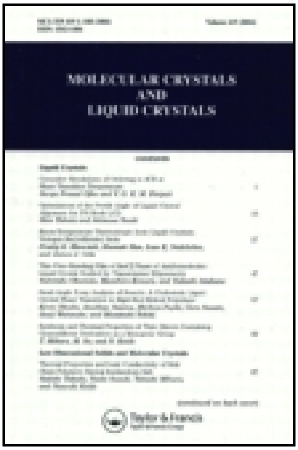

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Time-Resolved Polarized FTIR-Spectroscopy on the Molecular Structure and Mobility of Ferroelectric LC Elastomers (FLCE)

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Time-resolved FTIR-spectroscopy is employed to study structure and mobility in ferroelectric LC polymers and elastomers (temperature range 20°C...130°C, dynamic range 0.1 Hz...10^5 Hz). Due to its specifity the analysis of the (polarized) IR-spectra enables to determine the average orientation, the orientational order and the mobility in response to an electric field for the different molecular moieties (phenyl group, the polar groups, the methylene spacer and the polymer backbone). Furthermore the phase relationship in the motion of the different molecular groups can be extracted.

Keywords: Ferroelectric LC Elastomers; FTIR-spectroscopy

INTRODUCTION

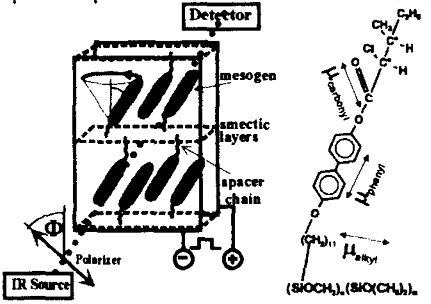
The synthesis of ferroelectric liquid crystalline elastomers (FLCE)[1,2] supplies a new class of materials that combines the optical and electrical characteristics of ferroelectric liquid crystals with the mechanical properties of an elastic network. The interaction between the Coulomb energy of the FLC in an external electric field with the elastic energy of the network plays a key role for the understanding of these features. Till present there are just a few publications that elucidate this interaction for surface stabilized FLCE cells[3,4].

Time-resolved FTIR-spectroscopy enables to study the reorientation dynamics in response to an external electric field on a molecular level and has given yet a variety of information about low molecular and polymeric FLC cells[4-10]. FTIR studies on different kinds of FLCE and FLCP samples (shear oriented in cells, freestanding films and microtomized sections of single crystalline (SC-) FLCE) give a detailed view on the molecular reorientation behavior and thus on the influence of the elastic network forces.

EXPERIMENTAL PART

The FTIR investigations were performed in the Sm-C* phase of sidechain FLC polymers and elastomers. The polymer shown in Fig.1 is used as precursor of a photocrosslinkable FLCE whereas in the single crystal (SC-) FLCE the network is formed by thermally crosslinking groups. These two substances consist of different mesogenic groups being attached to the polymethylsiloxane backbone. For FTIR measurements under influence of an external electric field this bulk SC-FLCE is microtomized to 5μm thick sections of different orientations and these sections are placed between CaF_2 plates coated with conductive ITO layers. These cells are also used for shear orientation of the photocrosslinkable FLCP melts. Freestanding films of this FLCP are prepared by suspending the substance on the edge of two small glass slides. By variation of the gap between these slides the thickness of these films can be controlled. In contrast to the bookshelf geometry of the shear oriented cells the freely suspended films have a homeotropic orientation and the electrical field has to be applied in the plane of the film.

In a time-resolved experiment the FTIR spectra are collected for a whole set of fixed polarizer angles ($\Phi = 0°$ to $180°$) with a time resolution of 5 μs. Then the obtained data are reorganized in order to determine for each time and each IR band the polarizer angle dependent absorbance plot A(Φ) from which the polarizer angle of maximum absorbance A_{max} and the dichroic ratio $R = A_{max}/A_{min}$ is derived. By that for the different molecular moieties the average orientation projected in the plane perpendicular to the beam propagation is obtained. The angle between this average orientation and a reference axis (layer normal in case of Fig. 1) is denoted "apparent angle γ of the corresponding molecular segment". The orientational order of these segments is determined. All spectra were recorded with a spectral resolution of 4 cm^{-1}. The temperature of the sample was stabilized within ± 0.1 °C. The attachment of an IR microscope (BioRad UMA 500) to the spectrometer (BioRad FTS 6000) enables to measure ferroelectric domains as small as 30μm x 30μm in the infrared and in the visible (between crossed polarizers).



Assignment	wavenumber [cm^{-1}] film & cell	SC-FLCE
ν^{phenyl} I	1499	1500
ν^{phenyl} II	1608	1609
$\nu^{carbonyl}$	1765	1736
ν_{as}^{nitro}	–	1540
ν_{s}^{nitrp}	–	1350
ν_{as}^{CH2}	2924	2924
$\nu_{as}^{C-O-C}; \delta^{Si-CH3}$	1261	1261

FIGURE 1 Experimental setup for a shear oriented FLCP in a CaF_2 cell and assignment of the infrared bands for the different samples.

RESULTS AND DISCUSSION

For the determination of the orientation of the different molecular units we used the infrared bands listed in Fig. 1. The transition moments of the phenyl bands are about parallel to the para-axes of the phenyl rings. Hence the polarizer angle of their maximal absorbance delivers the projection of the average long mesogenic axis ("apparent angle γ of the director"). The polar groups (carbonyl and nitro) are studied in detail as they play a major role for the existence of a spontaneous polarization in FLC. The alkyl vibrations can be used to characterize the orientation of the spacer chains. The methylsiloxane vibration band is overlapped by the C-O-C band assigned to the mesogen so that their interpretation is less straightforward.

Shear Oriented FLCE

The reorientation behavior of the different molecular moieties in the shear oriented and UV-crosslinked FLCE in a CaF_2-cell is studied in response to a rectangular field of $\pm 5\times 10^5$V/cm. From the polarizer angle dependent absorbance $A(\Phi)$ determined in steps of 5μs for the switching process the polarizer angle of extremal absorbance is derived[4]. This angle of the average orientation for the different corresponding molecular units (apparent angles γ) in dependence of the evolution time is presented in Fig. 2. The polarizer angle $\Phi = 0°$ is normal to the shearing direction and normal to the smectic layers.

The apparent angle of the phenyl vibration changes from $\gamma = -17°$ to $+17°$ when the field polarity is reversed. This reflects the reorientation of the director on a cone with a tilt angle of 17°. Measuring the time that the mesogens need to reorient (from the initial apparent angle to 90% of the final apparent angle) one obtains 2.2 ms as switching time from negative to positive field and 1.2 ms as switching time from positive to negative field. This result shows that these two states are not equivalent with respect to their free energy density due to the additional elastic energy caused by the crosslinking network. For similar results on the electrooptical switching Brehmer[3] introduced a Hook energy term $g(\vartheta) = 0.5\ D\ (\vartheta-\vartheta_0)^2$ depending on the tilt angle ϑ of the mesogen where ϑ_0 is the tilt where the FLCE has been crosslinked. Comparing the switching time of this FLCE with that of the

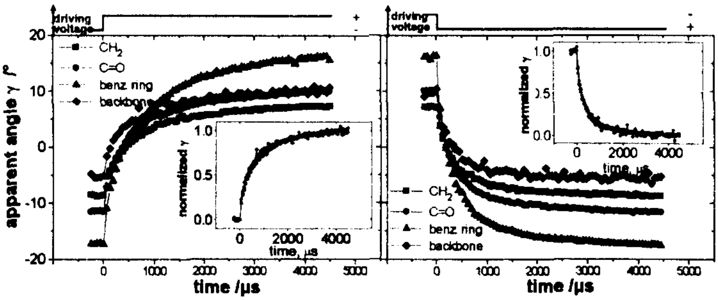


FIGURE 2 Evolution of the apparent angle γ for the shear oriented UV crosslinked FLCE (Sm-C*, $E = \pm 5\times 10^5$V/cm). The corresponding normalized curves (inlets) prove the synchronous reorientation of the different molecular units.

corresponding uncrosslinked polymer of 0.45 ms[4] one must conclude that the crosslinking has increased the viscosity for the mesogen rotation on the tilt cone. The other bands under investigation exhibit smaller apparent angles than the phenyl bands throughout the whole switching process. For those bands that indicate the orientation of the spacer and the polymer backbone, this deviation shows that these molecular segments are tilted less than the mesogens with respect to the smectic layer normal. Thus it is obvious that the reorientation of the mesogens is decoupled from the polymer backbone by the alkyl spacer. For the carbonyl band this deviation in the apparent angle proves the biased rotational distribution around the mesogenic long axis[4-8] and thus shows the molecular origin of the macroscopic spontaneous polarization. In order to check if asynchronicities in the reorientation of different molecular moieties exist, the time dependent apparent angle plots have been normalized (inlet in Fig. 2). The coincidence of these normalized curves proves a synchronous switching of the different molecular units.

Mechanically Oriented Single Crystalline (SC-) FLCE

FTIR-spectroscopy on microtomized sections of mechanical oriented SC-

FLCE enables to determine molecular structure and mobility in different sample geometries. Furthermore by placing the sections into ITO coated cells the influence of different field directions with respect to the spontaneous polarization can be analyzed[9]. In contrast to the shear oriented FLCE a mictrotomized section in bookshelf geometry ("A-section") does not show any changes in its polarizer dependent absorbance if a field of up to 2.5×10^5 V/cm is applied. This is obviously due to a rigid crosslinking in SC-FLCE. Nevertheless, the interdependence between these strong elastic forces and the mesogen reorientation behavior could be analyzed for a section microtomized in the plane formed by the layer normal and the tilt plane normal ("B-section")[9]. Under influence of an external field the changes in the polarizer dependent absorbance A(Φ) (Fig. 3) prove a mesogen reorientation on a restricted path of the tilt cone. The observed changes can be well explained if the tilt azimuth angle is assumed to change from 0° to ±35° under influence of the applied field of ±2.5×10^5 V/cm.

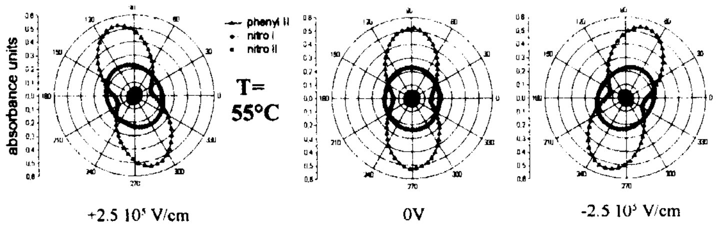


FIGURE 3 Polarizer dependent absorbance for the microtomized SC FLCE "B-section" under influence of external electric fields.

Freely Suspended Thin Films In Homeotropic Geometry

In μm-thick homeotropic films of the FLC polymer the mesogens are azimuthally oriented in the ferroelectric Sm-C* phase by application of an electric field of 10^3 V/cm. The IR beam forms an angle of about 10° to the film normal which allows to distinguish between molecular structures in which the director is tilted in the same plane but with opposite signs. By analysis of the dichroic ratio of the phenyl bands an orientation order parameter of $S = 0.66$ is measured which reflects the uniform orientation of the sample under study. The influence of the elastic network on the molecular mobility is studied for samples being crosslinked by a step-wise UV-irradiation (Fig. 4).

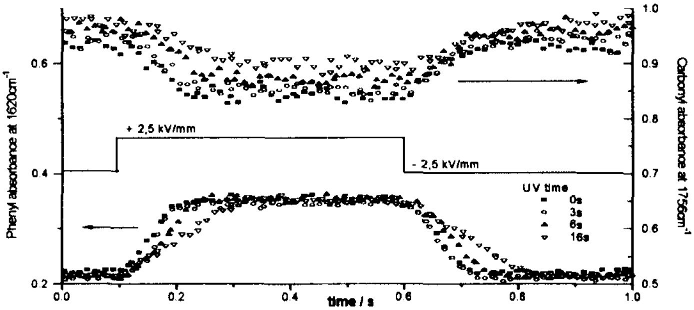


FIGURE 4 Evolution of the phenyl and carbonyl absorbance at reversal of the electric field polarity for a homeotropic μm thick freestanding FLCP film being UV crosslinked in steps of different duration (field strength: 2.5×10^4 V/cm).

For the uncrosslinked film (0 s UV irradiation time) measured with a fixed IR-polarization the field reversal leads to different absorbance plateaus due to the inclination of the IR-beam to the layer normal. The height of the absorbance plateaus is not influenced by the crosslinking. The switching time increases from 0.1 ms (uncrosslinked sample) to 0.2 ms (crosslinked sample (16 s UV irradiation)). This shows that the crosslinking increases the rotational viscosity of the FLCP but does not restrict the angular excursion of the mesogen reorientation. In contrast to the FLCE-cell no elastic memory effect (different reorientation times for + to - switching and for - to + switching) in freestanding films has been observed.

CONCLUSION

In conclusion one can state that time-resolved FTIR-spectroscopy is a powerful tool to analyze the molecular structure and mobility in FLC polymers and elastomers. In shear oriented and in freely suspended films of a photocrosslinkable FLCE as well as in mechanical oriented single liquid crystal elastomers the influence of the elastomeric network on the reorientation dynamics was studied. Depending on the crosslinking density and the type of sample, a decrease of the mesogen mobility, a restriction of the reorientation path and a strong memory effect can be observed in FLCE.

Acknowledgments

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