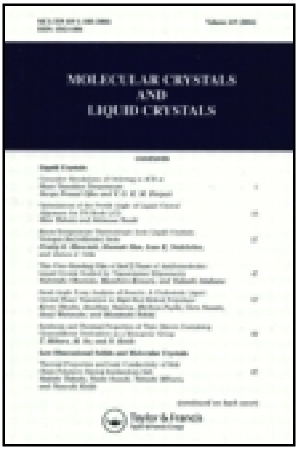

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Liquid Crystalline Polymers under Uniaxial Mechanical Stress as Observed with Modulated Waveguide Spectroscopy

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Liquid Crystalline Polymers under Uniaxial Mechanical Stress as Observed with Modulated Waveguide Spectroscopy

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The reorientation of a liquid crystalline statistical side chain polymer under application of a dynamic uniaxial stress is studied using mechanical modulated waveguide spectroscopy (MMWS). It is found that a tilt angle of the order of 5° is induced in the SmA phase by compressions of 19 nm of the originally homeotropic orientation with a pronounced orientational profile normal to the cell. The dependence of this mechanical reorientation process on the thickness modulation amplitude and frequency is discussed.

Keywords: liquid crystalline polymer; waveguide spectroscopy

INTRODUCTION

In liquid crystalline polymers the mesogenic parts are attached to a polymeric backbone. Liquid crystalline polymers therefore combine the anisotropic features of liquid crystals with the mechanical behavior of polymers. While low molecular liquid crystals usually have a low viscosity in their SmA and SmC* phase in polymeric liquid crystals the tendency to flow is suppressed. In liquid crystalline elastomers flow is no longer possible giving rise to interesting coupling between stress and orientation. In fact ferroelectric liquid crystalline elastomers are piezoelectric materials. A voltage induces a deformation whereas a compression of the elastomer causes electrical currents to flow across the sample. These electromechanical effects are believed to be associated with coupling of the elastic stress of the crosslinked polymer to the orientation of the ferroelectric spontaneous polarization. Electrooptical investigations and time resolved FTIR spectroscopy of ferroelectric liquid crystalline elastomers revealed that with increasing crosslinking density the reorientation time of the mesogens becomes slower[1,2]. The asymmetric switching in these samples due to a "memory effect" of the elastic network has been analyzed[1,2]. For mechanically oriented FLCE which exhibit piezoelectric effects as large as conventional piezoelectric ceramics[3] it was shown that the reorientation is restricted as the elastic energy exceeds the electric energy even if fields up to 2.5×10^5 V/cm are applied to reorient the mesogens[4]. The change of orientation induced by mechanical fields has not been studied in detail so far.

We investigate the amount of deformation needed to induce a reorientation of the mesogens for a liquid crystalline polymer which may be understood as a precursor of a liquid crystalline elastomer. In a previous paper we have shown that optical waveguide modes in liquid crystalline cells excited at defined incident angles react very sensitively to changes in both thickness of the cell and orientation profile of the director normal to the cell[5]. Changes in both parameters are reflected by shifts in the angular resonance position of those modes and an analysis of the data enables to determine these quantities simultaneously. We applied mechanical modulated waveguide spectroscopy to a homeotropically aligned liquid crystalline polymer revealing that an uniaxial compression of 19 nm of the polymer leads to a tilting of the director of the

EXPERIMENTAL

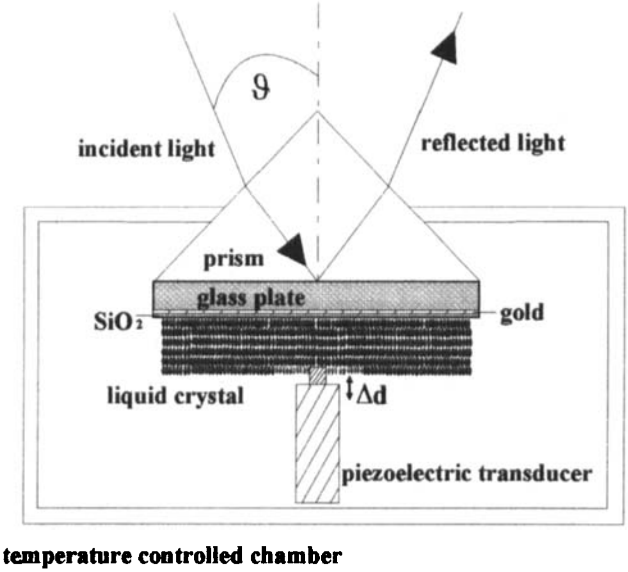

FIGURE 1 Schematic illustration for the temperature controlled waveguide cell for mechanical field modulated measurements.

The experimental setup of the mechanical modulated optical waveguide spectrometer has been published elsewhere[5]. Only the heart of the setup - the temperature controlled sample cell - is presented in Fig. 1. The sample cell consists of a glass slide (BK7 n=1.5151) evaporated with a thin (45 nm) gold cladding layer and a SiO_2 protection layer (33 nm). The free surface liquid crystalline polymer film is prepared by spin coating. The homeotropic orientation was checked using polarization microscopy. At the front of the glass slide a 90° prism with the same refractive index as the glass slide is attached to the sample using index matching oil.

For fixed orientation and thickness of the liquid crystal in the sample cell waveguide modes are excited at defined incident angles with p- or s-polarized light (λ = 632,8 nm). Due to coupling into the resonance cavity and guiding of the optical wave in the liquid crystalline polymer the intensity of the reflected light is strongly reduced at the resonant angles.

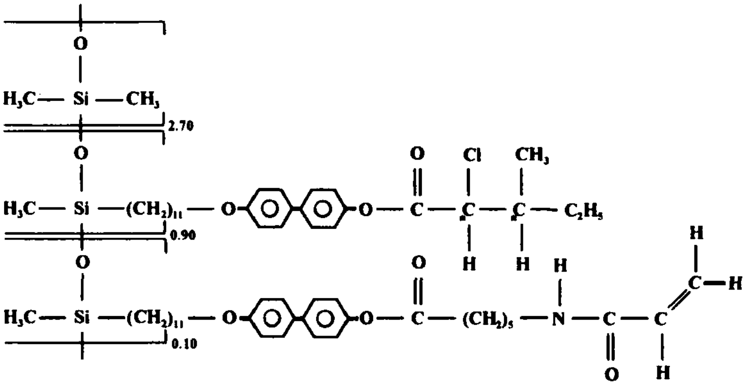

FIGURE 2 Chemical structure of the liquid crystalline side chain polymer EG-035.

Uniaxial compression is achieved using a piezoelectric transducer slightly bending the liquid crystalline polymer, inducing a uniform change of thickness over the spot of measurement (200 μm). As a result the reflectivity in the surrounding of the resonant angles is modulated and the modulation at the piezoelectric transducer frequency is recorded using lock-in technique.

The chemical structure of the liquid crystalline polymer under study is shown in Fig. 2. The phase sequence was found to be SmX-30°C-SmC*-61°C-SmA-86°C-isotropic. All experiments have been performed in the SmA phase at T = 63°C.

RESULTS AND DISCUSSION

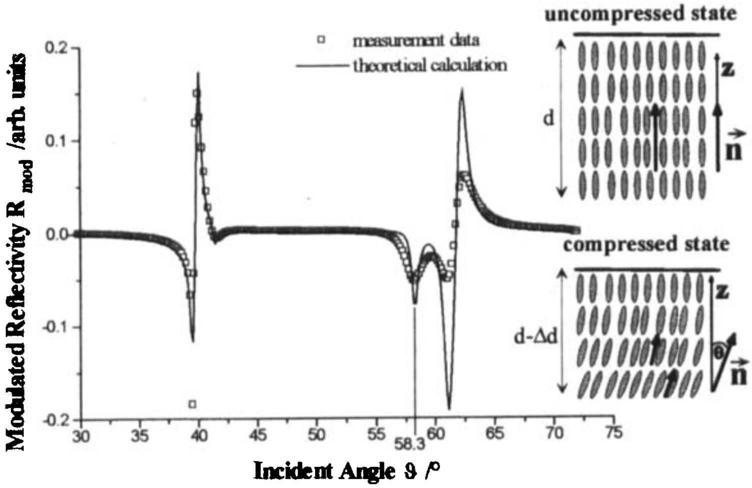

FIGURE 3 Modulated waveguide spectrum for p-polarized light of the liquid crystalline polymer EG-035 in the SmA phase at T = 63°C with sketches of the molecular director orientation in the uncompressed and the compressed state. The frequency of the applied mechanical field is 500 Hz, the voltage is 2 V.

The modulated waveguide spectrum obtained for p-polarized light at a frequency of 500 Hz is shown in Fig. 3. The dynamical spectrum consists of characteristic extrema corresponding to waveguide resonances in the stress free and the uniaxial compressed state. The maxima correspond to the stress free state, while the minima occur under compression. The minimum at the angle $\vartheta = 58.3°$ is an indication of tilt within the director profile of the sample, coupling p- and s-polarized light. The shift in the resonance position, i. e. the angle difference between maxima and minima is a measure for the thickness modulation amplitudes. Amplitudes of Δd = 5 nm - 50 nm were applied. For low amplitudes Δd < 30 nm the occurrence of an additional minimum is clearly visible, while at larger amplitudes an additional minimum could no longer be resolved (Fig. 4). The modulation spectra were fitted using a numerical program based on the Berremann 4×4 matrix formalism[6]. The fitting parameters for the data of Fig. 3 are listed in Table I.

TABLE I The optical parameters used for the calculated solid curves in Fig. 3.

layer	thickness	dielectric constant
gold	45.3 nm	-12 + 1.1i
SiO_2	33.5 nm	2.61
liquid crystal	1.0305 μm Δd = 19 nm θ ≈ 5°	$\varepsilon_\perp = 2.625$ $\varepsilon_\parallel = 2.225$

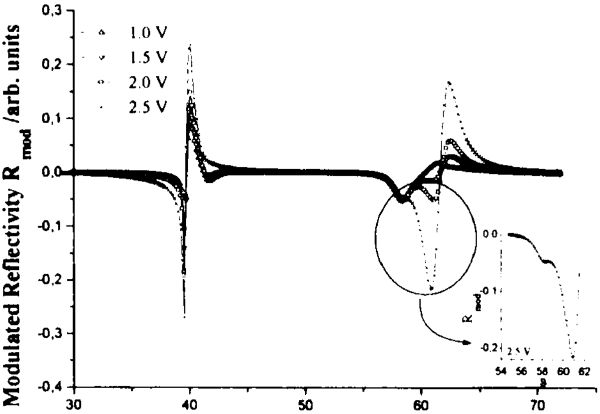

FIGURE 4 Modulated waveguide spectra for p-polarized light for different piezoelectric transducer voltages. The frequency of the applied field is 500 Hz.

Strong anchoring of the director at the upper glass boundary and week anchoring at the lower free boundary is expected in the compressed state. Therefore there will be a profile perpendicular to the film surface in tilt angle through the sample. In the analysis this is encountered for by assuming a linear tilt angle profile:

$$\theta(z) = \frac{10^\circ \cdot z}{(d - \Delta d)} \quad ; 0 \le z \le (d - \Delta d). \qquad (1)$$

It is not predictable in which direction this tilt occurs and averaging of the theoretical modulation spectra over the tiltazimuthal directions were performed. The according fit is shown as the solid line in Fig. 3. Fits with similar accuracy could be obtained for other tilt profiles. The average tilt angle θ = 5° seems to be independent of the assumed profile used for the analysis.

A homogeneous tilting through the sample, however, led to a fit which could not be brought into accordance with the data. It is concluded that a

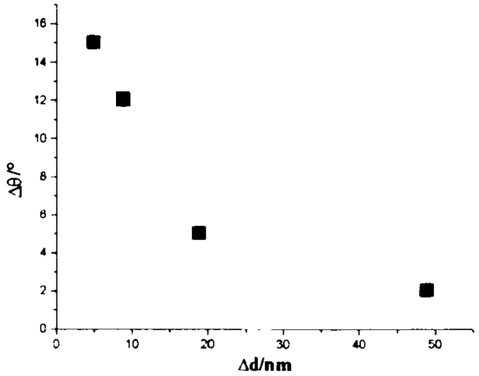

FIGURE 5 The calculated relations between changes in thickness of the liquid crystalline polymer and tilt angle during the modulation process without consideration of the tiltazimuthal scattering.

variation on scattering of the tilt through the sample is therefore necessary for the description. This can be seen in Fig. 4 where the modulation spectra are plotted for 4 different thickness amplitudes. At very high amplitudes the orientational change is broadened and the additional resonance minimum completely overlaps the other minimum indicating that the scattering in tilt angle is increasing with the thickness modulation amplitude while the average tilt angle is decreasing (Fig. 5).

Only slight changes in intensity and no shifts in the resonance angles are observed when increasing the frequency from 10^2 Hz - 10^5 Hz.

CONCLUSION

Uniaxial compression of a liquid crystalline side chain polymer EG-035 in homeotropic orientation causes an induced tilt angle θ of the order of 5° when compressing the film by approximately 20 nm. This change in orientation is caused by a coupling between stress and director orientation which decreases with increasing thickness modulation amplitude.

Acknowledgment

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References

[1] M. Brehmer, R. Zentel, F. Gießelmann, R. Germer, P. Zugenmaier, *Liq. Cryst.*, **21**, 589 (1996).

[2] S.V. Shilov, H. Skupin, F. Kremer, E. Gebhart, R. Zentel, *Macromolecules*, submitted (1998).

[3] W. Lehmann, P. Gattinger, M. Keck, F. Kremer, P. Stein, H. Finkelmann, *Ferroelectrics*, in press (1998).

[4] H. Skupin, F. Kremer, S.V. Shilov, P. Stein, H. Finkelmann, *Macromolecules*, submitted (1998).

[5] A. Fahrwald, H. Skupin, Th. M. Fischer, F. Kremer, *Rev. Sci. Instr.*, in press (1998).

[6] D.W. Berreman, *J. Opt. Soc. Am.*, **62**, 502 (1972).