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Axially Polar Columnar Phase Made of Polycatenar Bent-Shaped Molecules

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Although, in general, the mesoscopic order is a result of interplay between many competing and/or cooperative molecular interactions, it can be argued that to a great extent the type of mesophase, lamellar or columnar, is simply determined by the shape of molecules. The columnar phases are predominantly formed by molecules having disklike[1] or bowlike[2] shapes. The other mechanism, observed for polycatenars,[3] i.e., molecules having a rodlike mesogenic core and multiple terminal alkyl chains, involves the microsegregation induced by the incompatible space required to accommodate the aromatic and alkyl parts of molecules. The polar order in columnar phases is rather rare. It was claimed to exist for bowlike molecules;[2] however, recent studies do not confirm ferroelectric properties for these materials.[4] So far, polar properties of columnar phases were unambiguously proved only for chiral disklike molecules.[5] In 1996, it was shown that bent-shaped molecules offered a new opportunity to design polar, lamellar, and *broken-layer* columnar mesophases made of achiral materials.[6−8] In this contribution, we combined the ability of polycatenar molecules to form columnar phases with induction of polar order by bent-shaped core molecules to obtain an axially polar columnar phase.

The DSC, optical, and X-ray studies revealed three columnar mesophases for the studied compounds (Figure 1). The highest temperature mesophase was identified as a columnar one with a two-dimensional hexagonal lattice (Col_h). The optical texture shown in Figure 2a is characteristic of a Col_h phase (smooth fans with extinction brushes aligned along the polarizers were observed). In the X-ray studies (Table 1), a few low-angle Bragg reflections corresponding to a two-dimensional hexagonal lattice of columns and the diffused high-angle reflection, corresponding to the liquidlike order of molecules within the columns with a mean intermolecular distance of 4.5 Å, were detected. The calculated unit cell dimension correlates to the molecular length (distance between the terminal chain ends), which is 70 and 73 Å for Pol12 and Pol14, respectively. As usual, the intercolumnar distance is smaller than the molecular diameter because the alkyl chains are in disordered conformations and interpenetrate between neighboring columns. Calculated from density (~1 g cm^{-3}) and lattice volume, the number of molecules that are necessary to fill a 4.5 Å stratum of each column was found to be ~4 molecules.

Thus, it can be assumed that a few molecules self-assemble to form an overall disk-shaped object (Figure 3a) in a similar way as in dendrimeric materials.[9] Such a structure would have compensated dipole moments, which is in agreement with results of electrooptic studies. The Col_h phase is not sensitive to electric field: no current peak or any optical changes upon applying electric field have been detected. In the Col_h phase, the clear dielectric mode is observed, which on approaching the lower temperature phase departs from Arrhenius-type $f_r \sim \exp(-E_a/kT)$ temperature behavior. Close to the phase transition, the mode intensity critically increases and its relaxation frequency critically decreases (Figure 4a). This behavior is similar to the soft mode observed in the paraelectric SmA phase in the vicinity of lower temperature polar SmC* or SmC*$_A$ phases.[10]

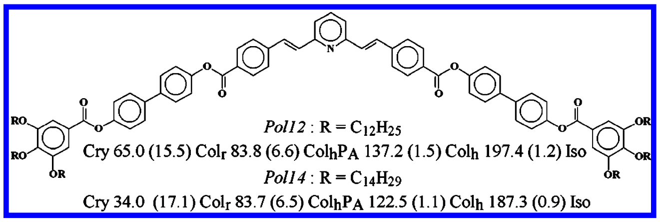

Figure 1. Chemical formula and phase sequences for the studied materials. The transition temperatures are given in °C along with the transition enthalpy changes (in parentheses) in J g^{-1}.

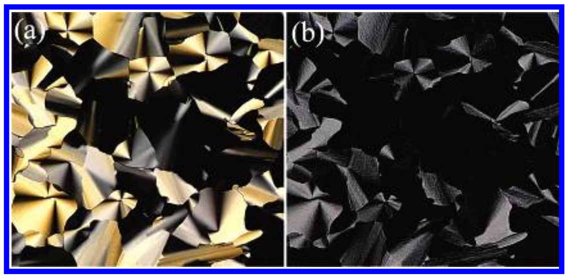

Figure 2. Textures of compound *Pol14* in the Col_h phase at $T = 170$ °C (a) and Col_hP_A phase at $T = 110$ °C (b). Appearance of black, pseudoisotropic regions in the texture confirms the hexagonal structure of the phase.

Table 1. Low-Angle Bragg Reflections (in Å) and, in Parentheses, Their Miller Indices[a]

Pol12	$T = 150$ °C, Col_h	55.0 (10), 31.7 (11), 27.5 (20)	$a = 63.5$ Å
	$T = 110$ °C, Col_hP_A	51.7 (10), 29.7 (11), 25.7 (20), 34.7, 19.5 (21)	$a = 59.7$ Å
	$T = 70$ °C, Col_r	50.4 (11), 31.6 (20), 29.0 (21), 25.3 (22), 20.2 (31)	$a = 63.2$ Å, $b = 83.5$ Å
Pol14	$T = 170$ °C, Col_h	55.8 (10)	$a = 64.4$ Å
	$T = 110$ °C, Col_hP_A	53.1 (10), 32.1, 27.4 (20)	$a = 61.3$ Å
	$T = 70$ °C, Col_r	53.5 (11), 32.8 (20), 30.8 (21), 26.7 (22)	$a = 65.6$ Å, $b = 92.4$ Å

[a] Indices are assigned assuming a hexagonal lattice for Col_h and Col_hP_A phases and a rectangular lattice for the Col_r phase. Unit cell parameters are given in the last column. The additional signal that could not be indexed into the hexagonal structure in Col_hP_A corresponds to the size of the blocks made of broken columns (see the text and Figure 4).

The phase transition from Col_h to lower temperature phase is marked by a distinct lowering of the optical birefringence (from 0.07 to 0.03) (Figure 2). The texture of the low-temperature phase can be rebuilt to give zero birefringence by applying an electric field. This suggests that, under the electric field, the columns reorient to have their axes perpendicular to the glass plate. A clear current peak is observed upon reversal of the applied voltage (Figure 4b), which proves the polar nature of the phase. The switching occurs without optical changes. Thus, it can be assumed that polarization exists along the columns. The low dielectric response

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† IPCMS.

10.1021/ja044597k CCC: $27.50

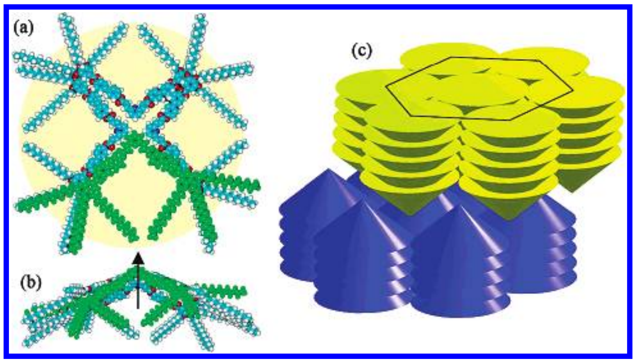

Figure 3. (a) Schematic drawing of the column cross-section made of four bent-shaped molecules. (b) In the $\mathrm{Col_hP_A}$ phase, the molecules form a conelike structure with noncompensated dipole moment depicted by an arrow. (c) Broken-column-type structure of $\mathrm{Col_hP_A}$ phase.

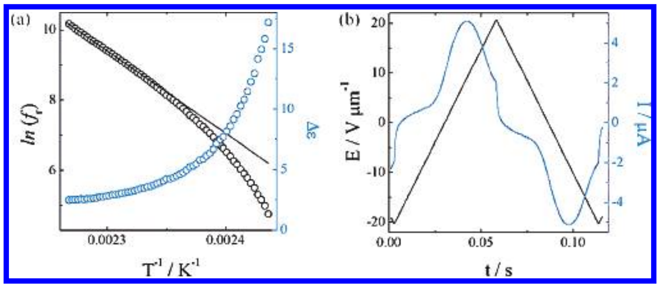

Figure 4. (a) Inverse temperature dependence of the relaxation frequency f_r and the mode strength $\Delta\epsilon$ in the $\mathrm{Col_h}$ phase of *Pol12* compound. Far from the $\mathrm{Col_h}-\mathrm{Col_hP_A}$ phase transition frequency follows Arrhenius law (solid line) with $E_a = 195$ kJ mol^{-1}. (b) Current peak registered for *Pol12* compound in the $\mathrm{Col_hP_A}$ phase at 130 °C upon applying the triangular waveform voltage. The calculated spontaneous electric polarization is $\sim$70nC cm^{-2}.

is observed ($\epsilon \sim 3.5$), which together with the switchable nature of the phase reveals its antiferroelectric properties. Surprisingly, the X-ray studies showed that the hexagonal structure is preserved in the switchable phase (Table 1). Thus, the phase will be referred to further as $\mathrm{Col_hP_A}$, where $\mathrm{P_A}$ stands for polar, antiferroelectric properties. The column diameter in the $\mathrm{Col_hP_A}$ phase is only slightly smaller than in the $\mathrm{Col_h}$ phase, so it is reasonable to assume that the number of molecules in the column stratum remains the same in both phases; however, in the low-temperature phase, the molecules depart from coplanar geometry, forming a cone with a noncompensated dipole moment along the cone axis (Figure 3b). Simple geometrical considerations show that the cone angle is about 150−140°. This assumption is also consistent with measurements of birefringence. It is expected that for light propagation perpendicular to the column axis, Δn should decrease upon transition from a flat disk to a conelike structure of the phase. However, the question arises how to compromise the two-dimensional hexagonal structure and antiferroelectric order of columns, as it is well-known that antiparallel dipoles cannot be accommodated without frustration in a lattice of triangular symmetry.[11] One possibility is that the lattice is quasihexagonal, i.e., dipoles are randomized in the two-dimensional triangular structure. The other possibility is the existence of an additional three-dimensional superstructure (Figure 3c). In the *xy* plane perpendicular to the column axis the ferroelectric hexagonal order exists but the columns are broken along the *z* direction and polarization direction alternates between the blocks. It should be noticed that for the phase made of conelike objects, the best space filling is obtained if the blocks are shifted in the *xy* plane by half of the cell lattice distance and the ABAB stacking of blocks with alternating polarization is enforced. This three-dimensional superstructure is supported by X-ray studies in which an additional, very weak signal was recorded that does not match with a hexagonal structure (Table 1). The estimated height of column fragments is 30−35 Å in both compounds.

Upon further decrease in the temperature, another disordered columnar phase is observed. The X-ray studies confirm the rectangular columnar structure ($\mathrm{Col_r}$) with *p*2*gg* symmetry. The distortion from the hexagonal lattice is not significant, as the ratio b/a is 1.3 and 1.4, for *Pol12* for *Pol14*, respectively, while $b/a = \sqrt{3}$ for an ideal hexagonal structure. The transition from the $\mathrm{Col_hP_A}$ phase to the $\mathrm{Col_r}$ phase occurs with a decrease of birefringence to almost zero, without any noticeable change of the domain's shape. The $\mathrm{Col_r}$ phase is not switchable under the electric field. The structure of this phase is not clear at present.

In summary, it was shown that polycatenar bent-shaped molecules are able to form columnar phases with column stratum built of few molecules, arranged in coplanar or conelike geometry. In the latter case, the phase becomes axially polar, with electric spontaneous polarization reorientable in an electric field. It should be noticed that previous attempts to obtain polycatenar bent-shaped molecules resulted only in nonpolar $\mathrm{Col_h}$ or smectic phases, most probably due to the much smaller bend in thienyl derivatives.[12] Although we cannot exclude that dipole interactions play some role in this system, it is more plausible that the cone formation is rather due to steric interactions. The filling of a column section with flat bent-shaped molecules might lead to some voids between molecule arms, and the tilting of the molecules improves packing by decreasing the distances between the aromatic parts of the molecules. To avoid an internal electric field, the antiferroelectric order is imposed by breaking the columns and forming a three-dimensional structure.

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Supporting Information Available: Chemical synthesis, spectral characterization of materials, and experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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