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Structure and switching behavior were studied in liquid crystals consisting of bent-shaped molecules with the linkage of an alkylene spacer, *m*(O)AM*n*AM(O)*m*, where *m* and *n* are carbon numbers of end and spacer chains, respectively. All the compounds exhibit a fan-shaped texture without a fringe structure in their smectic phase, different from the texture of conventional bent (banana)-shaped liquid crystals. In 12AM5AM12, two switching current peaks indicating the antiferroelectric phase were observed. The spontaneous polarization was about 600 nC/cm^2. The color change due to the birefringence change is associated with the switching, though the extinction direction between crossed polarizers remains the same. This clearly proves that the bent-molecules do not tilt with respect to the layer normal. In the dielectric measurements, there exist two relaxations at 600 kHz and below 100 Hz and they are suppressed by a biased voltage. Structure and switching in the other systems, 8OAM5AMO8, are also described briefly.

Keywords: bent-shaped molecule; antiferroelectricity; frustrated layer structure; switching current; dielectric constant

INTRODUCTION

Recently, ferroelectric/antiferroelectric switching was observed in achiral bent-shaped molecular systems[1,2]. The linkage of two mesogens in these compounds is 1,3-dihydroxybenzene. In this paper, we report the switching characteristics of the liquid crystals consisting of bent-shaped molecules

with the linkage of an alkylene spacer, *m*(O)AM*n*AM(O)*m*, where *m* and *n* are carbon numbers of end and spacer chains, respectively. These liquid crystal systems are interesting, since several phases with single layer, double layer, frustrated layer structures are realized depending on the choice of *m* and *n*, as shown in Fig. 1[3]. The number of the spacer carbon *n* must be odd to realize the herring-bone structure, otherwise the SmA and/or SmC phases arise. In the compounds with *m* smaller than or comparable to *n*, the single layer structure appears, while the double layer structure appears in the compounds with a larger *m* compared with *n*. In between, the frustrated layer structure is realized.

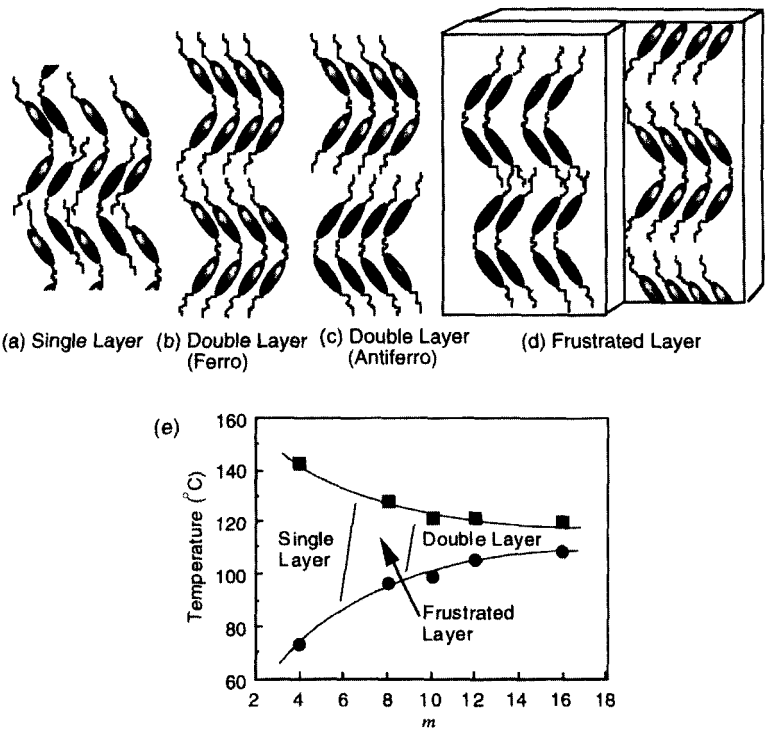

FIGURE 1 (a)~(d) Four smectic layer structures realized in bent-shaped molecular systems and (e) the phases exhibited in *m*OAM5AM*Om*.

In the following, the structure and switching of these materials are reported base on the experiments such as texture observation, switching current, dielectric and x-ray measurements.

EXPERIMENTAL

The sample used were achiral bent-shaped molecules, in which two mesogens are linked by an alkylene spacer, as shown in Fig. 2. The phases and the transition temperatures were also shown in the figure. The materials were sandwiched between two glass plates covered with ITO for the dielectric and electrooptic measurements. The glass plates were not coated with any polyimide nor rubbed, so that molecules were aligned almost homogeneously but randomly.

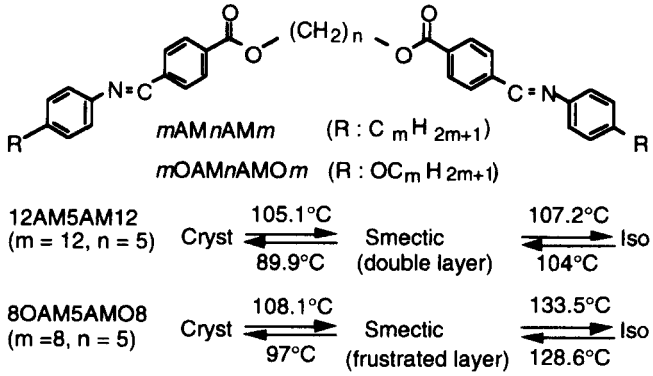

FIGURE 2 Chemical structure of the bent-shaped molecules used.

The anisotropy of the refractive indices, birefringence, was determined by analyzing the color, namely the transmittance spectra of the cell set between crossed polarizers. Switching current was observed by applying a triangular voltage wave. Dielectric response was measured with an oscillation field of 5 mV_{pp}~ 1.1 V_{pp} with or without a bias field using an impedance analyzer (HP, LF4192A).

RESULTS AND DISCUSSION

First of all, it was confirmed that the compounds exhibit a fan-shaped texture without a fringe structure in their smectic phase, different from the texture of conventional bent-shaped liquid crystals[4,5]. Figures 3(a) and 3(b) show the optical micrographs of (a) 12AM5AM12 and (b) 8OAM5AMO8, respectively, in the presence and the absence of an electric field. Two observations should be made. (1) The birefringence color changes by applying an electric field. The birefringence in the absence of the field was determined to be 0.244 (12AM5AM12) and 0.297 (8OAM5AMO8), which are smaller than that under the field, 0.262 (12AM5AM12) and 0.337 (8OAM5AMO8), respectively. (2) The dark position remains as is by applying a field, indicating that the extinction direction does not change. This fact indicates that the bent-shaped molecules do not tilt with respect to the layer normal, contrary to the conventional bent-shaped molecular systems[6].

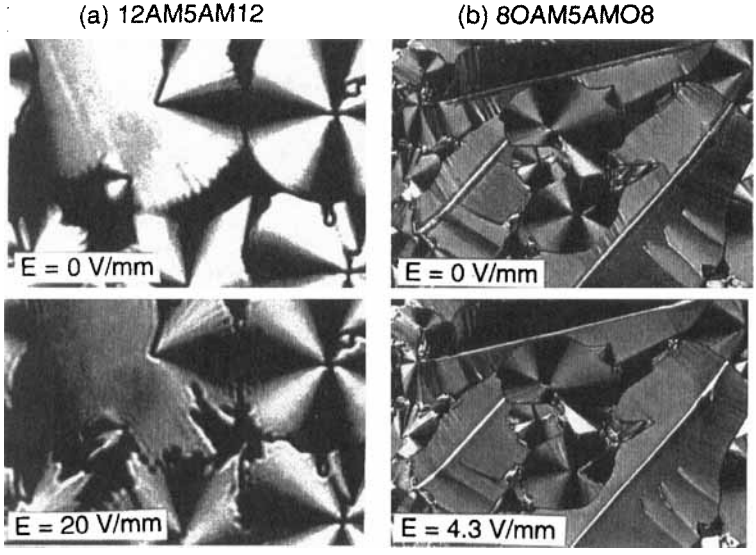

FIGURE 3 Optical micrographs of (a) 12AM5AM12 and (b) 8OAM5AMO8 in the presence and the absence of an electric field.
See color plate VI at the back of this issue.

12AM5AM12 clearly exhibits two switching current peaks (Fig. 4(a)), as already reported[7], while 8OAM5AMO8 shows a broad single peak, as shown in Fig. 4(b). The spontaneous polarization in 12AM5AM12 is very large, about 600 nC/cm^2 almost independent of temperature. According to the x-ray diffraction experiment, the layer spacing of 12AM5AM12 is 52.24 Å. This layer spacing and the two switching current peaks suggest the double-layered antiferroelectric structure, as shown in Fig. 1(c). Based on these observation, the orientational change shown in Fig. 5 could be imagined in 12AM5AM12 under the application of an electric field.

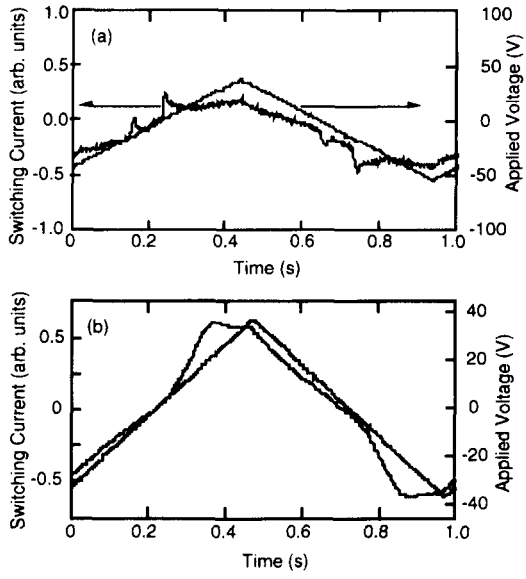

FIGURE 4 Switching current measured in (a) 12AM5AM12 and (b) 8OAM5AMO8.

In contrast, the powder diffraction pattern of 8OAM5AMO8 shows two peaks at 22.87 Å and 35.76 Å corresponding to (002) and (101) planes, suggesting the frustrated layer structure shown in Fig. 1(d). The lattice constants are a = 54.98 Å and c = 45.74 Å. Since the molecular distance is about 4.5 Å, six molecules form a cluster at each lattice point in the two-

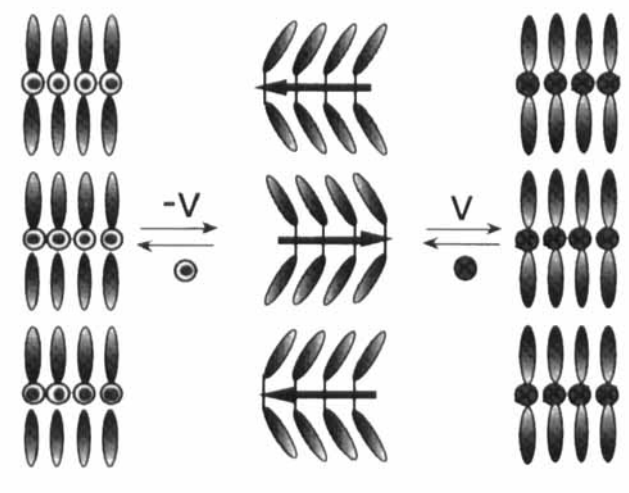

FIGURE 5 Structure of 12AM5AM12 without an electric field and switching by applying ±V.

dimensional (a-c plane) lattice. In the frustrated structure, the tip direction of the molecules was found to be perpendicular to the two-dimensional lattice by the following two experimental results; (1) x-ray measurements irradiated from the substrate normal of a monodomain planar cell exhibit (002) and (101) diffractions only when an electric field was applied, and (2) the large birefringence under the field assures that the tip of the molecules is perpendicular to the glass surface. This frustrated layer structure shown in Fig. 1(d) is the same as that in main-chain polymer liquid crystals[8]. It was found that the switching current observed in Fig. 4(b) could not be attributed to a ferroelectric switching according to optical second-harmonic generation experiments. The details will be published elsewhere.

Figure 6 shows the frequency dispersion of the dielectric constants at 95°C in a 13 μm thick cell of 12AM5AM12 (a) without a bias field and (b) under a bias field of 2.5 V/μm. Two relaxations at about 600 kHz and below 100 Hz are clearly observed in Fig. 6(a) and they are suppressed by the biased field. The lower frequency mode is observable only in the

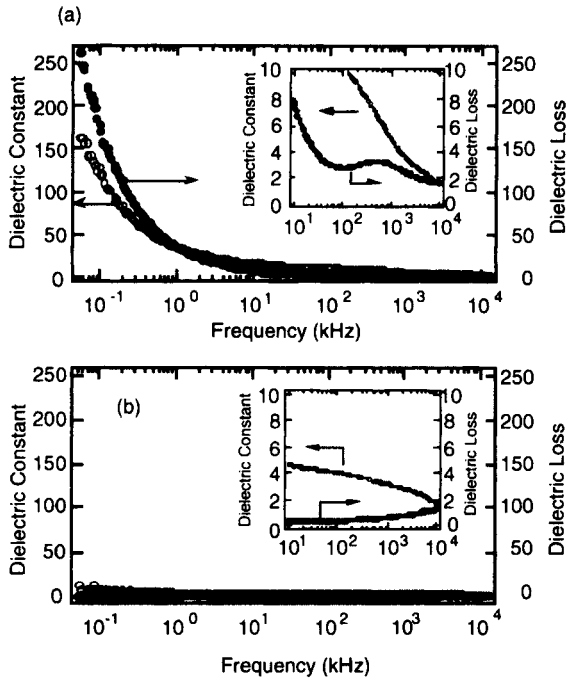

FIGURE 6 Frequency dispersion of the dielectric constant and loss in 12AM5AM12 at 95°C (a) without a bias field and (b) under a bias field of 2.5 V/μm.

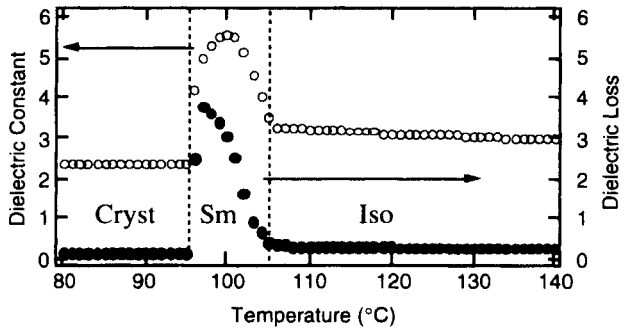

FIGURE 7 Temperature dependence of the dielectric constant and loss at 1 kHz in 12AM5AM12.

smectic phase but not in the isotropic and the crystalline phases, as shown in Fig. 7, where the dielectric constant and loss at 1 kHz are plotted as a function of temperature. Hence, this relaxation must be attributed to the antiferroelectric phase. The dielectric behavior is not clear at this stage.

CONCLUSION

The texture observation, the polarization current and the dielectric measurements were made in liquid crystals consisting of bent-shaped molecules with the linkage of an alkylene spacer to clarify the structure and the switching under an electric field. Two compounds used, 12AM5AM12 and 8OAM5AMO8, exhibit a fan-shaped texture without a fringe structure in their smectic phase, different from the texture of conventional bent-shaped liquid crystals. The color of the texture changes by applying an electric field, though the extinction direction between crossed polarizers remains the same. Therefore, the bent-molecules do not tilt with respect to the layer normal. Two and one switching current peaks were observed in 12AM5AM12 and 8OAM5AMO8, respectively, being attributed to the antiferroelectric and some nonferroelectric switchings. Two dielectric relaxations at 600 kHz and below 100 Hz were observed and were suppressed by a biased voltage in 12AM5AM12.

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