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Dielectric measurements on the 'isotropic smectic phase' of dyed side group polymers

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A comparative study of frequency domain dielectric relaxation in the SmA phase proper and in the TGB-like amorphous state (the 'isotropic smectic phase') is reported for two chiral photochromic copolymethacrylates. The phason mode of the helical TGB phase has been detected, and photoinduced ordering effects have been observed by dielectric methods. Temperature dependent dielectric measurements show Vogel–Fulcher behaviour on both heating and cooling cycles. A molecular relaxational mode with activation energy 1.04 eV was calculated from the Arrhenius plot in the higher temperature region of the SmA phase.

1. Introduction

An 'isotropic smectic phase' of chiral methacrylic homo- and co-polymers with phenyl benzoate side groups has been reported in previous papers [1, 2]. The observed mesophase possesses a layer structure according to DSC, X-ray and broad line NMR data, but shows no birefringence of visible light. A TGB-like amorphous smectic structure with extremely short helical pitch ($\lambda \sim 200$ nm) was suggested later for the mesophase [3]. For related dichroic copolymers—see SK8 in this work—with some proportion of azobenzene pendant groups, it has also been shown that the formation of the twisted TGB-like structure can be controlled by light illumination which induces a flip-flop of the azo fragment, thus changing the shape of the dichroic side group, its dipole moment, and (induced) chirality [4]. Detailed measurements were carried out [4] on such materials which are very interesting for optoelectronic and photorecording applications.

The detection of dielectrically active modes related to a helicoidal structure is well known from ferroelectric liquid crystals (FLCs) where they are called the Goldstone mode [5] or according to Musevic *et al.* [6] the 'phason mode'. It is relevant for common ferroelectric liquid crystals that we should point out a significant difference between the original theory by Goldstone [7] and the experimental observations on FLCs [8, 9]. The original definition [7] describes a symmetry restoring 'gapless' mode at zero frequency. Such a mode is not detectable by dielectric spectroscopy on a chiral SmC* phase [9] because it requires some perturbation of the spatial director configuration against elastic and surface interactions. The assignment as Goldstone mode demands a completely developed helicoidal ordering, at least in domains. However, since the name 'Goldstone mode' was introduced into literature, this term has been widely used, although its meaning is slightly different from that of the original concept. We would like to stress that 'phason mode' is a more generally applicable expression, whereas the term 'Goldstone mode' is somewhat too specialized to use in the case of chiral SmC* phase ordering. The idea of the structural habit inside the the polymers under investigation is better described as a periodical twist with some helicoidal aspects. That is the reason why we do not wish to be too precise about the exact definitions of this dielectrically active mode with its origin in collective fluctuations on helicoidal ordering. However, the materials above seem to be very interesting for investigation, as compared with conventional ferroelectric polymers [10].

Here we report the first results on the peculiarities of dielectric relaxation in the TGB-like 'isotropic smectic phase' (IsoSm* phase) of side chain polymers. The two particular copolymers, SK8 and SK16 (figure 1) were chosen for the investigation because they can form at any temperature below the clearing point either the SmA phase proper or the twisted TGB-like phase; these events depend moreover on previous history of the sample. This capability enables a comparative study of dielectric relaxation in both phases.

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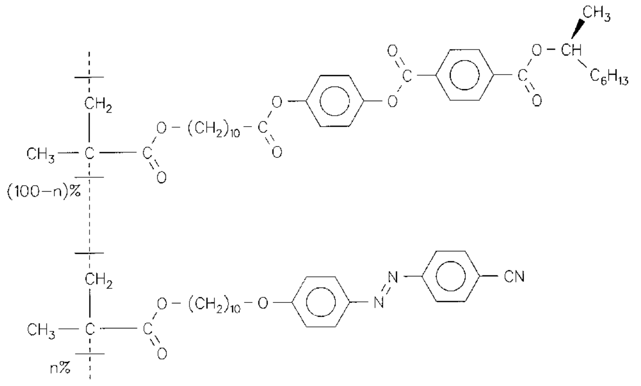


Figure 1. Chemical structure of the copolymers SK*n*, where *n* = 8 and 16 is the concentration of dichroic azobenzene side groups (mol %).

2. Experimental

The structure of the copolymers SK8 and SK16 is shown in figure 1 and their phase transitions (under different conditions) are summarized in the table. The synthesis of the copolymers has been described earlier [11].

Polarizing light microscopy (Leitz, Orthoplan Pol) in conjunction with an Instec hot stage, and differential scanning calorimetry (DSC2, Perkin Elmer) were used for the investigation of textures and phase transitions. Dielectric measurements were performed using an HP4192A impedance analyser controlled by an Atari 1040 computer [5]. The capacitor cell for measurements was a commercially available ITO covered cell (by E.H.C., Ltd) with $4 \times 4\,\mathrm{mm}^2$ sample area, 10 μm thickness and without any surfactant treatment. The substance was filled into the cell by capillary action at 70°C. During the measurements, the temperature of the oven was controlled using a Eurotherm 818 regulator with stability better then ±0.05 K. Dielectric measurements as a function of temperature were performed on heating and cooling cycles. For good temperature stabilization, a driving procedure with a decreasing cooling/heating rate was applied in the approach to the final temperature for the dielectric measurements.

Table. Phase transitions of the copolymers SK*n*.

Copolymer	Phase transition temperatures/°C
SK8	$\begin{tikzcd} \text{SmA* glass} \arrow[r, leftrightarrow] & \text{SmA*} \arrow[r, "62"] & \text{IsO} \arrow[dl, leftrightarrow, "53.3", "29.9"'] \\ \text{IsoSm* glass} \arrow[r, leftrightarrow, "\text{(fast)}"] & \text{IsoSm*} \arrow[u, "\text{slow}"] & \end{tikzcd}$
SK16	$\begin{tikzcd} \text{SmA* glass} \arrow[r, leftrightarrow] & \text{SmA*} \arrow[r, "63"] & \text{IsO} \arrow[dl, leftrightarrow, "58.5", "29.0"'] \\ \text{IsoSm* glass} \arrow[r, leftrightarrow, "\text{(fast)}"] & \text{IsoSm*} \arrow[u, "\text{slow}"] & \end{tikzcd}$

The dielectric spectra obtained were corrected by taking into account the residual impedance of cables, connections and the ITO electrodes. Characteristic relaxation parameters such as relaxation strength $\Delta\varepsilon''$, critical frequency f_0, and the distribution parameter α of the different processes were obtained by data analysis via a computational fitting procedure with the Cole–Cole equation (1) [12] and if needed, one additional term for the low frequency conductivity contribution to the spectra at higher temperatures.

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_S - \varepsilon_\infty}{1 + (\mathrm{i}\omega\tau)^{1-\alpha}} \tag{1}$$

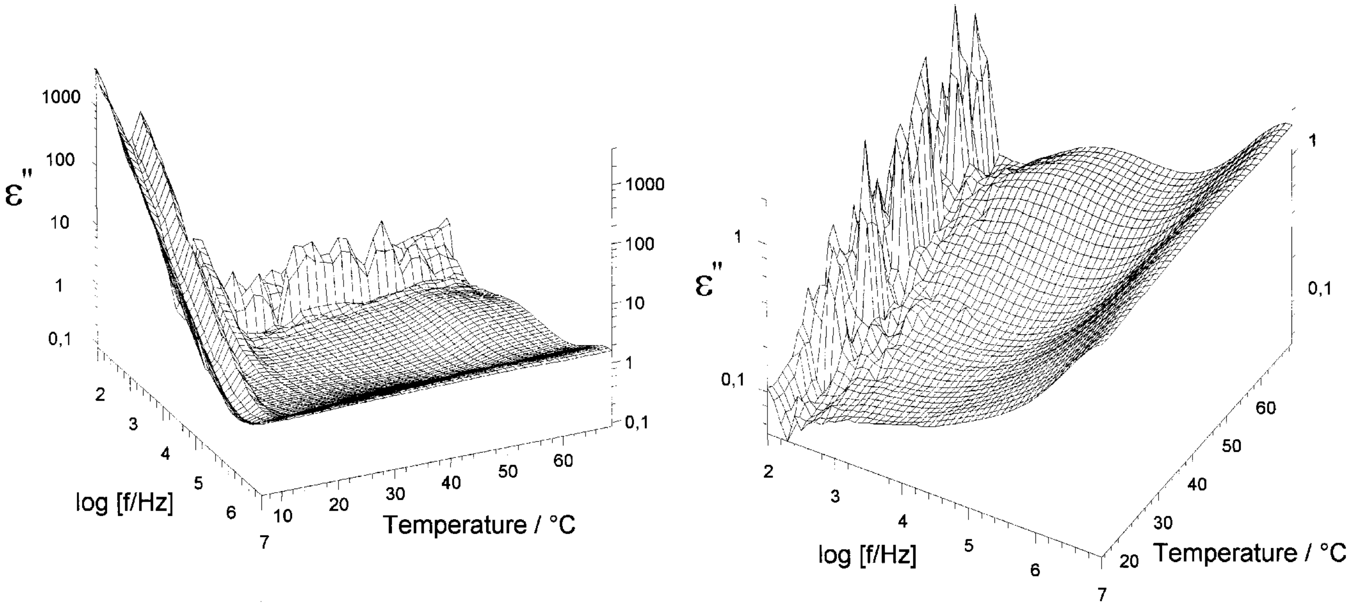
3. Results and discussion

The two states under investigation were the transparent, non-birefringent IsoSm* phase and the turbid, birefringent polydomain SmA phase which were obtained by spontaneous fast cooling of the polymer and first slow cooling at $3\,\mathrm{K\,h^{-1}}$, respectively. The dielectric spectra in relation to temperature of both phase states are shown in figure 2 as three dimensional graphs. For best viewing, the dielectric absorption ε'' was chosen on a logarithmic scale to cope with the enhanced contributions to the ε'' spectra at lower temperatures and frequencies in the IsoSm* phase. The frequency abscissa is also chosen on a logarithmic scale writing only the decadic exponents of the complementary frequency.

Figure 3 shows the retardation of a dielectrically active relaxational process. In the higher temperature region the process shows clear Arrhenius behaviour with an activation energy of 1.04 eV. The process obviously shows no change in the activation energy on passing from the isotropic smectic phase to the SmA* phase. Therefore we assume that this process is an ‘isotropic’ process prolonged into the SmA* phase. Below 48°C, Vogel–Fulcher behaviour is observed, i.e. a drastic decrease of the relaxational frequency along with broadening of the process.

Below 44°C, reliable fit data could not be obtained because of the low amplitude of the absorption process which turns into a broad absorption band with a large α-parameter. Such a broadening of the relaxation process on cooling is typical for polymers. As seen from figure 4, the α-parameter of the fits with the Cole–Cole-equation (1) increases non-linearly with cooling, starting from the value $\alpha \sim 0.5$ typical for polymers [13]. The temperature range shown in figure 4 corresponds to the mesophase and the parameters behave exactly in the same way on heating and cooling.

There is no difference in the dielectric behaviour between the IsoSm* and the SmA states at temperatures above 30°C. In the range 20 to 30°C, the deviations are quite small and not pronounced enough to give evidence



IsoSm* & SmA phase

SmA phase

Figure 2. Three dimensional plots of ε'' versus frequency and temperature for SK16 for the clear isotropic smectic phase and the turbid normal smectic A phase measured for a 10 μm EHC cell without surfactant. The ε'' axis is on a logarithmic scale.

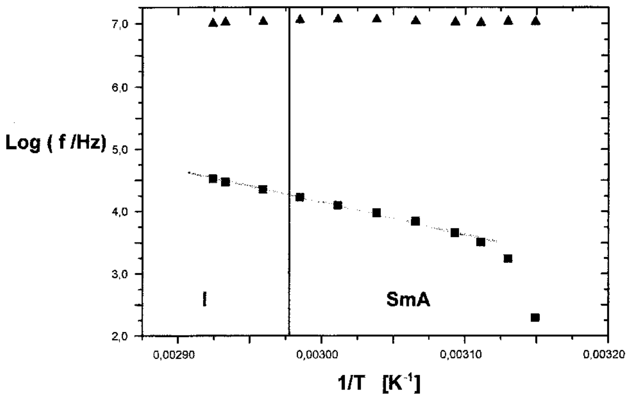


Figure 3. Arrhenius plot for SK16 on cooling: (■) the molecular mode, (▲) the mode connected with the resistivity of the ITO surface layer. The grey line is a guide line for the eye in the regime of Arrhenius-like behaviour.

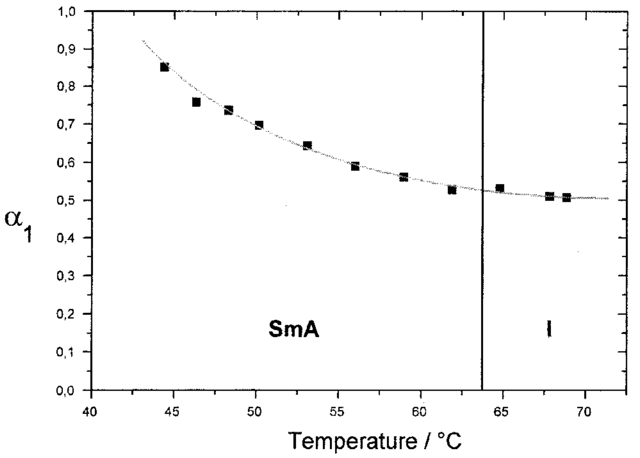


Figure 4. Distribution parameter α for the Cole–Cole fits of SK16 on cooling. The grey line is a guideline for the eye.

for any effect. In contrast, below 20°C there is a drastic difference in the ε'' (and tan δ) measurements for the two mesophases which is most probably connected with an internal tension of the quenched material. The dielectric dispersion, ε', shows no significant changes, but the measurements are more 'noisy' in the IsoSm* state. Figure 5 shows the dielectric absorption, ε'', versus frequency for the two phase states at 16.5°C. In contrast to the SmA state, the spectra for the IsoSm* phase exhibit a strong contribution at lower frequencies. Thus, for fit analysis we applied a single Cole–Cole function along with a term describing a non-linear conductivity contribution. The fit results are drawn into the figure and annotated as conductivity and phason mode.

Up to now it is not clear whether this process at low frequencies appears due to the tension created during the fast cooling of the sample and conserved in a glass (which is also worthy of investigation), or it is characteristic for the IsoSm* phase. We should note here however that the spontaneous cooling of the polymer sample in air from 70°C to ambient temperature during 0.5–5 min, resulting in conservation of the IsoSm* phase, was not fast enough to be interpreted as quenching or, moreover, shock cooling.

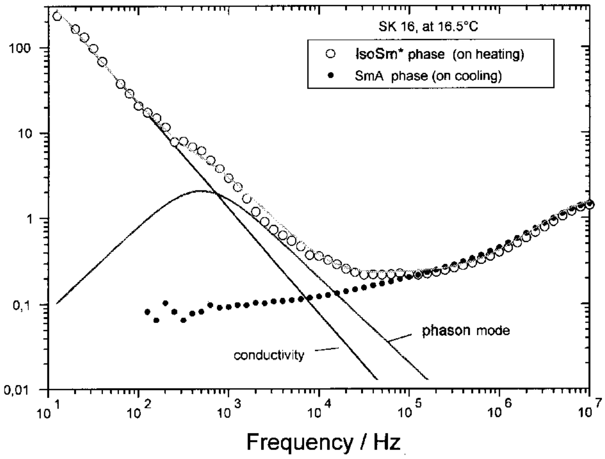


Figure 5. Dielectric absorption ε'' versus frequency for the IsoSm* phase (○) and SmA phase (●).

The strong absorption at lower frequencies may be explained by the assumption that the transparent, non-birefringent IsoSm* phase possesses a short pitch helical superstructure either of the TGB type, as suggested in previous papers [3, 4], or maybe similar to the newly described 'smectic blue' phase [14]. Such a twisted structure can show fluctuations around a helical axis parallel to the surface plane. The helical ordering in the IsoSm* phase has been confirmed by circular dichroism measurements and by UV data [3, 4]. If the fluctuations on the azimuthal angle of such a helical dipolar ordering exist, a phason mode should be detectable. For exhibition of a phason mode, formation of a complete helix is generally not required: some fractions like those existing in the twist grain boundary (TGB) phases can provide the necessary conditions. In the scope of the concept developed, the fluctuation process above is accompanied by charge transport across the sample, since the fluctuations of each helically ordered grain will move the charge carriers like a worm drive. For a better understanding, the original experimental values of tan δ are presented in figure 6 as a function of frequency.

4. Conclusions

The 'isotropic smectic phase' of chiral side group copolymers has been investigated for the first time by means of dielectric spectroscopy. The dielectric constant, ε^*, and dielectric loss, tan δ, have been measured as functions of frequency and temperature. Compared with the SmA phase proper of the same polymers, an additional phason absorption has been observed for the IsoSm* phase below room temperature; this could also be called 'Goldstone-like' according to this well known concept.

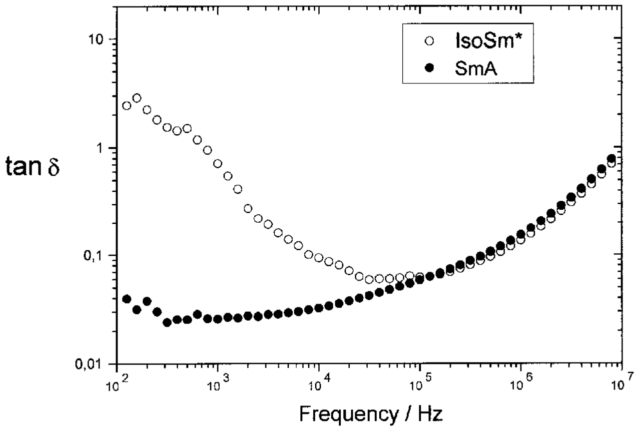


Figure 6. Dielectric loss, tan δ versus frequency for the IsoSm* phase (○) and SmA phase (●).

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