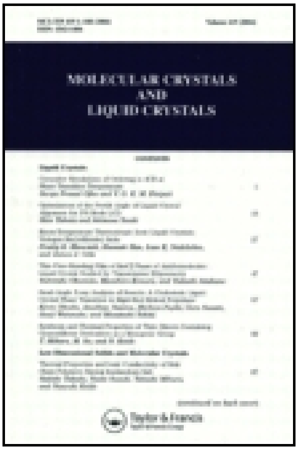

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Dielectric Investigations of a Chiral Monomer and Side Chain Polymer

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Dielectric Investigations of a Chiral Monomer and Side Chain Polymer

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The dynamics of different collective and non-collective modes in a chiral liquid crystalline monomer and its side-chain polymer have been studied by dielectric spectroscopy. The monomer system enabled us to study the temperature dependence of the dielectric permittivity when crossing the transition from the SmA* phase directly to the crystal phase. Although the polymer system has a SmA* to SmC* transition, we found that the temperature dependence of the dielectric permittivity is radically different from the normally observed behaviour in these phases. The contributions from the soft and Goldstone modes, respectively, are extremely low, a result which is related to the very low value of the spontaneous polarization of the material. At lower temperatures in the SmC* phase, a very weak dielectric absorption located around 50 kHz is observed and discussed in terms of the liberational motion of side chains around the polymer main chain.

Keywords: dielectric spectroscopy; liquid crystal; monomer; polymer; soft mode; Goldstone mode

INTRODUCTION

Since the realization of ferroelectricity in chiral smectic C* (SmC*) liquid crystals [1, 2], low molar mass and polymeric ferroelectric liquid crystals have been extensively investigated. The interest in optimizing their physical properties for device applications is growing rapidly. To this end, the study of the dynamics of different collective and non-collective processes is of great interest because of their relations to important material properties such as the rotational viscosity [3-4]. Dielectric relaxation spectroscopy has proven to be a powerful tool in studying these processes in both monomeric and polymeric systems [5-6].

In the present work, we have investigated the static and dynamic dielectric properties of a liquid crystalline monomer and its side chain polymer. Both possess a SmA* phase and the polymer also possesses a broad SmC* phase. Although a very narrow supercooled SmC* phase can be obtained in the monomer system, crystallization normally takes place directly from the SmA* phase. Thus, this monomer permits us to study a rare case of a strong first order transition (SmA* - crystal phase transition) which is not often discussed in literature.

EXPERIMENTAL

The monomer (figure 1a) consists of a bis-benzoate mesogenic unit bearing a chiral 2-methylbutoxy group and an undecenyloxyl flexible segment. The polymer (figure 1b) was synthesized by grafting the monomer onto a preformed poly(hydrosiloxan) by a Pt-catalyzed hydrosilylation reaction.

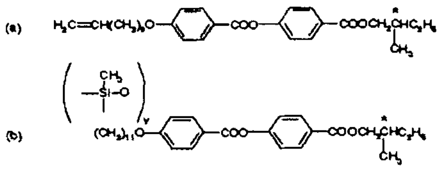

FIGURE 1. Structures of the studied monomer (a) and polymer (b).

The dielectric measurements were carried out in the frequency range 10 Hz to 13 MHz using the HP 4192A dielectric bridge, with a measuring voltage of 0.5 V_{pp} applied across the sample. The sample temperature was controlled with a Mettler hotstage and monitored using a PT-100 sensor connected to a thermometer.

The sample cells (8, 18 and 36 μm thickness) consisted of two glass plates coated with a conducting ITO (Indium Tin Oxide) layer with a sheet resistance of 20Ω/□. Two thin layers of SiO_x were further evaporated onto each surface. The first, which is evaporated normal to the surface, acts as an insulation layer to avoid electrical breakdown of the cell at high field strengths. The second layer produces a planar alignment with the smectic layers essentially perpendicular to the glass plates.

In addition to the contribution from the dipolar reorientation, the measured dielectric absorption ε'' contains spurious components (background) in the low and high frequency parts of the spectrum. At low frequencies the absorption increases drastically due to the conductivity contribution from the mobile charge carriers (ions), and at higher frequencies there is a spurious peak due to the resistance of the ITO layer. In polymer systems, where the phase transition temperatures can be quite high, the low frequency problem becomes more serious since the number of free charge carriers increases with temperature. In the present work the conductivity tail was found to be very large which made resolving the soft mode (tilt fluctuations [6]) and Goldstone mode (phase fluctuations [6]) absorption peaks non-trivial. The more so as these absorptions were found to be extremely weak.

For analyzing the results, equation (1), the Cole-Cole equation with two additional terms representing the background absorptions, was fitted to the experimental data.

$$\varepsilon'' = \frac{\sigma}{2\pi\varepsilon_0}\left(\frac{1}{f^n}\right) + Im\left(\varepsilon_\infty + \frac{\Delta\varepsilon}{1 + \left(j\frac{f}{f_r}\right)^{1-\alpha}}\right) + a(R, C)f^m \qquad (1)$$

Here σ and a are fitting parameters representing the low frequency ionic tail and the high frequency ITO absorption, respectively. The corresponding exponents n and m are both close to 1. A dielectric process is characterized by its contribution $\Delta\varepsilon$ to the dielectric permittivity, its relaxation frequency f_r and symmetric distribution parameter α.

RESULTS AND DISCUSSION

Static Dielectric Permittivity of the Monomer

The temperature dependence of the static dielectric permittivity ε' is shown in figure 2. On cooling, three phases could be clearly distinguished; isotropic, SmA* and crystal. In the SmA* phase, ε' increases linearly with decreasing temperature and at the onset of crystallization it decreases suddenly from 5.5 to 2.5. The observed increase in ε' is attributed to a soft mode. Note that ε' does not diverge close to the SmA* to crystal transition temperature, which is due to the first order nature of the transition. On heating, the melting from crystal to SmA* is observed 7°C above the crystallization temperature. On further heating a transition from the SmA* phase to the isotropic phase is observed at 53°C.

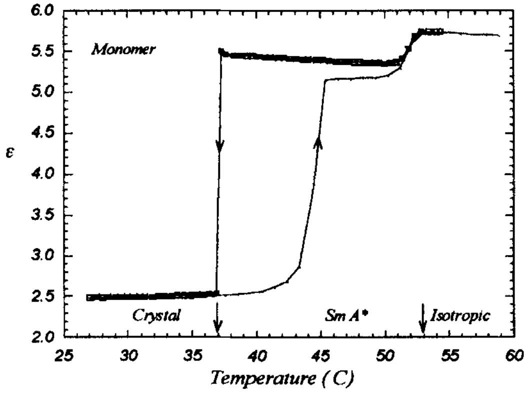

FIGURE 2. Temperature dependence of the static (200 Hz) dielectric permittivity of the monomer on cooling and on heating. The curves do not coincide in the SmA* phase, probably due to incomplete melting when heating from the crystal phase.

Quasi-static Dielectric Permittivity of the Polymer

Figure 3 shows the temperature dependence of the quasi-static (f=600 Hz) dielectric permittivity in the smectic phases of the polymer. Throughout the whole mesophase range, ε' increases linearly with sinking temperature but at the SmA* - SmC* transition there is a slight kink in the curve. The normally observed increase of the dielectric permittivity in the SmC* phase due to the Goldstone mode [6], is not present in this material. We explain this behaviour by the very low polarization values ($P_s \approx 2$ nC/cm^2) of the substance which leads to a very low Goldstone mode contribution $\Delta\varepsilon_G$ to ε', see equation (2).

$$\Delta\varepsilon_G = \frac{1}{2\varepsilon_0 K_\varphi}\left(\frac{1}{q}\frac{P_s}{\theta}\right)^2 \tag{2}$$

K_φ is the elastic constant for the cone motion and θ is the tilt angle.

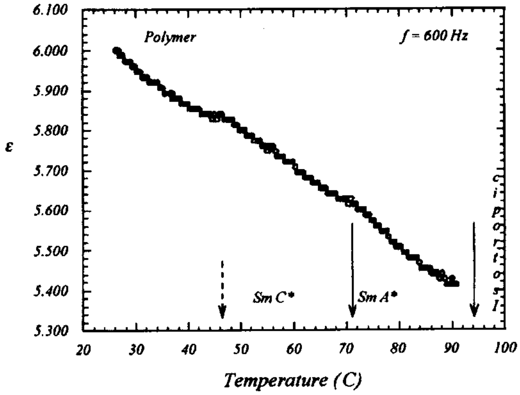

FIGURE 3. Temperature dependence of the quasi-static (f=600 Hz) dielectric permittivity in the SmA* and SmC* phases of the polymer compound.

At 46°C, in the SmC* phase, there is an appreciable change in the temperature dependence of the dielectric permittivity. This may be an indication of a glass transition.

Dynamic Dielectric Permittivity

Both the monomer and the polymer exhibit extremely weak absorptions which are hard to resolve experimentally. Therefore we present the values of relaxation frequency and dielectric strength only at some selected temperatures in different phases.

The monomer system

Figure 4 shows the frequency dependence of ε'' in the isotropic, SmA* and crystal phases of the monomer. In the isotropic phase an absorption has been observed around 1 MHz, which could be connected to the molecular reorientation around the short axis. In the SmA* phase, an absorption with a characteristic frequency in the kHz regime, is observed. This is interpreted as a soft mode. In the crystal phase the dielectric spectrum, as expected, does not contain any absorption in the studied frequency range, thus indicating that all dipolar reorientations are frozen out.

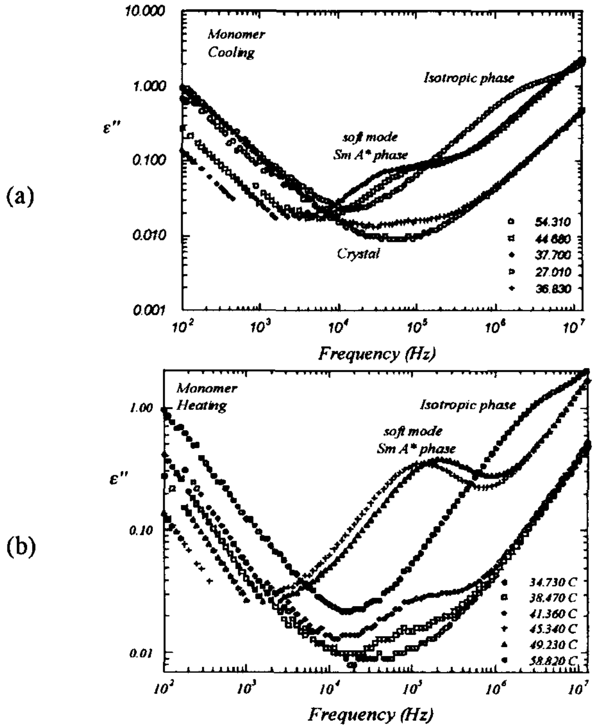

FIGURE 4. (a) Frequency dependence of the dielectric absorption of the monomer in different phases on cooling. (b) Corresponding results on heating.

The narrow supercooled SmC* phase of the monomer could not be resolved in the present study.

The polymer system

In the SmA* phase (see figure 5) one absorption, located in the kHz range and attributed to a soft mode, could be observed. As can be seen in the figure, the amplitude of this absorption is very weak which suggests that the perpendicular component of the dipole moment is very small. In the SmC* phase (figure 6a) the dielectric spectrum reveals a very weak maximum located at about 1 kHz which could be attributed to a Goldstone mode.

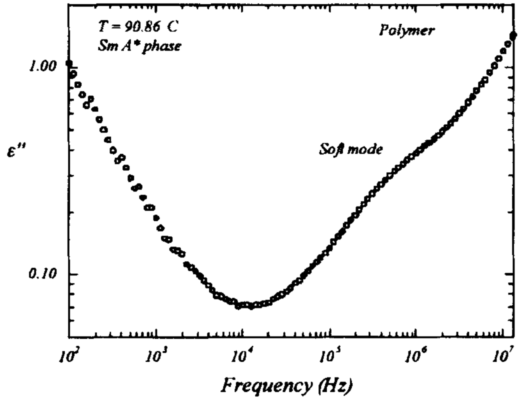

FIGURE 5. Frequency dependence of the dielectric absorption of the polymer in the SmA* phase.

At lower temperatures in the SmC* phase (see figure 6b) we observed an additional absorption at about 50 kHz. At higher temperatures this could not be resolved. This absorption may be attributed to a kind of liberational motion of the long axes of the mesogenic groups around the main chain. The appearance of this absorption at lower temperatures in the SmC* phase is correlated to the change in the temperature dependence of the dielectric permittivity at 46°C (see figure 3). As mentioned earlier this change could be connected to a glass transition of the polymer. If the system forms a glassy structure the viscosity increases rapidly, thus slowing down such rapid processes as the liberational processes so much that we can see them in our frequency window.

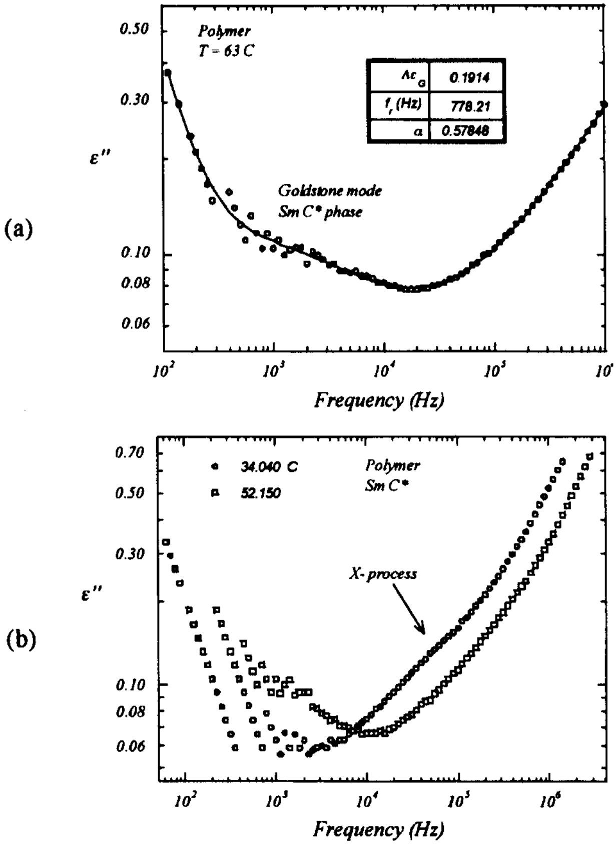

FIGURE 6. Frequency dependence of the dielectric absorption of the polymer in the SmC* phase at different temperatures.

CONCLUSIONS

We have studied the temperature dependence of the dielectric permittivity of a liquid crystalline monomer and its side-chain polymer, over a relatively broad frequency band. Both investigated compounds exhibit extremely weak absorptions which are difficult to resolve experimentally. The soft mode relaxation frequency of both the monomer and the polymer was found to lie in the high kHz region of the spectrum. The Goldstone mode has a relatively low frequency (800 Hz) but this was difficult to determine accurately as a good fit could only be obtained by using a very large distribution parameter α.

From the temperature dependence of the dielectric permittivity in the monomer, it is clear that ε' does not show any tendency to diverge at the SmA* to crystal transition. Contrary to the normal case with liquid crystals featuring a SmC* phase, the dielectric permittivity of the polymer did not increase drastically at the transition to this phase. The weak values of the Goldstone and soft modes are connected to the very low P_s values of the materials.

Based on the observed temperature dependence of the dielectric permittivity of the polymer system, and on the emergance of a new absorption in the low temperature region of the SmC* phase, we suggest that the material features some kind of glassy transformation within the SmC* phase range.

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