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Novel Chiral Effects on the Molecular Organization in the Liquid-Crystalline Phases

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Introduction of chirality into smectic liquid-crystalline systems produces a variety of helical,[1] polar,[2] and/or frustrated[3] macrostructures. The chirality-induced helical structures can be seen in the tilted smectic phases such as a smectic C phase and also in a family of Twist Grain Boundary (TGB)[4] phases. More complex helical structures can be generated by the strong chirality. One is the smectic blue phase where double helixes form due to a strong desire for the molecules to form helical structures.[5] The other example is the smectic Q (SmQ) phase,[6] which is a kind of TGB variant of the antiferroelectric phase; however, due to the strong chiral effect, the distance between grain boundaries of the TGB structure becomes so short that the defects in the grain boundaries form a 3D crystalline network, that is, so-called "crystal of defects".[7]

Here, we report novel chiral effects that produce new liquid crystal phases. One of the antiferroelectric phases of newly prepared chiral twin homologues, bis{4′-(1-methylheptyloxycarbonyl)biphenyl-4-yl}alkanedioates (Chart 1), was found to change into two anomalous phases, neither smectic blue nor common SmQ phase, with an increase in the optical purity. The chiral twins investigated in this study were obtained by the esterification between optically active (*S*)- or (*R*)-1-methylheptyl 4-hydroxybiphenyl-4′-carboxylate[8] and the respective alkanedioic acids by the DCC/DMAP method.[9] The purification was carried out using column chromatography over silica gel using dichloromethane as the eluent followed by the recrystallization from ethanol. The structures were elucidated by elemental analysis, ^{1}H NMR, IR, and mass spectrometry.[10] The phase assignments and corresponding transition temperatures were determined by thermal optical microscopy, differential scanning calorimetry (DSC), and X-ray scattering experiments, as reported earlier.[11] Viscoelastic properties were evaluated by the measurement of the longitudinal mechanical transfer function using piezoelectric ceramics, of which the details have been reported elsewhere.[12]

Table 1. Phase Transition Behavior of SS2-5 and RR4[a]

compound	Cr		M_2		M_1		Iso
SS2	•	82.6 [21.48]	•		–	116.9 [10.00]	•
SS3	•		–		–	97.8 [33.83]	•
SS4	•	79.6 [16.50]	•	103.3 [1.08]	•	104.9 [8.63]	•
RR4	•	80.2 [18.00]	•	103.2 [1.20]	•	104.7 [8.71]	•
SS5	•		–		–	85.6 [29.97]	•

[a] Temperatures (°C) and transition enthalpies (in square brackets/kJ mol^{-1}) were determined by the combination of optical microscopy and DSC at 5 or 1 °C min^{-1}. Cr, crystal phase; M_2, parquet-like liquid crystal phase; M_1, optically isotropic liquid crystal phase; Iso, isotropic liquid phase.

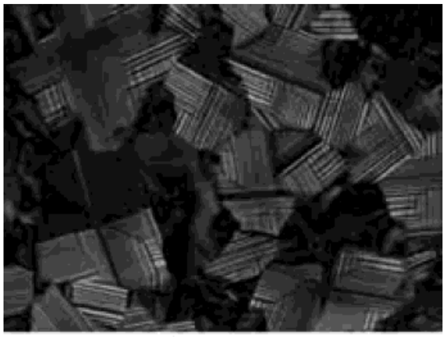

Figure 1. "Parquet-like" texture of the M_2 phase of **SS4** (magnification 100×).

Table 1 shows phase transition behavior of the homologues. Even-membered homologues (**SS2**, **SS4**, and **RR4**) showed a mesophase (designated as M_2 phase) exhibiting a characteristic texture with many stripes (Figure 1), which is similar to the so-called "parquet-like" texture[13] but is different from a common "mosaic" texture observed in the SmQ phase.[6] This is the first example of a chiral compound showing this unique parquet-like texture. Furthermore, **SS4** and **RR4** showed another mesophase (M_1 phase), which appeared between the isotropic liquid and the M_2 phases. The M_1 phase is optically isotropic regardless of the alignment conditions. DSC thermograms showed

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(10) Preparation procedures for **SS2**, **SS3**, **SS4**, **RR4**, and **SS5** with analytical data (^{1}H NMR, IR, mass spectrometry, and elemental analysis), a DSC curve for **SS4**, the electric field dependence of the optical tilt angle in the antiferroelectric phase, a *Schlieren* texture of the anticlinic phase of the 1:1 mixture between **SS4** and **RR4**, and an X-ray diffraction profile for **SS4** are available in the Supporting Information.

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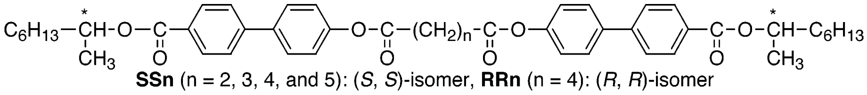
Chart 1. Structure of the Chiral Twin Investigated



SSn (n = 2, 3, 4, and 5): (*S*, *S*)-isomer, **RRn** (n = 4): (*R*, *R*)-isomer

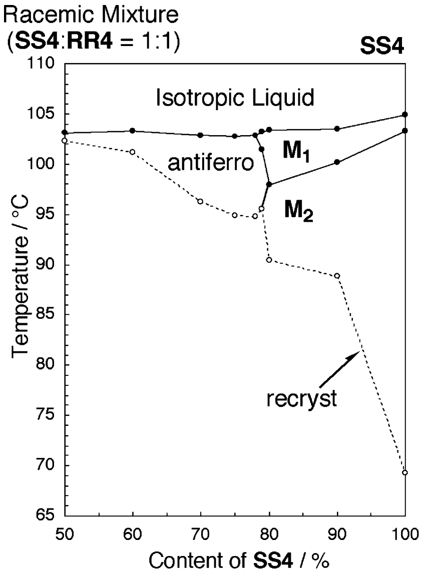


Figure 2. Phase diagram between **SS4** and the racemic mixture. Recrystallization temperatures slightly changed depending on the sample conditions; however, a tendency that the lower the optical purity, the higher the recrystallization temperature was well reproducible.

two peaks corresponding to the isotropic liquid–M_1 and M_1–M_2 transitions, respectively; therefore, the M_1 and M_2 phases do not just represent kinds of transient or metastable states of molecular alignments or orderings but are thermodynamically real phases.[10]

Figure 2 shows a phase diagram between optically active **SS4** and a racemic mixture (1:1 mixture of **SS4** and **RR4**) so that the effect of the chirality on the emergence of the M_1 and M_2 phases can be presented. With a reduction in the optical purity, these two phases changed into the antiferroelectric SmC* phase. The antiferroelectric character was observed in an optical tilt angle measurement as a function of the applied dc electric field, which shows typical threshold behavior.[10] The anticlinic character of the racemic mixture was confirmed by the appearance of both *two* and four brush singularities in a *Schlieren* texture[10] because *two* brush singularities are not allowed to be formed in the synclinic phase but can be generated in the anticlinic ordering.[14]

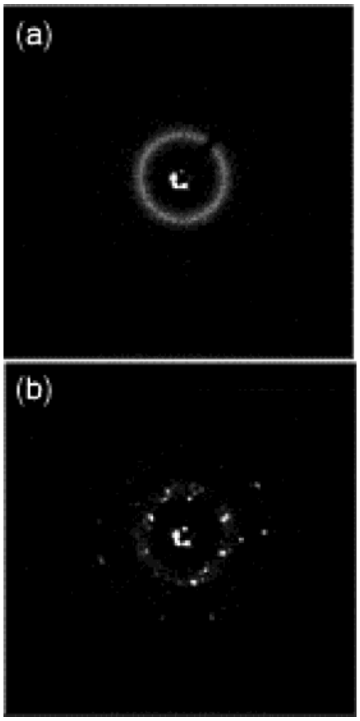


Figure 3. 2D X-ray scattering patterns in the small-angle region of **SS4** in the M_1 phase (104.4 °C) (a) and in the M_2 phase (99.1 °C) (b).

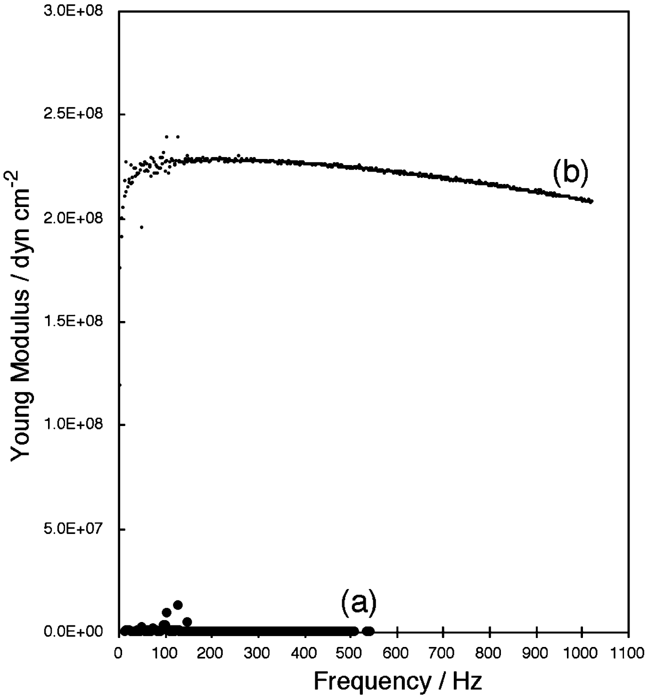


Figure 4. Frequency dependence of Young Modulus in the optically isotropic M_1 phase (a) and the parquet-like M_2 phase (b) of **SS4**.

Wide-angle X-ray diffraction patterns indicate that both the M_1 and M_2 phases only showed a broad scattering in the wide-angle region, which means these phases possess a liquid-like short-range order. Figure 3 shows the 2D scattering patterns in the small-angle region. A ring-shaped scattering was observed in the M_1 phase, suggesting the formation of the layered structure with a spacing of 38.0 Å. However, when the sample was gradually cooled into the M_2 phase, the ring-shaped diffraction disappeared but lots of spots appeared instead, indicating that the sample was oriented to some extent in the M_2 phase and that the 3D order was generated. The preliminary analysis of the scattering profile showed that the M_2 phase possesses a tetragonal structure with lattice constants of $a = 81.5$ Å and $c = 134.5$ Å.[10]

Figure 4 shows frequency dependence of Young Modulus in the M_1 and M_2 phases of **SS4**. A finite elasticity was clearly observed in the M_2 phase, which is consistent with the proposed 3D structure. However, there is no elasticity in the M_1 phase, indicating that this phase does not possess a macroscopic layered structure or a 3D superstructure responsible for the emergence of the elasticity. Therefore, the M_1 phase cannot be assigned as a variant of the smectic or cubic phase. A so-called "sponge" phase,[15] which possesses randomly interconnected layer planes, has been known to be optically isotropic and show no elasticity, but also reported to show the flow-induced birefringence.[16] Since the M_1 phase did not show such an induced birefringence under the shearing, it is not clear at present whether the M_1 phase belongs to the sponge phase.

In summary, two novel chiral effects were for the first time observed in the smectic liquid crystal phases: one is breaking the macroscopic layered structure of the antiferroelectric phase to produce the optically isotropic phase and the other stabilizing a three-dimensional "parquet-like" phase with a liquid-like short-range order. Further detailed studies on the structures of the M_1 and M_2 phases are now in progress.

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Supporting Information Available: Preparation procedures for **SS2**, **SS3**, **SS4**, **RR4**, and **SS5** with analytical data (^{1}H NMR, IR, mass spectrometry, and elemental analysis), a DSC curve for **SS4**, the electric field dependence of the optical tilt angle in the antiferroelectric phase, a *Schlieren* texture of the anticlinic phase of the 1:1 mixture between **SS4** and **RR4**, and X-ray diffraction profile for **SS4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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