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Huge dielectric constants of the ferroelectric smectic-A phase in bent-shaped dimeric molecules

In the image on the left, well-developed fan-shaped textures of the SmAP_{p} phase is observed, indicating the homogeneous alignment of the molecules, in other words, the alignment of the smectic layers perpendicular to the cell's surface. The image on the right indicates the texture under the DC bias fields. The texture does not change at all, but the birefringence color changes. This indicates that the bent (polar) direction of the molecules that are initially parallel to the cell's surface become perpendicular to it because of the ferroelectric response.

As featured in:
Huge dielectric constants of the ferroelectric smectic-A phase in bent-shaped dimeric molecules†

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We present the dielectric relaxation properties of the ferroelectric smectic-A (SmAPs) phase formed by a mixture of bent-shaped dimeric molecules \(\alpha_2\omega\)-bis(4-alkoxyanilinebenzylidene-4'-carbonyloxy)pentanes with different alkyl chain lengths. The SmAPs phase shows a Goldstone-like mode at approximately 500 Hz, which can be attributed to the ferroelectricity and huge dielectric strength \((\Delta \varepsilon)\). \(\Delta \varepsilon\) varies dramatically with the cell thickness; in particular, it attains more than 7000 in a 50 \(\mu\)m-thick cell, which is much higher compared to that reported in the bent-shaped molecules.

Introduction

Since the reports on bent-shaped molecules with unique polarity by Watanabe et al.,\(^1\) bent-shaped molecules have become an important field in the investigation of liquid crystals. In particular, the ferroelectric and the antiferroelectric smectic phases that comprise bent-shaped molecules are of great interest because they can be switched between different polar ordered states by electric fields.\(^2\) Various bent-shaped molecules, with ferroelectric and antiferroelectric behaviors, have been synthesized and investigated to clarify the structure–property relationships associated with their profound mesomorphic properties.\(^4,5\)

Bent-shaped dimeric molecules with two aromatic mesogens linked by an odd-carbon numbered alkylic spacer are another type of bent-shaped dimeric molecules that form polar phases.\(^5,9\) Two mesogens in a molecule are forced to be relatively tilted to each other by the conformational constraint of the alkylic spacer.\(^3,10\) The typical molecules are \(\alpha_2\omega\)-bis(4-alkoxyanilinebenzylidene-4'-carbonyloxy)pentanes \((mOAM5AMOm)\) with the formula shown in Fig. 1. These bent-shaped dimeric molecules form three types of smectic liquid crystals (refer to Fig. S1, ESI†), depending on the alkylic tail group.\(^7\) When the tail length was short \((m = 4\) and 6\), the SmCA\(^*\) phase was formed. Here each mesogen, but not a bent-shaped dimeric molecule, participated to form each smectic layer. When the tail length was medium \((m = 8\)–12\), the frustrated SmCA\(^*\) phase was formed. When the tail length was long \((m = 14\)–18\), the smectic structure was identified as the antiferroelectric SmC\(_{AP}\) phase, where each bent-shaped dimeric molecule participates in each layer comprising a bilayer of mesogenic groups. Within a layer, the bent-shaped dimeric molecules are packed with significant tilting of the molecular axis and with the same direction of the bent (polar) axis. The polar directions are opposite between the neighboring layers. Furthermore, the mixture of \(4OAM5AMO4\) forming the SmCA\(^*\) phase and \(16OAM5AMO16\) forming the SmC\(_{AP}\) phase with antiferroelectricity formed the ferroelectric smectic-A (SmAPs) phase in a specific ratio. The ferroelectricity of the SmAPs phase was identified by a single current peak under a triangular wave field (refer to Fig. S2, ESI†) and clear second harmonic generation.\(^9\)

The SmAPs phase generally shows that the molecules lie perpendicular to the layer, with ferroelectric alignment of the polar directions (refer to Fig. S1(d), ESI†). Bent-shaped dimeric molecules and general bent-shaped molecules form SmC\(_{AP}\) and SmC\(_{PA}\), but the SmAPs phase is not commonly observed in these systems.\(^5,8\) For example, W586 consisting of a bent-shaped molecule with a carbosilane group at the terminal chain suppresses out-of-layer fluctuations, favoring anticlinic tail orientation and thus the SmAPs phase due to the influence of carbosilane.\(^11,13\) In bent-shaped dimeric molecules, mixing of \(4OAM5AMO4\) and \(16OAM5AMO16\) with different alkylic chain lengths obviously prevents the tilted association of molecules, although the reason is not clear.\(^6\) As one of the properties of the SmAPs phase with a bent-shaped molecule, Guo et al. reported that W586 has high dielectric constants.\(^14\)

In this study, we examined the dielectric relaxation properties of the SmAPs phase in bent-shaped dimeric molecules and showed extremely large dielectric constants of 2000–7000 attributable to the collective fluctuation of the polar molecules.
Fig. 1  Molecular structures and phases sequence for mOAMSAMOm (m = 4, 16, and 4 + 16). The transition temperatures are taken from the DSC cooling run and the switching current curve.9

Fig. 2  (a) and (b) Frequency dependence of the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the complex dielectric constants of the SmC_A $P_A$ (at 114 °C), SmC_A $P_A$ (at 90 °C) and SmAP_F (at 98 °C) phases, measured in a 3 μm-thick cell. In the insets, the vertical axis is expanded to clarify the high frequency mode. The dashed curves are obtained by fitting eqn (1). (c) Cole–Cole plot for the high frequency mode of the SmC_A $P_A$ and SmC_A $P_A$ phases, and (d) Cole–Cole plot for the Goldstone-like mode of the SmAP_F phase, based on the data of Fig. 2(a and b). The dashed curves are obtained by fitting eqn (1).
Results and discussion

The molecular structures and the phase sequence (refer to Fig. S3, ESI† as a differential scanning calorimetry (DSC) chart) of the bent-shaped dimeric molecules 4OAM5AMO4 and 16OAM5AMO16, and the mixture (4OAM5AMO4 (65 mol%) + 16OAM5AMO16 (35 mol%)) are given in Fig. 1.

To clarify both the non-collective and collective motions of the molecules, dielectric dispersion measurements were performed in the SmCA* ($m = 4$), SmC$_A$P$_A$ ($m = 16$), and SmAP$_F$ (mixture of $m = 4$ and 16) phases. Here, it should be noted that the domain size is small especially in the SmAP$_F$ and the SmC$_A$P$_A$ phases just as cooled from the isotropic phase. Hence, the domains of SmAP$_F$ and SmC$_A$P$_A$ were enlarged by applying an AC field of $5 \, V_{pp} \, \mu m^{-1}$ and $33 \, V_{pp} \, \mu m^{-1}$, respectively; they were grown by agitation of molecular motion due to ferroelectric switching. In Fig. 2(a) and (b), the real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts of the dielectric constants are plotted against the frequency from $10^4$ to $10^7$ Hz, respectively. Two relaxation modes are observed in this frequency range. One is a low frequency mode which is observed at approximately 500 Hz in the SmAP$_F$ phase and possesses huge dielectric constants. The low relaxation frequency ($f_r$) of the order of 1 kHz or less, 14–16 as well as the suppression under DC bias fields (mentioned later), shows that this mode is a Goldstone-like mode, collective fluctuation of polarization that is attributable to the ferroelectric phase. The other is a high frequency mode observed in the SmCA* and the SmC$_A$P$_A$ phases. The isotropic phase also exhibits this mode.

The molecular structures and the phase sequence (refer to Fig. S3, ESI†) parts of the dielectric constants are plotted against the inverse absolute temperature for the SmCA*, SmC$_A$P$_A$, and SmAP$_F$ phases in a 3 $\mu m$-thick cell.

$\Delta \varepsilon$ has been reported in the ferroelectric phases of bent-shaped molecules. 14,20–22 W586 showed the maximum value of $\Delta \varepsilon$ (~300) as observed in a 3 $\mu m$-thick cell. 14 Furthermore, a bent-shaped azo molecule consisting of nonsymmetrical molecules with a lateral fluoro substitution on one of the wings achieved the maximum value of $\Delta \varepsilon$ (~400) in a 9 $\mu m$-thick cell. 22 The present $\Delta \varepsilon$ of 1800 exceeds these values substantially.

Fig. 3 shows the temperature dependence of the characteristic $f_r$ of the relaxation processes observed in the SmCA*, SmC$_A$P$_A$, and SmAP$_F$ phases in a 3 $\mu m$-thick cell. The high frequency mode observed in the SmCA* and SmC$_A$P$_A$ phases follows the standard Arrhenius equation 20,22

$$f_r = A \exp \left( -\frac{E_{act}}{k_B T} \right)$$

(2)

where $f_r$ is the relaxation frequency, $A$ is the pre-exponential factor, $E_{act}$ is the activation energy, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. Eqn (2) is fitted to the experimental data points in order to obtain $E_{act}$. The estimated $E_{act}$ of the SmCA* and SmC$_A$P$_A$ phases is 4 and 40 kJ mol$^{-1}$, respectively. In the higher temperature region, $f_r$ of the SmAP$_F$ phase is somewhat temperature dependent, but seems to be independent in the lower temperature region as expected for the Goldstone mode.

As another feature of the Goldstone-like mode of the SmAP$_F$ phase, $f_r$ and $\Delta \varepsilon$ strongly depend on the cell thickness (refer to Fig. 4). As the thickness increases from 3 to 50 $\mu m$, $f_r$ decreases from 500 to 300 Hz. On the other hand, $\Delta \varepsilon$ almost linearly grows; although $\Delta \varepsilon$ is approximately 1800 in a 3 $\mu m$-thick cell, it is 3200, 4500, and 7400 in 10, 25, and 50 $\mu m$-thick cells, respectively.

A similar thickness dependence of $\Delta \varepsilon$ for Goldstone-like modes has been observed in the ferroelectric chiral Sm-C* 24 and SmAP$_F$ phases. 14 Ozaki et al. found that some chiral Sm-C* materials possess dielectric constants larger than 7500 in a 250 $\mu m$-thick cell. 24 Guo et al. mentioned that by linear extrapolation of $\Delta \varepsilon$ for W586 an even larger value (~20 000) is expected for this cell thickness. 14 We estimated $\Delta \varepsilon$ by linear extrapolation similar to Guo et al. The expected $\Delta \varepsilon$ of 30 000 exceeds these values. One may speculate that such a cell
thickness dependence is caused by strong anchoring of the molecules to the cell surfaces, which can prevent the collective fluctuations of dipoles near the cell surfaces. However, anchoring can cause significant suppression only in a thin cell, but not lead to a linear increase with the cell’s thickness. A theoretical approach to explain this trend has been carried out by Guo et al.\textsuperscript{14} They collected $\Delta\varepsilon$ with the cell where the bent direction of the bent-shaped molecules lay perpendicular to the cell’s surface by strong surface anchoring. In such a cell, it is speculated that a splay of polarization arises across its thickness that can induce the cell thickness dependence in $\Delta\varepsilon$ and $f_r$ in relation with the anchoring strength. Comparing the model and the experimental results, they have estimated the correlation length in the bulk and the surface to be approximately 10 and 1 $\text{nm}$, respectively.

In our case, however, the molecular orientation reported by Guo et al.\textsuperscript{14} is unlikely. Fig. 5(a, c, and e) show the optical microscopic textures of the SmAP$_F$ phase in 3, 10, and 25 $\mu$m-thick cells, respectively. In all these cells, well-developed fan-shaped textures are observed, indicating the homogeneous alignment of the molecules, in other words, the alignment of the smectic layers perpendicular to the cell’s surface by strong surface anchoring. In such a cell, it is speculated that a splay of polarization arises across its thickness that can induce the cell thickness dependence in $\Delta\varepsilon$ and $f_r$ in relation with the anchoring strength. Comparing the model and the experimental results, they have estimated the correlation length in the bulk and the surface to be approximately 10 and 1 $\mu$m, respectively.

The textures do not change at all, but the birefringence colors change. This indicates that the bent (polar) direction of the molecules that are initially parallel to the cell’s surface become perpendicular to it because of the ferroelectric response. On the basis of the retardation obtained from the general polarization color chart, the birefringence ($\Delta n$) is estimated to be 0.07 at 0 V $\mu$m$^{-1}$ and 0.18 at 1 V $\mu$m$^{-1}$, which are well expected from
the parallelly and perpendicularly aligned models, respectively. In such a molecular alignment, the splay of polarization does not arise across the cell’s thickness as reported by Guo et al. The effect of DC bias fields on the Goldstone-like mode of the SmAPF phase was also studied. As shown in Fig. 7, by applying DC bias fields, the Goldstone-like mode is quickly quenched. As a result, the high frequency mode can be clearly detected at 100 kHz. The disappearance of the Goldstone-like mode is explained by the suppression of the dipoles’ fluctuation due to the DC bias fields. Here, a cell thickness dependence is also observed in the critical voltage that suppresses the Goldstone-like mode. The critical voltage is 0.40 V/µm for a 3 µm-thick cell, 0.14 V/µm for a 10 µm-thick cell, and 0.06 V/µm for a 25 µm-thick cell (refer to Fig. S4, ESI†). This trend is the same as that reported by Shimbo et al. but opposite to that reported by Shimbo et al.

Conclusions

The dielectric relaxation properties were studied for the SmAPF phase in a bent-shaped dimeric molecule mixture of 40AM5AM04 (forming the SmCA phase) and 16OAM5AM016 (forming the SmC_A phase). Within a cell of the SmAPF phase, the bent-shaped dimeric molecules lie with their bent plane parallel to the surface. The SmAPF phase shows a Goldstone-like mode at approximately 500 Hz characteristic of the ferroelectric phase and a huge Δε of over 7000 in a 50 µm-thick cell, which is much higher compared to almost all the reported values in bent-shaped molecules. The highly
cooperative orientation of the bent-shaped dimeric molecule is considered to bring about the giant value of \( \Delta e \). It is also characteristic of the Goldstone-like mode that the cooperative fluctuation of dipoles is easily quenched under DC bias fields. The extremely large value of the dielectric constants of the ferroelectric bent-shaped dimeric molecules suggests high potential for application in highly processible elements in electromechanical energy conversion devices.

Experimental
The mOAM5AMO\( _m \) dimers with \( m \) values of 4 and 16 were synthesized following the methods reported in a previous report.\(^7\) The bent-shaped dimeric molecule mixture of 4OAM5AMO4 (65 mol\%) + 16OAM5AMO16 (35 mol\%) was prepared by evaporating a chloroform solution of the two molecules at a predetermined molar ratio.\(^9\) The phase transition temperatures were determined by DSC (SHIMADZU DSC-60 Plus) at a rate of 5 °C min\(^{-1}\) under cooling and heating runs. Texture observation and the identification of the mesophases were carried out using a polarizing optical microscope (OLYMPUS BX53) equipped with a hot stage and a temperature controller (Metert Toledo FP 82HT). Electro-optical and dielectric investigations were performed using glass cells, having indium tin oxide (ITO) electrodes commercially available from EHC Co., Ltd. The area of the ITO electrodes was 100 mm\(^2\), and the cell thicknesses of the ITO electrodes were 3, 10, 25, and 50 \( \mu \)m. In these cells, the bent-shaped dimeric molecules was homogeneously aligned with the bent plane parallel to the cell plane. Before the measurements, AC applied fields of 33 and 5 V\(_{pp}\) \( \mu \)m\(^{-1}\) were applied to 16OAM5AMO16 and 4OAM5AMO4 (65 mol\%) + 16OAM5AMO16 (35 mol\%) for the growth of liquid crystals, respectively. The complex dielectric constants were measured in the frequency range between 10\(^4\) and 10\(^7\) Hz with an impedance analyzer (FRA51615). The electric field was 1 V\(_{pp}\).

Conflicts of interest
There are no conflicts to declare.

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