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DIELECTRIC BEHAVIOR IN CHIRAL SMECTIC PHASES OF MAIN-CHAIN POLYESTERS

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Abstract We have investigated the SmA-SmC* phase transition of main-chain polyesters having a mesogenic *p,p'*-bibenzoate unit by means of the dielectric and electrooptic measurements. In the SmC* phase, a relaxation due to the Goldstone mode was observed at several 10 Hz. In addition, we recognized the other relaxation exhibiting softening behavior around the SmA-SmC* phase transition temperature.

INTRODUCTION

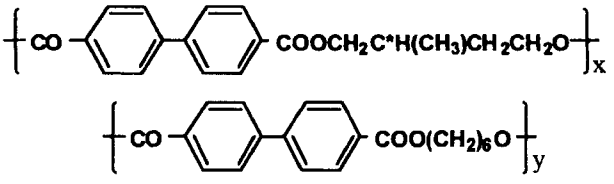
Since the realization of surface stabilized ferroelectric liquid crystalline devices,[1] a variety of materials have been synthesized in order to improve the material properties for the device application. Recently, the search for new ferroelectric liquid crystalline materials has expanded to the field of liquid crystalline polymers (LCPs).[2,3] Using chiral mesogenic groups already used in low molar mass ferroelectric liquid crystals (FLCs), numerous ferroelectric liquid crystalline polymers (FLCPs) have been synthesized. While mesogenic groups can be incorporated into a polymer not only as side chains but also as part of the main chain, most of the FLCPs described so far belong to the former case which gives rise to the so-called side-chain LCP. Since the polymeric and mesogenic effects are relatively uncoupled in the side-chain FLCPs, the physical properties are usually predictable from those of the low molar mass FLCs.[4,5] On the other hand, few studies about the main-chain FLCPs have been done,[6-8] and the details of the physical properties are not disclosed.

Recently, Watanabe *et al.* confirmed the ferroelectricity of the chiral smectic C* (SmC*) phase of a main-chain LCP which is constructed from *p,p'*-bibenzoate

and mixtures of (*S*)-2-methylbutanediol and hexanediol.[9,10] In this letter, the fluctuation behavior of the main-chain FLCP is investigated by means of dielectric spectroscopy as well as electrooptic methods. In the polymeric SmC* phase, a relaxation of the Goldstone mode due to the contribution of the spontaneous polarization is easily observed at several 10 Hz. In addition, we recognize the other relaxation exhibiting softening behavior around the SmA-SmC* phase transition temperature. We will report the experimental details and discuss the fluctuation models responsible for the dielectric and electrooptic behavior.

EXPERIMENTAL

The sample used was designated as BB-4*/6 which has a following chemical structure,[7,9]



The polymer was synthesized by melt transesterification of dimethyl *p,p'*-bibenzoate and a 50/50 w/w mixture of (*S*)-2-methylbutanediol and hexanediol. Here, the dimethyl *p,p'* -bibenzoate and hexanediol were used as received from Tokyo Kasei Kougyou Co., Ltd. The chiral (*S*)-2-methylbutanediol (optical purity;86%) was kindly supplied by Nippon Oil Co., Ltd.

The inherent viscosity of the prepared polymer, as determined at 25°C by using 0.50 g/dL solutions in a 60/40 w/w mixture of phenol and tetrachloroethane, ranged about 0.27 dL/g. The polymer showed a following phase sequence;

Solid-(114°C)-SmC*-(134°C)-SmA-(221°C)-Iso.

The transition temperatures listed above were determined by differential scanning calorimetry (DSC) in the heating cycle. DSC measurements were carried out at the rate 10°C/min. The phase sequence almost agrees with that already reported.[9]

In order to measure both of the dielectric constants and the electrooptic responses, homogeneously aligned cells were prepared. The material was sandwiched between glass plates separated by 12 μm thick spacers. The glass plates were coated with ITO as electrode. The dielectric measurements were carried out using an impedance analyzer (Solartron, 1260) as described in our previous paper.[11] In electrooptic measurements, the optical response was detected by a photomultiplier (Hamamatsu, R955) attached to a polarizing optical microscope under a sinusoidal wave, and the signal was amplified by a lock-in amplifier (NF, 5610B).

RESULTS AND DISCUSSION

We show the temperature dependence of the dielectric constants in Figure 1, where three temperature regions corresponding to the phase sequence confirmed by DSC are recognized. Two vertical dotted lines indicate the Solid-SmC* and SmC*-SmA phase transition temperatures determined by DSC. In the temperature dispersion curve measured at 10 Hz, the dielectric constant of the SmC* phase becomes larger than those of other phases because of the contribution of the spontaneous polarization. In addition, the effect of the soft mode is recognized in the curve measured at 300 Hz, where the contribution of the spontaneous polarization almost vanishes; the dielectric constant increases in SmC* with increasing temperature until it attains the maximum around SmC*-SmA phase transition point, and then decreases in the SmA phase.

In order to consider the detail of the fluctuation behavior, typical frequency dispersion curves in the SmA and SmC* phases are plotted in Figure 2. The contribution of the spontaneous polarization is seen in the frequency region less than 100 Hz, besides the conductivity contribution. A relaxation due to the spontaneous polarization is clearly observed at several 10 Hz in the dispersion curve of SmC*. Since the helical structure of BB-4*/6 has already confirmed,[7,9] the relaxation of the polymeric SmC* phase is probably due to the Goldstone mode associated with the helical fluctuation. In addition, the relaxation frequency is about the same as the Goldstone mode of the low molar mass FLC.[12]

For further discussion, we investigated the electrooptic properties of the BB-4*/6. Figure 3 shows the temperature dependence of the intensity of the electrooptic response under a sinusoidal electric wave of frequency 10 Hz. The measurements were carried out in a cooling process. The intensity is due to the field-induced apparent tilt angle. The softening behavior is clearly seen around the SmA-SmC* phase transition; the intensity of the response, namely the induced tilt angle increases gradually with decreasing temperature in SmA until it attains the maximum at SmA-SmC* phase transition point, and then decreases in the SmC* phase. Observing the softening behavior, we can easily determine the SmA-SmC* phase transition temperature which is indicated by a vertical dotted line in Figure 3. In the frequency dispersion curves of electrooptic response, we also observed the contribution of the Goldstone mode in the polymeric SmC* phase, in which the relaxation frequency of the electrooptic response corresponded to that of the dielectric measurements.[13] These electrooptic properties of the main-chain FLCP are similar to those exhibited by the low molar mass FLCs.

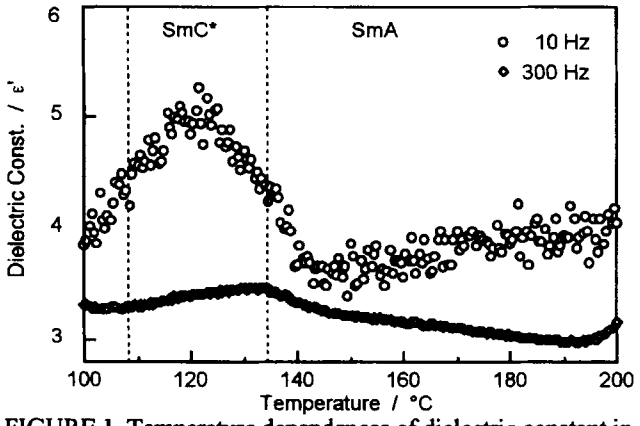


FIGURE 1 Temperature dependences of dielectric constant in a main-chain ferrolectric liquid crystal designated as BB-4*/6.

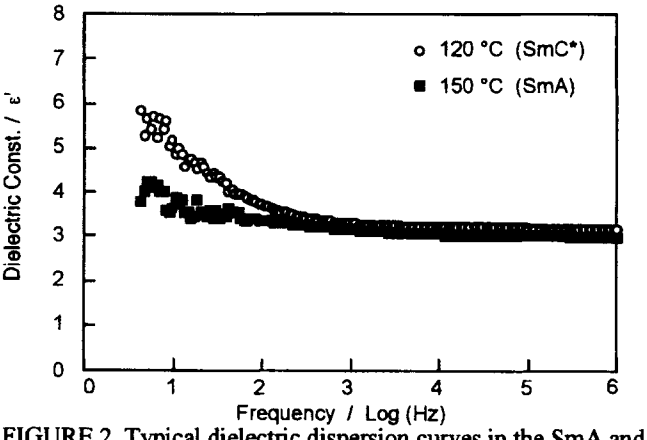


FIGURE 2 Typical dielectric dispersion curves in the SmA and SmC* phases of BB-4*/6.

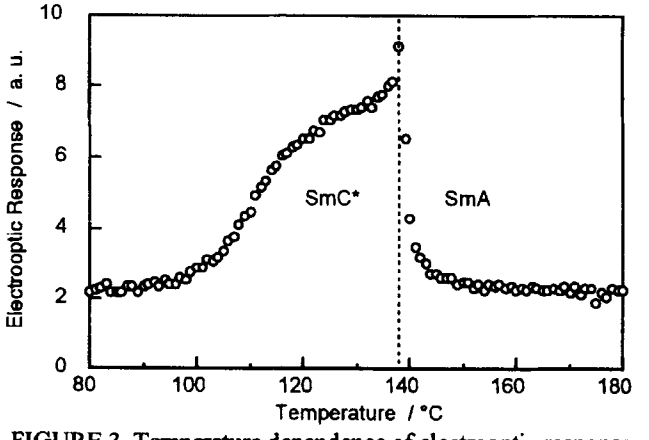


FIGURE 3 Temperature dependence of electrooptic response of BB-4*/6. Measuring frequency is10 Hz.

Let us consider the fluctuation processes of the Goldstone and soft modes of the main-chain FLCP, using the models speculated in Figure 4. For the sake of simplicity, we assumed that the length of the spacer part does not change in the fluctuation processes. We would like to say that the polymeric effect might not suppress the Goldstone mode described as the fluctuation of azimuthal angle ϕ around the helical axis, because no conformational change of the polymer is caused by the helical fluctuation as shown in Figure 4(a). We expect, therefore, that the Goldstone mode of the main-chain FLCP behaves in a similar way to that of the low molar mass FLC. On the other hand, we notice the tilt fluctuation bringing about the deformation of the polymeric chain in Figure 4(b), which shows that the polymer bends at a joint between the mesogenic core and the spacer part in the fluctuation process of the tilt angle θ. In the case of the material used, namely BB-4*/6, we can easily suppose that the deformation is attributed to the conformational change of the alkylene spacer. It seems that the alkylene spacer is too flexible to hinder the fluctuation of the tilt angle θ, because the softening behavior of the induced tilt angle was clearly seen in the electrooptic measurements.

Lastly, we would like to consider the SmA-SmC* phase transition behavior of BB-4*/6. The softening behavior of the field-induced tilt fluctuation implies that the mesogenic core also becomes tilted to the layer normal through the phase transition from SmA to SmC*. The conformation of the flexible alkylene spacer might vary according to the mesogenic tilt angle θ, as shown in Figure 4(b). In the previous paper, however, the X-ray diffractions indicated that the conformation of the polymer chain remains unchanged through the mesophase temperature region from SmA to SmC.[14] We would like to explain the discrepancy by the difference of the degree of polymerization. The inherent viscosities of the polymers used in the X-ray measurements were much higher than those in the electrooptic measurements. Moreover, the small angle X-ray scattering studies recently revealed that the chain foldings exist in the SmA phase.[15] Therefore, it is expected that the physical properties of the smectic phases strongly depend on the degree of polymerization: the change of the physical properties might occur, when the length of the polymer chain becomes longer than the correlation length between the chain foldings.

CONCLUSIONS

We have investigated the fluctuation behavior in the chiral smectic phases of a main-chain FLCP designated as BB-4*/6 by means of the dielectric and electrooptic measurements. The collective fluctuation processes such as the Goldstone and soft

modes are similar to those exhibited by the low molar mass FLCs, although the polymer molecule must adopt a conformation and packing that is compatible with the structure of the mesophases.

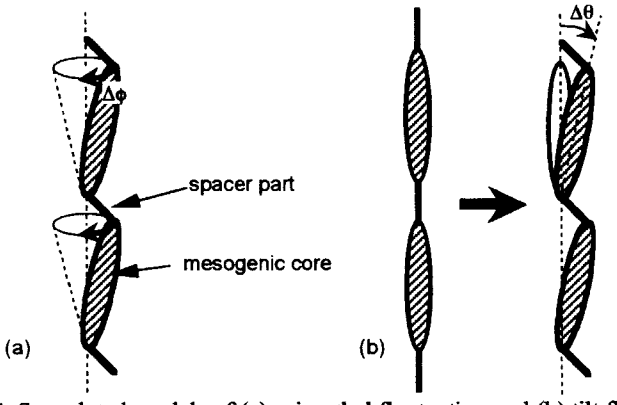


Figure 4 Speculated models of (a) azimuthal fluctuation and (b) tilt fluctuation of a main- chain FLCP. Note that the length of spacer part does not change in the fluctuation processes.

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