Angewandte
Chemie

Polymerizable Bent-Core Mesogens: Switchable Precursors to Ordered, Polar Polymer Materials**

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Bent-core (that is, banana-shaped) liquid crystals (LCs) have recently emerged as one of the most significant discoveries in the area of ferroelectric LCs.[1–3] These polar, chevron-shaped molecules have the ability to form switchable ferro- and antiferroelectric liquid-crystalline phases, even though the molecules are achiral.[1–3] Prior to the discovery of these materials, ferroelectric and antiferroelectric liquid-crystalline phases had only been possible with chiral, rodlike mesogens that adopt tilted layered phases (that is, smectic C (SmC) phases).[4] There is currently a great deal of interest in bent-core mesogens because they exhibit complex phase behavior not seen in other liquid-crystalline molecular architectures. They also offer certain advantages over traditional rodlike chiral SmC mesogens as switching materials in ferroelectric LC displays[5] and as building blocks for ordered, noncentrosymmetric polar polymer materials (for example, for nonlinear optical (NLO), piezoelectric, and pyroelectric applications).[2,6–8] For example, bent-core LCs can be more readily designed, synthesized, and modified since enantiomerically pure or enriched starting materials are not required. Unfortunately, bent-core mesogens generally form liquid-crystalline phases at relatively high temperatures (greater than ca. 140 °C).[1,2] This not only limits their usefulness in device applications, but also makes detailed analysis of their mesophases more difficult. It has also not yet been possible to synthesize a polymerizable derivative of a bent-core mesogen that retains the desired liquid-crystalline properties. Polymerizable or cross-linkable bent-core LCs would afford the ability to stabilize/trap the switchable liquid-crystalline mesophases. This situation would not only aid in their structural characterization, but the resulting polar polymers could also be used for

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[**] Financial support for this work was provided by the National Science Foundation (DMR-0111193) and the NSF Ferroelectric Liquid Crystal Materials Research Center at the University of Colorado, Boulder (DMR-0213918). The authors also thank Dr. E. Körblova, Dr. R. Zhao, Mr. A. Klittnick, and Profs. D. M. Walba and N. A. Clark for their assistance in the analysis of the bent-core liquid-crystalline phases.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200250680

NLO and transducer applications if aligned.[2,9] Ikeda and coworkers recently made a diacrylate derivative of a bent-core mesogen for this purpose; however, this compound was found to be completely nonmesogenic, which suggests that there is a certain sensitivity or incompatibility of this bent-core platform to polymerizable groups in the tails.[9] Blending with a large fraction of a conventional bent-core mesogen was required to obtain a switchable liquid-crystalline mixture that could be gelled.

Herein, we report the first example of a family of intrinsically polymerizable and cross-linkable bent-core mesogens (**1**, see scheme 1). These bent-core LC monomers are based on the 1,3-phenylenebis[4-(4-alkoxyphenyliminomethyl)benzoate] structure,[1] but contain a pair of reactive 1,3-dienoxy tails.[10,11] These tails more closely resemble *n*-alkyl and *n*-alkoxy tails than most other polymerizable tail systems and thereby allow retention of the desired liquid-crystalline properties. Some of the bent-core homologues exhibit a switchable smectic (Sm) phase which appears to be ferroelectric SmC in nature. They can also be thermally or photochemically cross-linked with retention of the phase microstructure. Ordered polymer films with pyroelectric properties have been obtained by aligning and cross-linking these mesogens under an electric field. This result demonstrates the viability of these monomers as precursors to ordered, polar polymer materials.

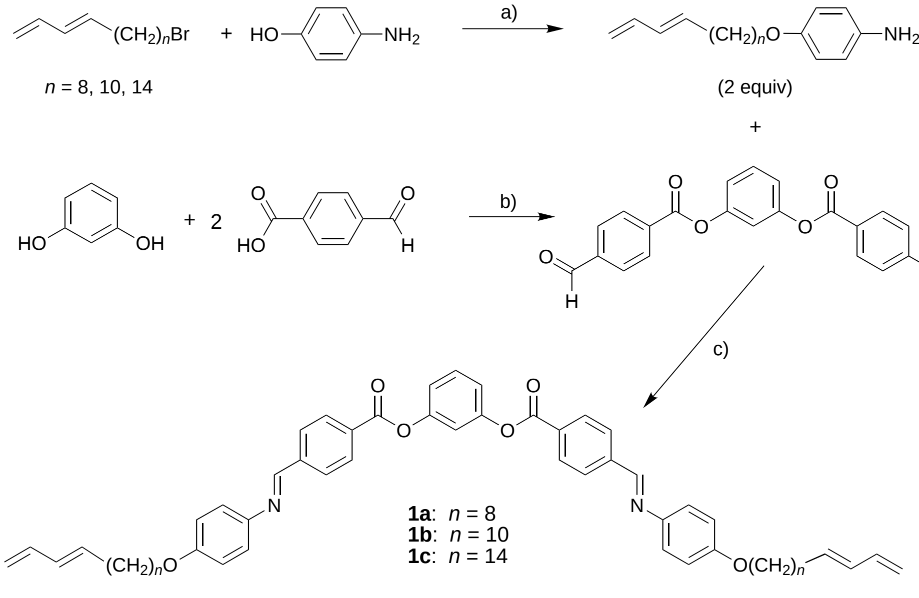
Three homologues (**1a**–**c**) containing an even number of methylene units in the tails were initially synthesized to investigate the properties of a system comprised of a bent-core and 1,3-diene tails. These diene tail units were originally developed by our group as a means of making polymerizable analogues of LCs which were sensitive to or incompatible with conventional polar or bulky polymerizable moieties in the tails.[10,11] Compounds **1a**–**c** were synthesized as shown in Scheme 1, using ω-bromoalkan-1,3-dienes as modular polymerizable tail units.[10,11] The detailed procedures for the synthesis, characterization, and property testing of these compounds are provided in the Supporting Information. The one drawback with the 1,3-diene tail system is that it tends to undergo spontaneous thermal polymerization at about 90 °C when coupled to a rodlike mesogenic core.[10] However, the effect of tail unsaturation on thermotropic liquid-crystalline behavior is a complex function of both the nature of the mesogenic core and the olefin units in the tails.[12] It was hoped that the unprecedented combination of diene tails with a bent core might afford lower phase-transition temperatures and reduced susceptibility to thermal cross-linking.

The thermotropic liquid-crystalline behavior of compounds **1a**–**c** was studied by polarized light microscopy (PLM), differential scanning calorimetry (DSC), and powder X-ray diffraction (XRD; Table 1). Upon heating, **1a** ($n=8$) begins to change from a crystalline solid to a liquid-

Table 1: Thermotropic liquid-crystalline phases and transition temperatures of compounds **1a**–**c**.[a]

Compound	*n*	Transition	*T* [°C]
1a	8	K→LC[b]	90–95
1b	10	K→B_4	107
		B_4→SmC	141
		SmC→I	145
		I→SmC	143
		SmC→B_4	128
		B_4→K	101
1c	14	G→SmC	119
		SmC→I	135
		I→SmC	136
		SmC→G	125

[a] K = crystalline phase, LC = unknown liquid-crystalline phase, G = ordered glassy phase, I = isotropic melt. [b] Cross-links upon entering the liquid-crystalline phase.



Scheme 1. Synthesis of cross-linkable bent-core mesogens **1a**–**c** containing 1,3-diene tails. a) K_2CO_3, methyl ethyl ketone, Δ, b) 4-dimethylaminopyridine (DMAP), *N,N'*-dicyclohexylcarbodiimide (DCC), CH_2Cl_2, c) molecular sieves, CH_2Cl_2.

crystalline phase at about 90–95 °C. However, the monomer spontaneously cross-links in a matter of seconds as it begins to enter the liquid-crystalline phase, which makes phase identification difficult. In contrast, **1b** ($n = 10$) exhibits well-defined enantiotropic liquid-crystalline behavior without premature diene polymerization. Thermally induced polymerization of **1b** only occurs if samples are held at temperatures above 90 °C for several hours. Upon cooling from the isotropic melt at 5 °C min^{-1}, **1b** initially enters a stable liquid-crystalline phase with a fan-type optical texture at 143 °C, which persists down to 128 °C (see Supporting Information). XRD analysis of this mesophase revealed a single diffraction peak at 49.6 Å, consistent with a lamellar phase with a layer spacing of that magnitude (Figure 1 a). Based on the calculated length of **1b** of 54 Å[13] and assuming there is little or no tail interdigitation, the observed layer spacing is consistent with a SmC phase with a tilt angle of 23°. Upon cooling below 128 °C, **1b** forms an anisotropic phase with a blue fan-type texture that does not respond to applied pressure, which is consistent with the so-called solid B_4 phase.[1] Below 101 °C, **1b** forms a solid crystalline phase which has the same optical texture as the "B_4 phase" but lacking the blue color. The longest homologue **1c** ($n = 14$) is a glassy solid at ambient temperature and also forms a reversible SmC phase upon heating, but the phase transitions are weaker and much harder to observe. In addition, **1c** partially thermally polymerizes upon initial heating. These diene mesogens exhibit very different trends with respect to their initial melting and final clearing temperatures as a function of tail length compared to *n*-alkoxy and *n*-alkenoxy analogues with the same bent core.[1,14] As a consequence of the susceptibility of **1a** and **1c** to thermal polymerization in the liquid-crystalline state, all subsequent studies were performed with **1b** since it has the most stable and most well-defined liquid-crystalline behavior.

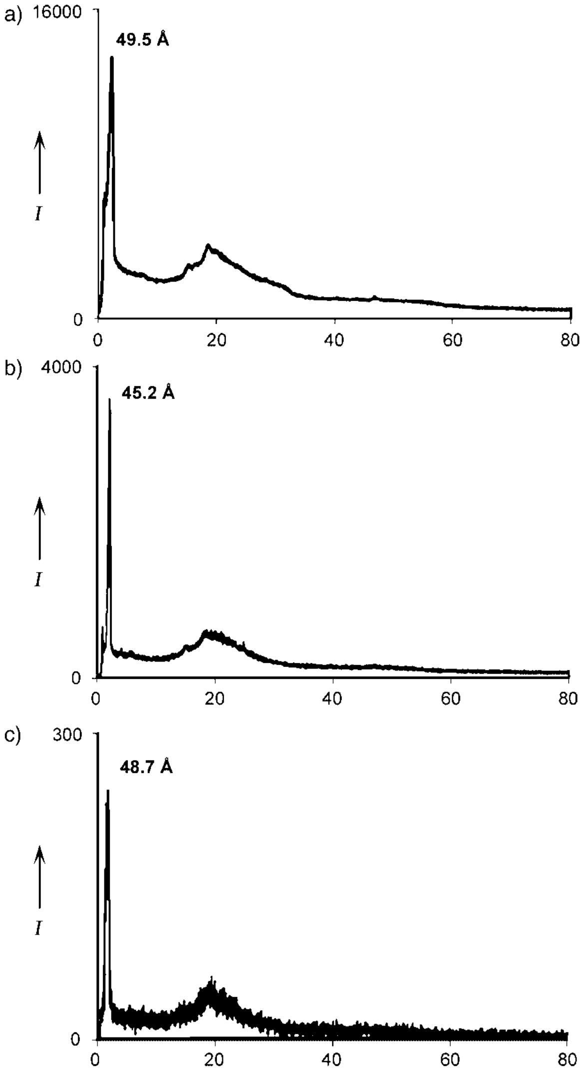


Figure 1. XRD profiles of **1b** taken at a) 133 °C in the SmC phase before polymerization; b) 180 °C after thermal polymerization; and c) 160 °C after photopolymerization.

Bent-core mesogens can adopt four general SmC packing configurations (not including enantiomeric forms), depending on the nature of the layer interface (namely, synclinic ($_S$) or anticlinic ($_A$)), and whether the mesogens are parallel or antiparallel in adjacent layers (that is, ferroelectric (P_F) or antiferroelectric (P_A)).[3] Only two of these four possible geometries (the SmC_SP_F and SmC_AP_F phases) are ferroelectric (Figure 2).[3] To help identify the SmC phase observed in our bent-core monomers, the electro-optic switching behavior of **1b** at 135 °C was examined in a 4-μm thick ferroelectric test cell using the triangular wave method.[2,3,11] The resulting current versus applied voltage curve (Figure 3) exhibits a single peak during voltage ramp-up and ramp-down, with a maximum polarization of 210 ± 30 nC cm^{-2} and a rise-time of 190 μs (averaged from five runs). This single-peak response is characteristic of ferroelectric behavior.[3,12,15] No signs of a double peak response indicative of antiferroelectric switching were observed, even when the frequency was varied from 10 to 1000 Hz,[3,12] so there is a high degree of confidence that the phase is ferroelectric in nature. Unfortunately, the magnitude of the observed polarization and the switching behavior steadily decrease over several minutes until a nonswitching sample with a fixed optical texture is formed. This behavior is

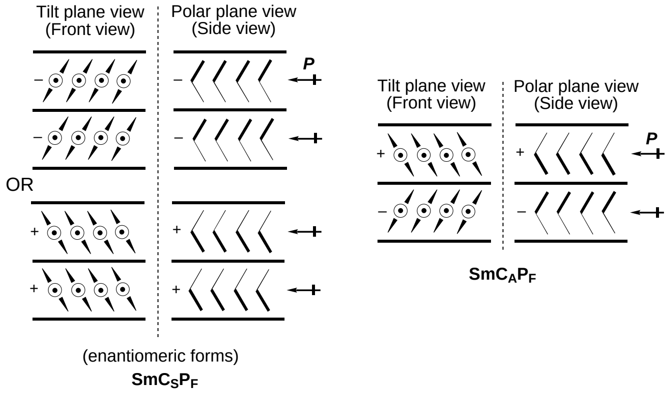


Figure 2. Schematic representations of the ferroelectric SmC_AP_F and SmC_SP_F bent-core phases. The symbols + and − indicate the enantiomeric layer configurations, and *P* is the layer polarization.

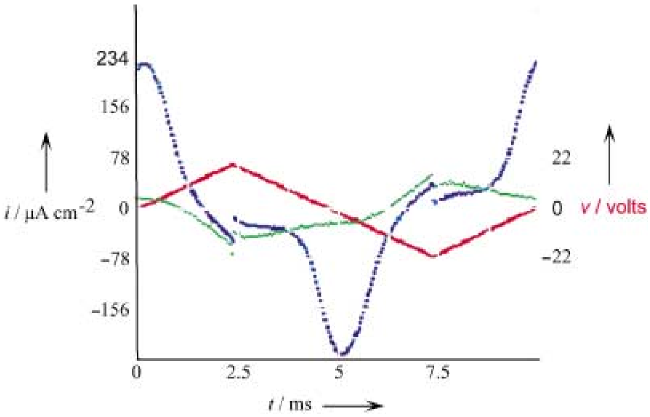


Figure 3. Triangular wave switching curve for **1 b** in the SmC phase at 135 °C. The blue curve is the initial switching response, and the green curve is the switching response after 15 min.

consistent with accelerated thermal cross-linking under the oscillating electric field. It also accounts for the unusual broadness of the switching curve (which complicates phase identification), since the sample is polymerizing and becoming more viscous as switching proceeds. It should also be noted that the current response appears to lead the applied voltage by a small amount. This phenomenon is a characteristic artifact of an electro-optic switching system with little or no hysteresis, which has been observed before in surface-stabilized ferroelectric LC cells.[16] Only small changes in optical texture were observed upon switching,[17] so it was not possible to unequivocally determine whether the observed phase has a SmC_SP_F or SmC_AP_F configuration. Nevertheless, **1b** does form a switchable Sm phase that can be aligned for subsequent polymerization.

Compound **1b** was subjected to both thermal and radical photopolymerization experiments to investigate the polymerization behavior of the bent-core dienes and whether they can be cross-linked with retention of the liquid-crystalline microstructure. Samples of **1b** were thermally cross-linked by maintaining the samples in the SmC phase at 135 °C for 16 h, which resulted in completely insoluble samples that no longer responded to pressure. XRD analysis of the resulting material shows retention of the phase order even at temperatures well above the clearing point of the original monomer (Figure 1 b), and even down to room temperature. Only a slight decrease in the primary XRD peak occurs upon cross-linking. The optical textures of the materials before and after thermal polymerization were essentially unchanged. Similar results were observed for samples of **1b** that were mixed with 2 wt % of a radical photoinitiator and irradiated with 365-nm UV light for 30 min (Figure 1 c). The extent of 1,3-diene conversion in both polymerization cases was estimated to be approximately 50 % using FTIR analysis as previously described.[10,11]

To demonstrate that the bent-core monomer can be aligned and cross-linked to form an ordered, polar noncentrosymmetric network, a sample of **1b** was placed in a 4-µm thick ITO cell and thermally cross-linked in the SmC phase for 3 h under a static 10 V electric field. Retention of order in the polymerized sample was confirmed by observation of the optical texture of the LC even down to room temperature. Pyroelectric measurements were performed on the sample to confirm the presence of a permanent net polarization.[18] As can be seen in Figure 4, the polymer exhibits a well-defined electrical response to changes in temperature, indicative of an aligned material with a permanent net polarization.[18] In contrast, a sample of **1b** similarly cross-linked in the absence of an applied field yields no pyroelectric response. The calculated pyroelectric coefficient for the material is 4.8 $\mu C\,m^{-2}K^{-1}$, which is similar to values observed for noncentrosymmetric Langmuir–Blodgett films (10–20 $\mu C\,m^{-2}K^{-1}$) and poled polymers (30–40 $\mu C\,m^{-2}K^{-1}$).[18,19] The optical texture of **1b** aligned and cross-linked in the field shows that it is still a polydomain sample (see Supporting Information). Samples with more uniform alignment under applied field and better bulk noncentrosymmetric properties might be possible if methods can be developed for aligning bent-core mesogens at the surface.

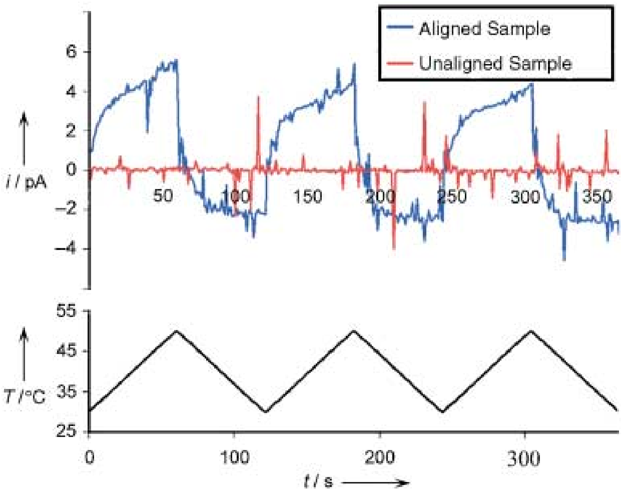


Figure 4. Pyroelectric response curve for **1 b** thermally cross-linked in the SmC phase under a 10 V electric field.

In conclusion, we have designed and synthesized the first example of a cross-linkable bent-core mesogen. This achiral mesogen adopts a SmC phase with switching behavior consistent with a ferroelectric phase. When aligned and cross-linked in the liquid-crystalline state under a static electric field, ordered polymer networks with a net polarization are generated that exhibit pyroelectric properties. Studies are currently underway to identify the exact structure of the liquid-crystalline phase formed and to examine the noncentrosymmetric properties of the resulting networks in more detail.

Received: December 2, 2002 [Z50680]

Keywords: liquid crystals · mesogens · nanostructures · polymerization · polymers

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