Polymer-Stabilized Ferroelectric Liquid Crystals and their Spontaneous Polarization

Hirokazu Furue, Ryosuke Uchino and Jun Hatano

Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

A photocurable mesogenic monomer was mixed into ferroelectric liquid crystals (FLCs) in which dipole moments of carbonyl groups are the main source of the spontaneous polarization, and then polymer-stabilized ferroelectric liquid crystal (PSFLC) cells were fabricated. The effect of polymer stabilization on the spontaneous polarization of FLC was researched by analyzing the hindered rotational motion of the carbonyl groups measured using a polarized Fourier transform infrared spectroscopy (FT-IR). Although the degree of hindrance increases due to the polymer stabilization, the polymer stabilization rather strongly influences the tilt angle of FLC molecules which is in proportion to the spontaneous polarization.

Keywords: polymer-stabilized ferroelectric liquid crystal, spontaneous polarization, hindered rotational motion, tilt angle

1. Introduction

Surface-stabilized ferroelectric liquid crystal displays (SSFLCDs) form the basis of a rapidly developing technology of significant potential impact in display applications, in particular, such as video image displays by taking advantage of their fast response speed [1-4]. However, the bistability of SSFLC is disadvantageous for LCDs that possess grayscale or full-color capability, because the size of bistable switching domains may become almost equal to the pixel size of LCDs. In previous papers we reported a polymer-stabilized (PS) FLC fabricated by a UV photocure of doped photocurable monoacrylates, which have mesogenic side chains, at a temperature where the LC medium is in the SmC* phase under the application of a monopolar electric field [5-8]. This PSFLC exhibits monostable electrooptical characteristics with grayscale capability without a threshold. While lots of paper mainly concerned with the application research of PSFLC have been reported, it has not been clear in detail yet how the polymer stabilization influences the molecular orientation and the physical property. For an investigation of the molecular conformation and orientation, polarized Fourier transform infrared (FT-IR) spectroscopy can be used as a powerful tool [9, 10]. Here we report a result obtained by the polarized FT-IR spectroscopy and refer to the relationship between the spontaneous polarization and the hindered rotational motion of the carbonyl group near the chiral center (hereafter abbreviated as the chiral carbonyl group) which produces the spontaneous polarization in the ferroelectric chiral smectic-C (SmC*) phase. Then we discuss the effect of polymer stabilization on the hindered rotational motion and the spontaneous polarization.

2. Experimentals

Three FLC materials were used in this research [9-11]. The structural formulae of these materials are shown in Fig. 1. The photocurable mesogenic monoacrylate was UCL-001 (Dainippon Ink and Chemicals) which were doped with 1wt% photoinitiator [5-8] and the LC alignment film was polyimide RN-1199 (Nissan Chemical Industries) which induced a defect-free FLC alignment [12, 13]. A solution of polyimide was spun on BaF2 substrates coated with indium-tin-oxide (ITO) and then baked.

Received March 19, 2005
Accepted April 25, 2005
After the thermal treatment, the substrates were rubbed. Then the FLC, which was doped with the photocurable mesogenic monomer, was injected in the isotropic phase via capillary action into an empty cell, in which the rubbing directions were parallel and the cell gap was 10µm. Next, the cell was cooled gradually to the temperature where the LC medium is in the SmC* phase. After that, the LC medium was photocured with a UV light source (365nm, 2mW/cm²) under the application of a monopolar electric field. The concentration of monoacylate in the LC medium was set at 0, 2 or 4wt%.

The spontaneous polarization was measured by the polarization current method utilizing a triangular electric field [14]. Using a Fourier transform infrared spectrophotometer FTIR-8400 (Shimadzu), polarized FT-IR spectra were measured as a function of the sample rotation angle. The measuring geometry is illustrated in Fig. 2. The rotation angle $\omega$ is defined as zero when the polarization direction of incident infrared light coincides with the rubbing direction of the cell. Three absorption peaks investigated are listed in Table 1. The chiral carbonyl group and the carbonyl group in the core part (abbreviated as the core carbonyl group) give well-separated absorption peaks, while
three phenyl rings give absorption peaks at the same wave number. Since the average stretching direction of phenyl rings is parallel to the long molecular axis, the information of the FLC molecular orientation can be obtained from the angular dependence of the phenyl ring stretching peak.

3. Results and discussion

Figure 3 shows the temperature dependence of the spontaneous polarization. It is guessed that the spontaneous polarization of the PSFLC is lower than that of a conventional FLC over the wide range of temperature because the UV photocure was done at the slightly lower temperature than the transition

Fig. 3. Temperature dependence of spontaneous polarization (0wt%: a conventional FLC; 2 and 4 wt%: PSFLCs). Tc is the SmA to SmC* phase transition temperature.

Fig. 4. Absorbance as a function of the cell rotation angle under the quiescent condition and the application of an electric field.
temperature of SmA to SmC\(^*\) (Tc) and then the rather low spontaneous polarization at the UV photocure temperature would be stabilized. It is attractive that the polymer stabilization technique can be controlled the temperature dependence of the spontaneous polarization of FLC.

In order to determine why the polymer network can stabilize the spontaneous polarization, we investigated the influence of the polymer stabilization on the hindered rotational motion by using the polarized FT-IR. Figure 4 demonstrates the sample rotation angular dependence of the absorbance for the phenyl rings, the chiral carbonyl group and the core carbonyl group stretching peaks in conventional FLCs. It is confirmed that the molecules freely rotate around the long molecular axis in the helicoidal structure of FLC at the quiescent condition, since the phase difference of the angular dependence between the phenyl ring and the carbonyl groups is \(\pi\). On the other hand, the hindered rotational motion is observed under the application of an electric field, since the phase difference is neither 0 nor \(\pi\). As the hindered rotational motion may be described by the distribution function of the carbonyl group

\[
f(\psi) = \left(\frac{1}{2\pi}\right)\{1 + a \cos(\psi - \psi_0)\}
\]

(1)

where \(a\) is the degree of hindrance and \(\psi_0\) is the most probable orientation, we can simulate the absorbance as a function of the cell rotation angle; \(A(\omega')\) in which \(\omega' = \omega - \theta\) (\(\omega\) is the cell rotation angle and \(\theta\) is the molecular tilt angle) [10]. When the absorbance takes the maxima at \(\omega' = \omega'_{\text{max}}\), the relationship between \(\omega'_{\text{max}}\) and \(\psi_0\) is shown in Fig. 5. Since the core carbonyl group is distantly separated from the chiral center, the mirror symmetry exists so that \(\psi_0 = 0\) in Eq. (1); i.e. the core carbonyl group appears to lie on the tilt plane [10]. Therefore, we can obtain the value of \(a\) for the core carbonyl group from the experimental result of \(\omega'_{\text{max}}\); as an example, \(a = 0.075\) for FLC-2 (\(\omega'_{\text{max}} = 84^\circ\) in Fig. 4(b)). Assuming that \(a\) for the chiral carbonyl group is equal to \(a\) for the core carbonyl group, \(\psi_0 = -70^\circ\) for the chiral carbonyl group of FLC-2 (\(\omega'_{\text{max}} = 87.5^\circ\) in Fig. 4(b)). Figure 6 shows the \(a\) dependence of the spontaneous polarization \((P_s)\) in all FLC media used in this research at the temperature much lower than \(Tc\). It is found that \(P_s\) is proportional to \(a\) in the both cases of a conventional FLC and a polymer-stabilized FLC. However, although the \(a\) increases in the respective FLCs due to the polymer stabilization, \(P_s\) decreases. Therefore, the decrease of spontaneous polarization owing to the polymer stabilization as shown in Fig. 3 does not originate in the variation of the hindered rotational motion.

It is well known that the spontaneous polarization is proportional to the tilt angle of FLC molecules (\(\theta\)). So,
Fig. 6. The dependence of spontaneous polarization on the degree of hindrance \( a \) (0 wt%: a conventional FLC, 2 and 4 wt%: PSFLCs).

we investigated the effect of polymer stabilization on the tilt angle. Figure 7 demonstrates the temperature dependence of the tilt angle. It is confirmed that both temperature dependences of \( P_s \) and \( \theta \) are very similar. Thus, it is concluded that the variation of the spontaneous polarization due to the polymer stabilization is mainly caused by that of the tilt angle.

4. Conclusions

A photocurable mesogenic monomer was mixed into ferroelectric liquid crystals (FLCs) in which dipole moments of carbonyl groups are the main source of the spontaneous polarization, and then polymer-stabilized ferroelectric liquid crystal (PSFLC) cells were fabricated. In this study, we researched the effect of polymer stabilization on the spontaneous polarization of FLC by analyzing the hindered rotational motion of the carbonyl groups in terms of a polarized FT-IR spectroscopy. It has been confirmed that the polymer stabilization technique can be controlled the temperature dependence of the spontaneous polarization. For this mechanism, it has been found that although the degree of hindrance increases due to the polymer stabilization, the polymer stabilization rather strongly influences the tilt angle of FLC molecules which is in proportion to the spontaneous polarization.

Acknowledgements

We gratefully thank Mr. S. Saito of Chisso Petrochem., Dr. H. Takatsu and Dr. H. Hasebe of Dainippon Ink & Chem. and Mr. H. Fukuro and Mr. H. Endoh of Nissan Chem. Ind. for supplying liquid crystal, photocurable monoacrylate and polyimide materials, respectively.

References

3. D. Armitage, J. I. Thackara and W. D. Eades,