroalkyl tails between the smectic layers plays an important role on the micro-segregation. In addition, since Compound **1i** possesses highly fluorinated phenyl rings, the arene–perfluoroarene interaction [10,11] may have some effects on the molecular ordering in the liquid crystal phases.

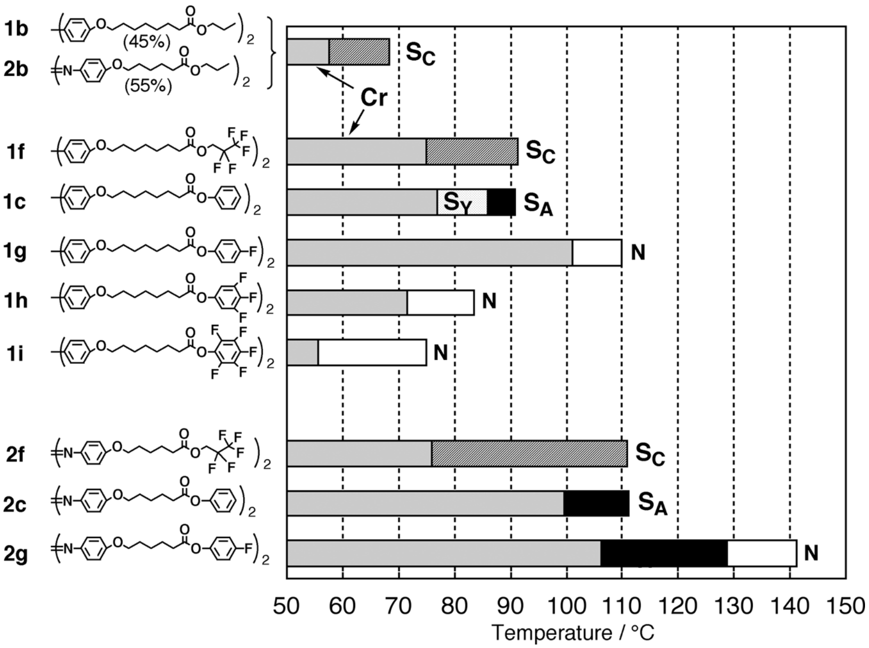

FIGURE 4 Transition temperatures of the fluorinated compounds.

3.4. Introduction of Further Peripheral Tails – *Pseudo* Core Structure

Next, the *para*-position of the terminally positioned phenyl ring was systematically modified. The non-*para*-substituted compound (**1c**) showed the S_A phase, however, introduction of rather a short tail resulted in the appearance of the N phase (**1g**, **1k**, and **1m**) as shown in Figure 5. With increasing the length of the peripheral alkyl chain of the *para*-substituent from methyl (**1m**) to heptyl (**1n**), the N phase disappeared and the S_C phase was again produced. This behaviour i.e., the smectic phase is preferred with ascending the peripheral alkyl chain, is commonly observed effect of the alkyl chains attached to the central rigid core, even though the peripheral alkyl chain of **1n** is not attached directly to the central biphenyl core. The obtained phase sequences and the molecular structures are compared in Figure 6. The original compounds possessing flexible alkyl chains showed the S_C phase (the mixture between **1b** and **2b**), where the biphenyl or azobenzene is considered to be a core part as usual. However, the introduction of *para*-substituted phenyl rings produced a different situation, where the region including two *para*-substituted phenyl rings, as indicated in Figure 6, behaves as a *pseudo*-core part, resulting in the appearance of the N and S_C phases for **1m** and **1n**, respectively. One of the important effects produced by the

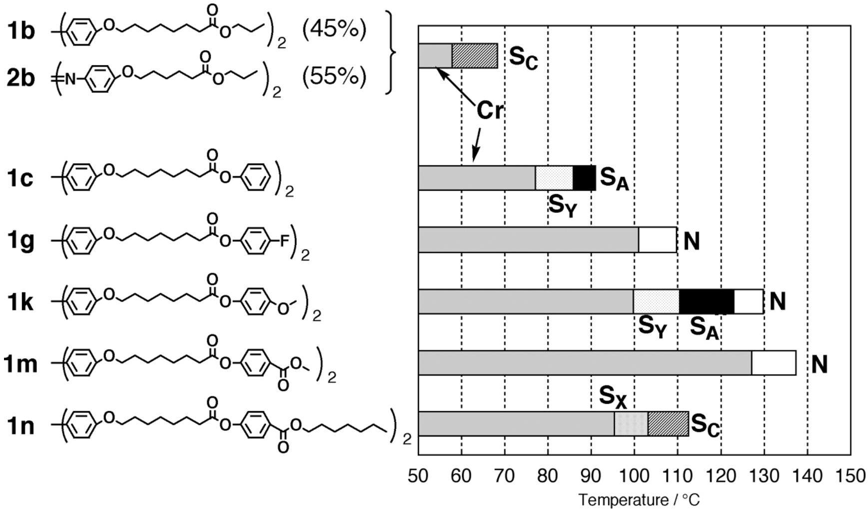

FIGURE 5 Transition temperatures of the *para*-substituted compounds.

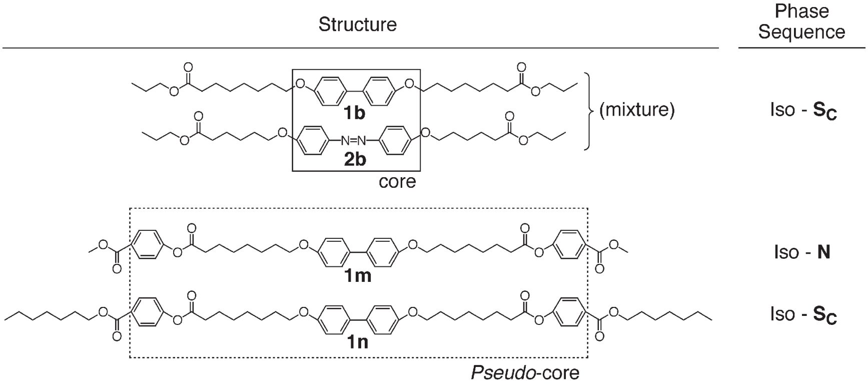

FIGURE 6 Molecular structures and phase sequence showing a *pseudo*-core model.

pseudo-core structure may be the emergence of the clear periodicity of the smectic layers. Figure 7 shows the wide angle X-ray scattering patterns in the S_C and smectic X (S_X) phases of **1n**. Clear second-order diffraction peaks were obtained corresponding to the smectic layer spacing, indicating the formation of the well-defined layered structure.

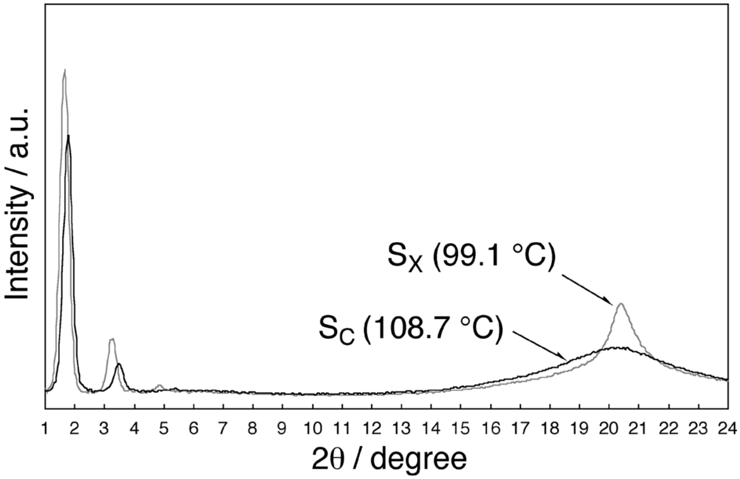

FIGURE 7 Wide angle X-ray diffraction patterns obtained in the S_A and S_Y phases of **1n**.

3.5. Steric Effect of the Terminal Structure on the Clinicity

Further peripheral modification was made by introducing another phenyl ring into the molecular structure of **1n**, which produces a compound **1r**. Related compounds having a different parity of the peripheral alkyl chains were also prepared (**1p** and **1q**) and the transition temperatures compared (Fig. 8). Compounds **1n**, **1p**, and **1q** showed the usual "synclinic" S_C phase, in which typical broken-fanand *Schlieren* textures with only four brush singularities were observed. However, Compound **1r**, which is a homologue of **1q** possessing one more methylene unit ($-CH_2-$) in each peripheral alkyl chain, showed completely different textures. This homologue, **1r**, showed a fan texture which is quite similar to that obtained for the S_A phase where extinction direction seems to be normal or parallel to the polarizers, but also showed a *Schlieren* texture in a pseudo-homeotropically aligned region. Similar textures were obtained for Compound **2r**, which is an azobenzene analogue of **1r**. Figure 9 shows the *Schlieren* texture observed for Compound **2r**, which clearly showed both *two* and four brush singularities. The *two* brush singularities are not allowed to be formed in the synclinic S_C phase [12], thus, these results strongly indicate that **1r**, and **2r** exhibit an "anticlinic" version of the S_C ($S_C$anti) phase [4]. Figure 10 shows XRD scattering patterns obtained for **1q** and **1r**. The emergence of the second order peak in the small angle region indicates that the well-defined layered structure is also formed in the smectic phases of **1q** and **1r**. The $S_C$anti phases of Compound **1r** just showed a diffuse scattering in the wide angle

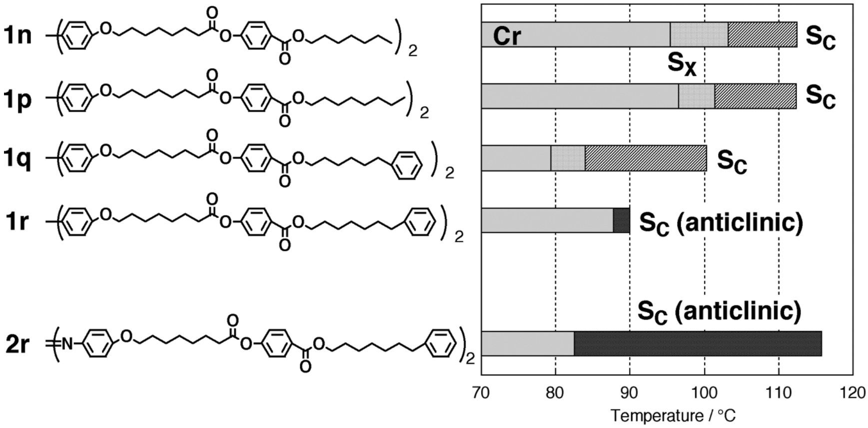

FIGURE 8 Transition temperatures of the compounds possessing different terminal structures.

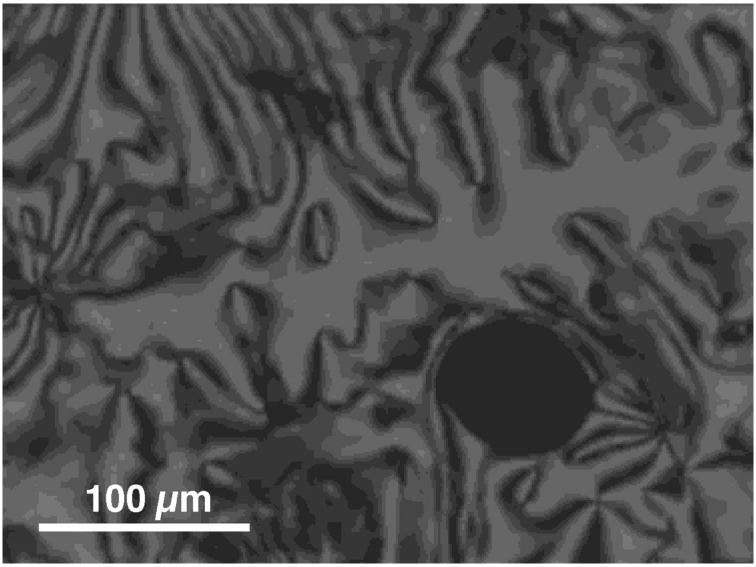

FIGURE 9 A *Schlieren* texture observed for the anticlinic S_C phase of **2r**, showing both *two* and four brush singularities (115.0°C).

region, indicating the fluid-like order within the layers, which is consistent with the phase assignment that the anticlinic phase of **1r** is a sub-phase of the S_C phase.

The anticlinic phase was obtained only for Compound **1r** among the analogous compounds, giving us an important clue on the appearance of the anticlinic structure. The effects on the stabilization of the anticlinic structure obtained in this study can be discussed as follows.

a. The over-all molecular structures are not bent but are rod-shaped. Thus, the bent configuration produced within each molecule, i.e., "intra"-molecular bent structure, is not the origin of the over-all anticlinic molecular assembly but the anticlinic ordering is stabilized by the "inter"-molecular interaction.
b. The "pseudo-core" structure produced the well-defined smectic layers, which supports the anticlinic zig-zag molecular assemblies.
c. Compounds **1r** and **2r** do not possess a strong polar group, such as ester and ether, at the peripheral position of the molecular structure, but just have phenyl rings and alkylene spacers, which suggests that the anticlinic ordering is not stabilized by the electric interaction produced by the molecular dipoles near to the smectic layer interfaces.

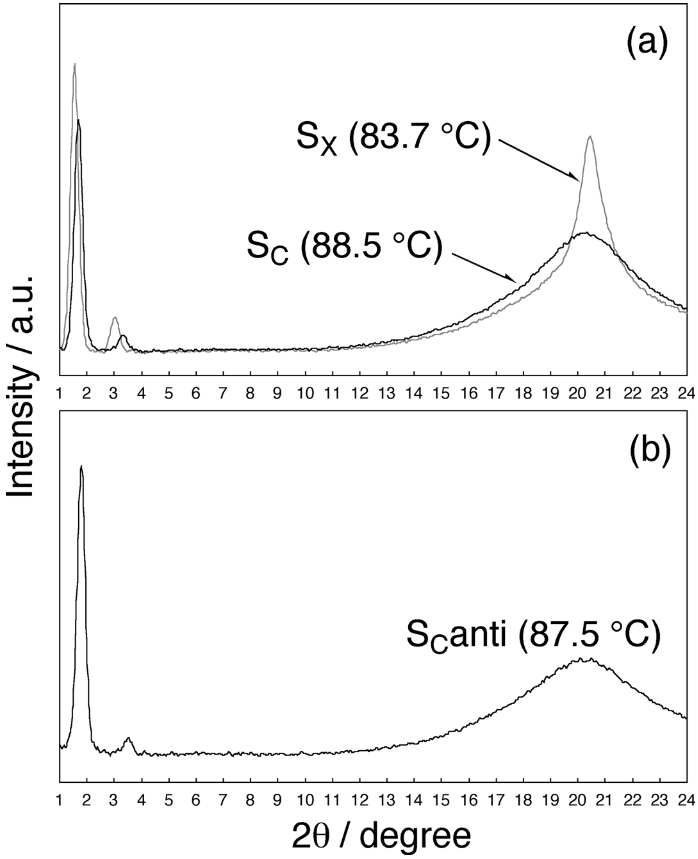

FIGURE 10 Wide angle X-ray diffraction patterns of two related compounds: (a) in the S_C and S_X phases of **1q**, and (b) in the anticlinic S_C phase of **1r**.

d. Compounds **1r** and **2r** do not possess branched alkyl chains, so that the bent conformation produced at the branching carbon atom [13,14] is not the origin of the anticlinic structure obtained in the present study.
e. Compound **1q** showed the synclinic structure, whereas **1r** exhibited the anticlinic phase. The difference in the molecular structures between these two homologues is just one methylene unit ($-CH_2-$) at each peripheral alkyl chain, however, the direction of the terminally attached phenyl rings with respect to the molecular long axis was found to be quite different between these homologues. The terminal phenyl rings of **1q** align to the same direction as the molecular axis so that the steric interaction at the interfaces of the

layer promotes the synclinic ordering. In the case of **1r**, however, the terminal phenyl rings align much more toward the off-axis direction, which may be favourable for the anticlinic ordering.

f. The effect mentioned in (e) is one of the "odd-even" effects of the alkyl chain. This effect, however, was not observed between **1n** and **1p**. The parity of the peripheral alkyl chains of compounds **1n** and **1p** are opposite, but both of the compounds exhibited the synclinic phase. The characteristic structural feature of the compounds **1q** and **1r** is that these compounds possess bulky terminal phenyl rings, whereas the compounds **1n** and **1p** have less bulky methyl groups at the molecular ends. The odd-even effect may be emphasized by the terminally attached bulky phenyl groups.

Finally, we would like to mention about the delicate balance of the synclinic/anticlinic structures observed in **1r**. Figure 11 shows the texture obtained at the transition from the isotropic liquid to the $S_C$anti phase, giving us important information about the molecular ordering. The texture of the yellow-coloured region is similar to that of the S_A phase because of the appearance of the anticlinic ordering. However, in some regions (blue in colour), the extinction direction is

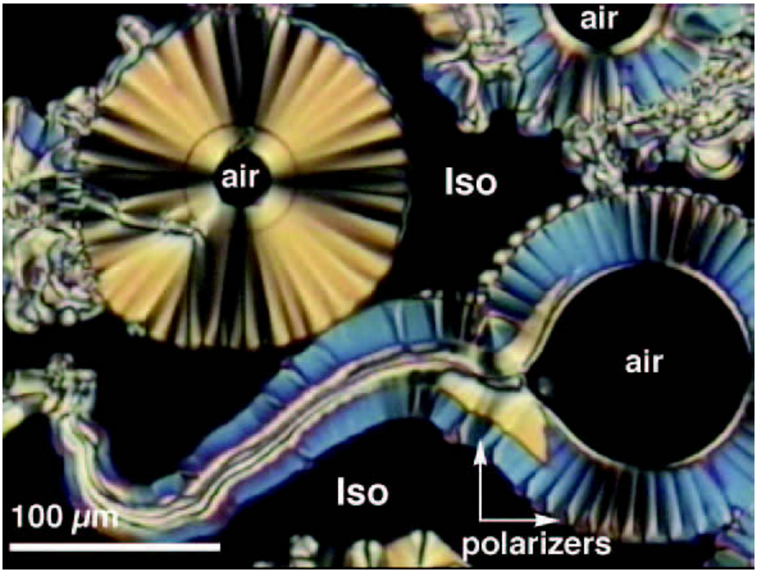

FIGURE 11 Photomicrograph showing the Iso-anticlinic S_C transition of **1r**. A dark region exhibits the isotropic liquid phase.

not exactly along to the direction of the polarizers, indicating the emergence of a slightly tilted molecular ordering. The molecular tilt in this domain is estimated to be ca. 10 degrees which is quite small for the materials showing direct isotropic-tilted smectic phase transition. Thus, one possible explanation for the molecular ordering in the blue-coloured domain is that some synclinic structures appeared and co-existed in the intrinsic anticlinic structure, which makes a slight over-all tilt. This is a kind of mixed synclinic/anticlinic structure, which can be produced if the anticlinic interaction is not too strong, and is considered to possess similar molecular assemblies to the ferrielectric phase.

4. CONCLUSIONS

The modification of both peripheral ends of the molecular structure was found to be a powerful tool for controlling the smectic stability and clinicity. The fluorination of the peripheral alkyl chains stabilized the smectic phase, whereas that of the terminal phenyl ring did not. Introduction of the *para*-substituted phenyl ring at the end of each alkyl chain formed a "*pseudo*-core" structure. Increase in the length of the alkyl chain attached to the *pseudo*-core produced a well-defined smectic layer structure. Another phenyl ring was again introduced at the molecular ends and it was found that the anticlinic ordering was stabilized when the direction of the terminally attached phenyl rings is different from the molecular long axis. The steric interlayer interaction was proposed to have more important effect than the dipolar interaction on the appearance of the anticlinic ordering obtained in this study.

REFERENCES

[1] Goodby, J. W. (1997). *Mol. Cryst. Liq. Cryst. 292*, 245.

[2] Yoshizawa, A. (1999). *Recent Res. Devel. Applied. Phys.*, *2*, 453, and references therein.

[3] For reviews, (a) Osipov, M. A. & Fukuda, A. (2000). *Phys Rev. E*, *62*, 3724.
  (b) Matsumoto, T., Fukuda, A., Johno, M., Motoyama, Y., Yui, T., Seomun, S.-S., & Yamashita, M. (1999). *J. Mater. Chem.*, *9*, 2051.
  (c) Fukuda, A., Takanishi, Y., Isozaki, T., Ishikawa K., & Takezoe, H. (1994). *J. Mater. Chem.*, *4*, 997.
  (d) Nishiyama, I. (1994). *Adv. Mater.*, *6*, 966.

[4] Nishiyama, I., Yamamoto, J., Goodby, J. W., & Yokoyama, H. (2003). *J. Mater. Chem.*, *13*, 1868.

[5] Faye, V., Nguyen, H. T., Laux, V., & Iseart, N. (1996). *Ferroelectrics*, *179*, 9.

[6] Paratibha, R. & Madhusudana, N. V. (1992). *J. Phys. (France) II*, *2*, 383.

[7] Naito, H., Okuda, M., & Zhong-can, U.-Y. (1997). *Phys Rev. E*, *55*, 1655.

[8] Guittard, F., Taffin de Givenchy, E., Geribaldi, S., & Cambon, A. (1999). *J. Fluorine Chem.*, *100*, 85.

[9] (a) Tschierske, C. (2002). *J. Mater. Chem.*, *11*, 2647.
(b) Tschierske, C. (2002). *Current Opinion in Colloid and Interface Science*, *7*, 298.

[10] Dai, C., Nguyen, P., Marder, T. B., Scott, A. J., Clegg, W. & Viney, C. (1999). *Chem. Comm.*, 2493.

[11] Weck, M., Dunn, A. R., Matsumoto, K., Coates, G. W., Lobkovsky, E. B., & Grubbs, R. H. (1999). *Angew. Chem. Int. Ed.*, *38*, 2741.

[12] (a) Takanishi, Y., Takezoe, H., Fukuda, A., & Watanabe, J. (1992). *Phys Rev. B*, *45*, 7684.
(b) Takanishi, Y., Takezoe, H., Fukuda, A., Komura, H., & Watanabe, J. (1992). *J. Mater. Chem.*, *2*, 71.

[13] Nishiyama, I. & Goodby, J. W. (1992). *J. Mater. Chem.*, *2*, 1015.

[14] Hori, K. & Kawahara, S. (1996). *Liq. Cryst.*, *20*, 311.