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Segmental orientation and mobility of ferroelectric liquid crystal polymers

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IR spectroscopy was used to study the orientation and mobility of different molecular segments in a side chain ferroelectric liquid crystalline polymer (FLCP) in the book-shelf geometry. It was directly shown that the tilt angles for the mesogenic units and the spacers are different. The data obtained allowed us to construct a detailed model of segmental orientation in the S_C^* phase for this FLCP. This model is consistent with the 'zigzag' model for tilted smectic phases. The rotational bias of carbonyl bonds is also confirmed and a possible orientation function for the carbonyl group is discussed. Time-resolved step-scan FTIR spectroscopy enabled us to follow the intra- and inter-molecular response of the FLCP to an external electric field with a time resolution of 5 μs. It was detected that mesogenic moiety, spacer and backbone take part in the reorientation process. The time responses of different molecular segments are similar on the time scale of a few hundred microseconds.

1. Introduction

The most important characteristics of ferroelectric liquid crystals (polarization, tilt angle, response time) are closely related to the mutual agreements of molecular segments in smectic layers and the mobility of these segments under an electric field. For that reason the study of segmental orientation and specific functional mobility is the key to an understanding of the mechanism of ferroelectric switching on a molecular level. The collective and molecular dynamics of ferroelectric liquid crystals have been extensively studied during recent years by dielectric spectroscopy [1–4]. On the basis of these data, the hindered rotation [4] or libration [2] of mesogens around the molecular long axis was proposed to explain the origin of ferroelectricity in the smectic layers of chiral liquid crystals. However, this method is not capable of separating the motion of different molecular segments. For non-polymeric smectic liquid crystals, the mutual arrangement of molecular parts was modelled on the basis of X-ray experiments [5, 6]. The data obtained fitted well with the 'zigzag' model, according to which the flexible tail and the mesogenic core tilt independently with respect to the smectic layer normal.

Detailed information about orientation and rotational bias of molecular moieties (in terms of orientation distribution functions of different molecular segments) can be obtained by IR spectroscopy. With current improvements in the mechanical stability and data acquisition electronics of a modern FTIR spectrometer, the segmental reorientation dynamics in an electric field can be probed with a time resolution of 5 μs. Recently the method of IR spectroscopy was applied to study the segmental orientation and mobility of ferroelectric and antiferroelectric liquid crystals [7–13]. It was detected that the distribution of carbonyl groups, not only in the chiral group but also in the mesogenic core, is not cylindrically symmetric with respect to the molecular long axis [10, 11]. According to the data of ref. [10], the directions of the mesogen long axis and the average orientation of the alkyl tail coincide. This is in strong contradiction to the 'zigzag' model.

It should be mentioned that previous studies were restricted to non-polymeric ferroelectric LCs. At present there are few reports of investigations involving ferroelectric liquid crystal polymers (FLCPs) by FTIR spectroscopy [12, 13]. The aim of this paper is to present the results of more detailed studies of segmental orientation and mobility of an FLCP.

2. Experimental

The chemical structure and transition temperatures of the FCLP investigated are presented in figure 1. The

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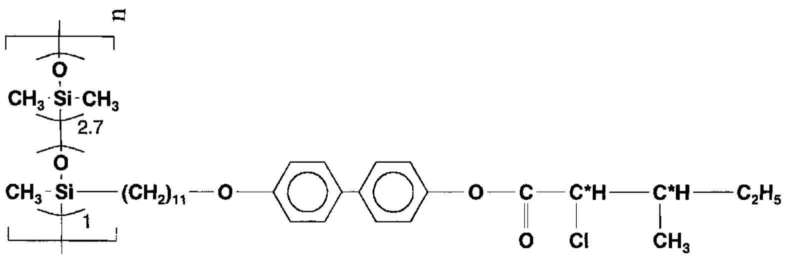

$S_X 29^\circ S_C{}^* 61^\circ S_A 89^\circ I$

Figure 1. Molecular structure and transition temperatures of the FLCP investigated.

molecular weight of this polymer is approximately $M_w \cong 21\,000$ and its polydispersity is about 1·66. The synthesis of this FLCP and results of studies by dielectric spectroscopy and electro-optical methods are described in ref. [14].

Our measurements were made with a cell consisting of two parallel CaF_2 plates coated with indium tin oxide. These plates are transparent to visible and IR light and served both as windows and electrodes. PET spacers with a thickness of 2 μm were used to keep a definite spacing between the electrodes. The empty cell and the FLCP were heated up to 100°C in order to fill the polymer into the cell through the gap between the windows by capillary forces. After filling the cell, it was slowly cooled down ($1^\circ C\ min^{-1}$) at first to the S_A phase in which the polymer was oriented by a parallel movement of one of the CaF_2 plates. An a.c. voltage of $20\ V_{pp}$ (peak to peak) and 5 Hz was also applied during the shearing to reduce defects in the oriented film. This procedure led to homogeneous orientation of the FLCP. Further cooling of the sample to the S_C^* phase with simultaneous application of the electric field resulted in book-shelf orientation of the mesogenic side groups.

A BioRad FTS 6000 FTIR spectrometer with an IR microscope was used to record the IR spectra. The experimental geometry is shown in figure 2. In the S_C^* phase there are two stabilized orientational states of the FLCP depending on whether the mesogenic units incline to the right or to the left relative to the direction perpendicular to the shear. Switching between these two states can be achieved by reversing the polarity of the applied electric field. The sample was positioned on a microscope stage using crossed polarizers and visible light, and the most extended region of uniform orientation ($100 \times 100\ \mu m^2$) was selected for the IR measurements. After positioning the sample, the microscope was switched from the visible light mode to the IR mode. The propagation direction of the polarized IR beam was perpendicular to the surface of the windows. In static experiments, DC voltages of +10 V and −10 V were applied to the sample and IR spectra were measured as a function of polarizer rotation angle ω from 0° to 180° in steps of 5°. To guide the eye, a data point obtained at an angle ω $(0^\circ < \omega < 180^\circ)$ is presented in the polar plots for an angle of $\omega + 180^\circ$ as well as for ω. The positions of maximal and minimal (ω_{max} and ω_{min}) absorption for the different absorption bands were calculated by the centre of gravity method [15]. With this method, the precision of determining these angles is improved to ±1°.

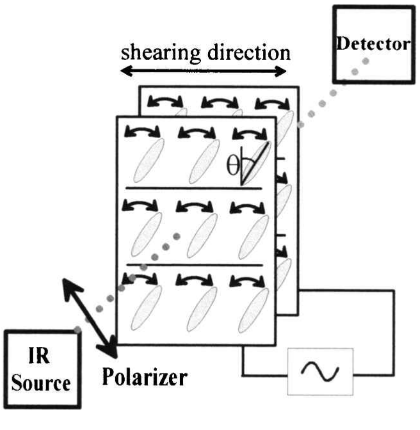

Figure 2. The principal scheme of the experimental set-up.

Time-resolved spectra of the FCLP during switching between the two stabilized states were recorded using a step-scan technique with a time resolution of 5 μs [16, 17]. The details of the present measurement set-up will be described elsewhere. Both time-resolved and static spectra were measured with a spectral resolution of $4\ cm^{-1}$.

3. Results and discussion

3.1. *Band assignment*

The static IR spectra of the FLCP investigated under a DC voltage of +10 V at a temperature of 35°C measured with polarized IR light are shown in figure 3. The 'parallel' polarization direction of the IR beam is defined as the polarizer direction at which the absorbance for the $1499\ cm^{-1}$ band (mesogenic unit) is maximal. A tentative band assignment based on the spectral analysis of similar compounds [18] is given in the table. The dichroic ratios calculated as $R = A_\parallel / A_\perp$

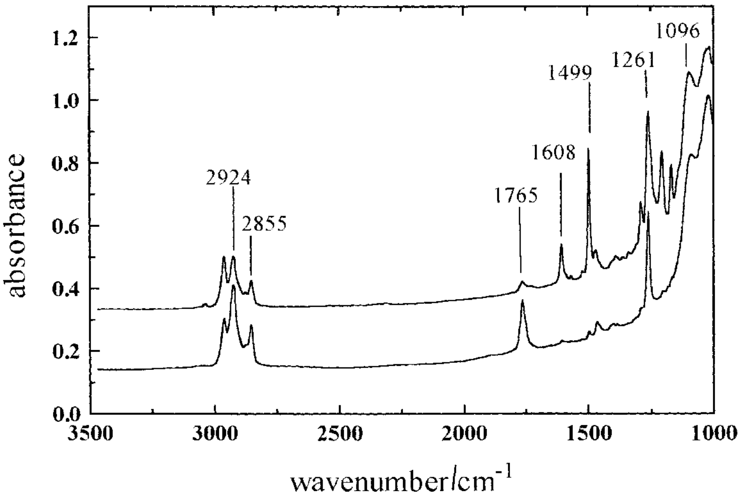

Figure 3. Polarized static spectra of the FLCP at +10 V, 35°C.

Table. Band assignment for the FLCP investigated.

Wavenumber/cm^{-1}	Dichroic ratio, R	Assignment
2963	1·05	$\nu(CH_3)$
2924	0·61	$\nu_{as}(CH_2)$
2855	0·63	$\nu_s(CH_2)$
1765	0·18	$\nu(C{=}O)$
1608	13·12	$\nu(C{-}C)_{ar}$
1499	21·61	$\nu(C{-}C)_{ar}$
1463	0·59	$\delta(CH_2)$
1261	1·29	$\nu_{as}(C{-}O{-}C) + \delta(Si{-}CH_3)$
1207	23·82	$\nu(C{-}O) + \nu(C{-}O{-}C)$
1168	12·22	$\nu(C{-}O) + \nu(C{-}O{-}C)$
1096	1·31	$\nu(C{-}O) + \nu(Si{-}O{-}Si)$

($A_{\parallel}$ and $A_{\perp}$ are the absorbance values measured with polarized light in parallel and perpendicular directions) from the polar plots are also included in the table. The 1608, 1499, 1207 and 1168 cm^{-1} bands are characteristic for the mesogenic units. The transition moments for these bands are nearly parallel to the mesogenic axis. For that reason, the very high dichroism of these bands (at 35°C, see the table) signifies that all the mesogenic groups are almost parallel to each other. The 2924 and 2855 cm^{-1} bands originate from asymmetric and symmetric CH_2 stretching vibrations. Since our molecule contains eleven CH_2 groups in the spacer and only one CH_2 in the tail, the intensity and dichroism of these bands characterize mainly the poly(methylene) spacer. The transition moments for these vibrations are nearly perpendicular to the poly(methylene) chain in an all-*trans*-conformation. Due to conformational disorder of the spacer, the dichroic ratio for these bands is lower than that for bands characterizing the mesogen units.

Unfortunately, the characterization of the polysiloxane backbone is not unequivocal. The band at 1096 cm^{-1} (Si–O stretching vibration) could be used for this purpose. However, in our case this broad band is overlapped by the ν(C–O–C) vibration from the ester function. Moreover, this intense band is located close to the transmission limit of CaF_2 windows, so that quantitative calculation based on this band is not possible. We chose the 1261 cm^{-1} band, $\delta(Si{-}CH_3)$, for characterization of the backbone, although the $\nu_{as}(C{-}O{-}C)$ band (related to the mesogenic units) also has a contribution in this spectral region. The transition moment for the 1261 cm^{-1} band is nearly perpendicular to the polysiloxane chain. In the FLCP samples investigated, carbonyl and C–Cl groups are mainly responsible for the spontaneous polarisation. C–Cl groups give absorption in the 800–600 cm^{-1} region [18], which is not accessible with CaF_2 windows. The carbonyl group absorbs at 1765 cm^{-1} and the transition moment for this band is nearly parallel to the C=O bond. The C=O bond itself is tilted to the mesogen long axis at an angle of 60–70° [19, 20].

3.2. *Smectic A phase of the FLCP*

The polar plot for the absorbance versus polarization angle ω in the S_A phase is presented in figure 4. In this

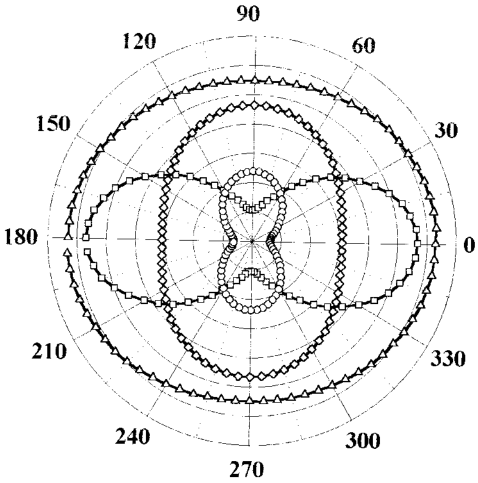

Figure 4. Polar plot of absorbance versus polarization rotation angle for the 1499 cm^{-1} (□), 1765 cm^{-1} (○), 1261 cm^{-1} (△) and 2924 cm^{-1} (◇) bands for the FLCP in the S_A phase at 70°C.

plot the 90° position of the polarizer corresponds to the shearing direction. According to common considerations, the orientation of the mesogenic units in the S_A phase is not biased and the orientation distribution function for the mesogenic units has a cylindrical symmetry around the director (or smectic layer normal). If the orientation function for a molecular segment is cylindrically symmetrical, the maximal or minimal absorption of all related IR bands must be observed for polarization either parallel or perpendicular to the director. As can be seen from figure 4, this rule is obeyed in the S_A phase: the absorption maxima for the 1499 and 1261 cm^{-1} bands are observed at 0° and those for the 2924 and 1765 cm^{-1} bands are observed at 90°. Taking into account the angles between the transition moments for these bands and the corresponding molecular segments (see above), it can be concluded that the polymethylene spacers are preferentially oriented in the direction of the long axis of the mesogenic groups, whereas the main chain segments orient perpendicular to it. The shearing of the sample in the S_A phase orients the mesogenic groups (and spacers) perpendicular to the shear direction and the backbone parallel to the shear direction.

3.3. *Smectic C* phase of FLCP*

In the S_C^* phase, electro-optical switching can be observed under an a.c. voltage between two crossed polarizers for visible light. The sample was rotated until a minimum in the transmission at voltage +10 V was reached. After that, the two visible light polarizers were replaced by one IR polarizer. The polarization direction of the IR polarizer was the same as that of one of the visible light polarizers. We define this direction as $\omega = 0$. The phenomenon of electro-optical switching in LC ferroelectrics is a consequence of the rotational bias of the mesogens. If the rotation around the molecular long axis is biased, the angular position of the maxima and minima of at least some bands should differ from each other. The polar plots of some absorption bands for the sample at 35°C under a voltage of +10 V are presented in figure 5 *(a)*. As can be seen from figures (4) and 5 *(a)*, there is a pronounced difference in the absorbance versus polarization angle dependency between the S_A and the S_C^* phase. In the S_C^* phase (figure 5 *(a)*), the bands corresponding to different molecular moieties have different positions of their absorbance maxima and minima. This is direct evidence that the cylindrical symmetry of the distribution function for segments is broken in the ferroelectric phase. It should be mentioned that the maxima in absorption for the 1608 and 1499 cm^{-1} bands are observed at $\omega = 0°$ and the minima at $\omega = 90°$. That means that the optical axis of the FLCP in the

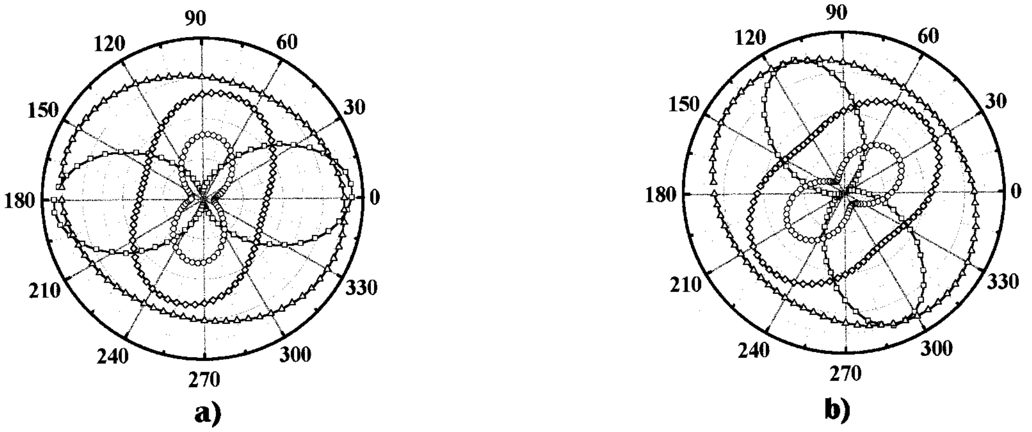

Figure 5. Polar plot of absorbance versus polarization rotation angle for the 1499 cm^{-1} (□), 1765 cm^{-1} (○), 1261 cm^{-1} (△) and 2924 cm^{-1} (◇) bands for the FLCP in the S_C^* phase at 35°C; *(a)* +10 V, *(b)* −10 V.

book-shelf geometry coincides with the long axis of the mesogen.

After changing the polarity of the electric field, the molecules reorient to the second stable state. The polar plot for this state is shown in figure 5 *(b)*. The graphs for positive and negative voltage (figures 5 *(a)* and 5 *(b)*) are symmetric relative to the bisector of the angle between the absorption maxima for the positive and the negative voltages. The temperature dependences of the apparent tilt angles (calculated as half of the angle between the direction in the absorption maxima for positive and negative voltage) are shown in figure 6. The temperature dependence of the dichroic ratio for the 1499 cm^{-1} band is also presented in this figure. The largest values for the ϑ angle are observed for bands corresponding to the benzoate ring of the mesogenic fragment, whereas the smallest values for ϑ are related to the backbone. Since the transition moments for the 1608 and 1499 cm^{-1} bands are parallel to the mesogen axis, the angles ϑ_{1608} and ϑ_{1499} are equal to the inclination angle of the mesogen to the smectic layer normal (figure 2). The data on the tilt angles of the mesogenic units obtained in this work by IR spectroscopy are in agreement with results from electro-optical investigations of that FLCP [14]. For the whole temperature range of the S_C^* phase, the values ϑ_{2924} and ϑ_{2855} (corresponding to the spacer) and ϑ_{1261} (corresponding to the backbone) are approximately half the values of ϑ_{1608} and ϑ_{1499} (corresponding to the mesogenic unit). The carbonyl group also belongs to the mesogen fragment (figure 1); however the ϑ_{1765} value is approximately two thirds the ϑ_{1499} value (see figure 6). A similar observation for carbonyl bands was made in the case of non-polymeric antiferroelectric liquid crystals [10, 11].

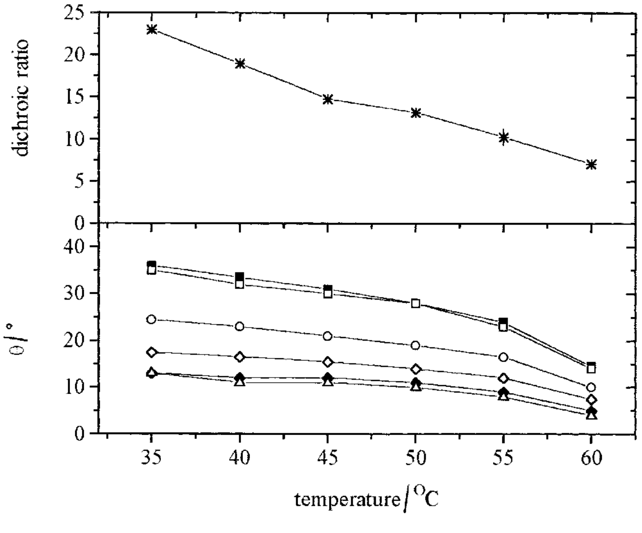

Figure 6. Temperature dependences of the dichroic ratio for the 1499 cm^{-1} band (∗) and the apparent tilt angle calculated from the absorbances of the 1499 cm^{-1} (□), 1608 cm^{-1} (■), 1765 cm^{-1} (○), 2924 cm^{-1} (◇), 2855 cm^{-1} (◆) and 1261 cm^{-1} (△) bands.

The shift in the position of the carbonyl maximum can be explained on the basis of the model proposed by Miyachi *et al.* [11]. Following this model we assume that the mesogenic units are aligned perfectly parallel, but that they can rotate (although biased) about their long axes. The relative positions of mesogenic moiety (x, y, z) and laboratory (X, Y, Z) coordinate system are shown in figure 7. The IR beam propagates along the Y-axis and its polarization vector forms the angle ω with the Z axis. The position of the carbonyl bond is characterized by the angle α (between mesogenic unit and C=O bond) and the torsion angle φ (rotation of the C=O bond out of the ZY plane). There are two equivalent configurations: with the carbonyl group tilted either to the left or to the right out of the ZY plane. The existence of these two equivalent configurations (figure 7) leads to a spontaneous polarization due to the carbonyl group which is perpendicular to the ZX plane. If $f(\varphi)$ is the rotational distribution function of the transition moment **M** around the mesogen long axis for one configuration, then the absorbance A relative to ω is given by the equation [11]:

$$A(\omega) = 0{\cdot}5 \int_0^{2\pi} M^2 f(\varphi)(\sin\omega \sin\alpha \sin\varphi + \cos\omega\cos\alpha)^2 \, d\varphi$$

$$+ \text{ a corresponding term with the distribution function for the other configuration} \quad (1)$$

In the case of free rotation the absorption will be [21]:

$$A(\omega) = 0{\cdot}5 M^2 \sin^2\alpha \sin^2\omega + M^2 \cos^2\alpha \cos^2\omega \quad (2)$$

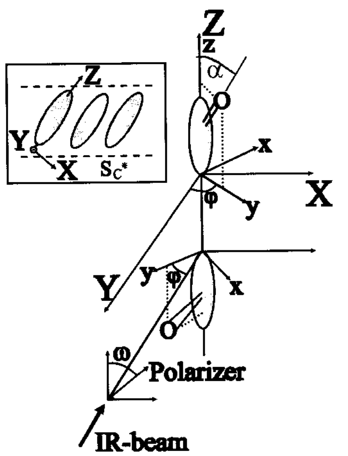

Figure 7. Laboratory (X, Y, Z) and molecular (x, y, z) coordinate system. The laboratory coordinate system is always chosen in such a way that the Z axis is parallel to the mesogen long axis.

If it is taken into account that the angle α for the carbonyl group vibration ($1765\,\mathrm{cm}^{-1}$) is approximately 60° and that for the benzoate ring vibration ($1499\,\mathrm{cm}^{-1}$) is 0°, equation (2) leads to $\omega_{\max,1743} = \omega_{\min,1499}$, that is that the maximum of the carbonyl absorption will be located at the minimum of the benzoate ring absorption (and vice versa). This situation actually takes place in the S_A phase (figure 4).

In the case of completely uniform orientation with the torsion angle $\varphi = 0$, the carbonyl band maximum appears at an angle $\omega_{\max} = 0$. If $\varphi = 90°$, the maximum should appear at $\omega = \alpha$. When the transition moments have some φ-distribution along the long axis, an assumption about the distribution function $f(\varphi)$ must be made before integration of equation (1) [11]. It was shown [11] that at $\varphi \neq 0$, a narrower distribution function moves the absorption maximum of the C=O group from $\omega_{\max} = 90°$ toward the value $\omega_{\max} = \alpha$. This behaviour of the C=O absorption is also observed for the FLCP under investigation (figure 5 *(a)*). On the basis of these discussions, it is possible to conclude that the detected shift in the position of $\omega_{\max}$ for the carbonyl band is a consequence of the non-cylindrical symmetry of the C=O orientation. The maximum of that distribution function lies out of the ZY plane ($\varphi \neq 0$, figure 7). It should be mentioned that the assumption of perfect parallel orientation of mesogenic units is valid only for temperatures close to the S_X phase transition where the high dichroic ratio for benzoate ring bands is observed. At higher temperatures the thermal fluctuations of the mesogenic axis must also be taken into account and should be included in the model as well.

The proposed model does not explain the difference in both $\omega_{\max}$ and ϑ values for bands corresponding to the spacer and for those corresponding to the benzoate ring. For the poly(methylene) spacer part, the angle α_{spacer} between the transition moment for the 2924 and $2855\,\mathrm{cm}^{-1}$ bands and the polymethylene chain axis is close to 90°. If the average axis of the spacer coincides with the mesogenic axis and $\alpha_{\text{spacer}} = 90°$, no difference between the $\omega_{\max}$ of these bands and $\omega_{\max}$ of the mesogen bands should be observed. Hence, the detected difference is direct proof of non-coincidence of the spacer and the mesogen axes. This result is in agreement with the 'zigzag' model proposed on the basis of X-ray data [5, 6]. If the distribution function for the methylene units is cylindrically symmetric relative to the average spacer axis, and this spacer axis is in the plane ZX (figure 6), then the detected angle θ for the spacer is the angle formed between the spacer axis and the layer normal. The similarity of θ_{2924} and θ_{2855} (figure 7) supports the contention that the orientation of the methylene units is unbiased.

The interpretation of the IR data on the dichroism of the backbone is not evident due to the uncertainty in assignment of the $1261\,\mathrm{cm}^{-1}$ band. Nevertheless the dichroic ratio 1·29 (table) leads to the conclusion that the backbone is on average oriented perpendicular to the smectic layer normal.

Summarizing the data obtained, the following static model of mutual arrangements of molecular segments in the S_C^* phase can be proposed (figure 8). At a temperature of 35°C, the mesogenic groups align parallel to each other and form an angle of 35° with respect to the smectic layer normal (**n**, figure 8), whereas the average spacer axis forms an angle of 18° with **n**, and finally the average backbone axis is perpendicular to **n**. The rotation of the carbonyl group of the mesogenic moiety is biased and its most probable position is out of the XY plane (turned to the left or to the right). Due to the equivalence of these two states, the spontaneous polarization appears along the Y axis. Reversing the polarity of the electric field rotates the LC group to a new position given by a rotation of 180° around **n** relative to the former one. The increase of temperature leads to an increase in the fluctuations in the orientation of the mesogenic moieties around their average orientation (manifested in the decrease of the dichroic ratio for the $1499\,\mathrm{cm}^{-1}$ band) and to a decrease of the θ angles of the mesogenic units and the spacer. In a S_A phase, the distribution functions of the molecular segments become cylindrically symmetrical.

3.4. *Segmental mobility of the FLCP in the S_C^* phase*

Since the spacer is effectively 'decoupling' the movement of the mesogenic units from the movement of the

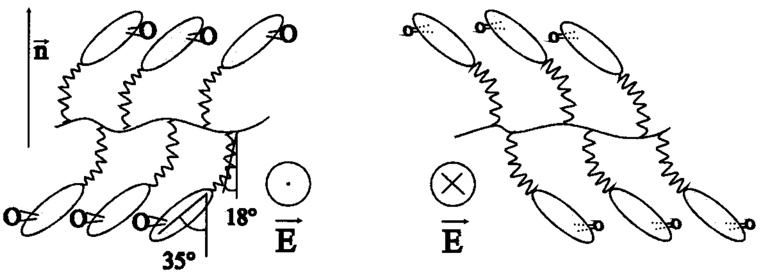

Figure 8. Model of mutual arrangements of molecular segments at 35°C.

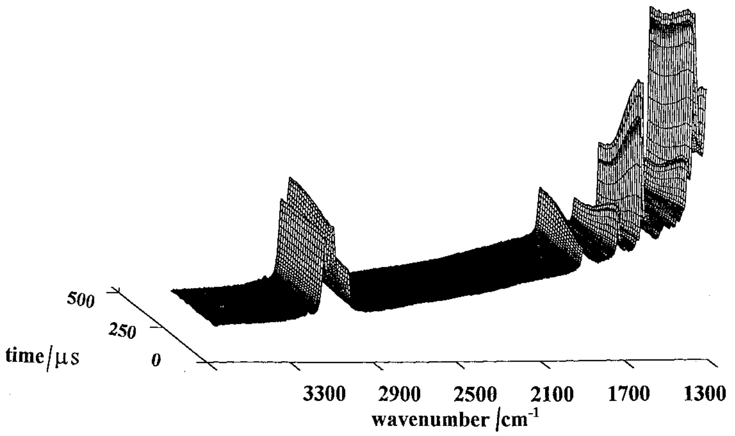

Figure 9. Time-resolved IR spectra of the FLCP during electro-optical switching.

polymer backbone, a different behaviour of mesogenic group, spacer and main chain can be expected in a switching process. This difference (if it exists at all) must be more pronounced in systems with a short response time. Since the response time decreases with increasing temperature and electric field strength, we carried out time-resolved experiments at a temperature of 50°C (close to the S_C^*–S_A phase transition) and at the highest available field strength of 30 V μm^{-1}. The IR polarization direction corresponded to the value $\omega = 0$ (see figure 5 *(a)*). A three-dimensional plot of time-resolved spectra recorded as a response to the reversal of polarity of the electric field is shown in figure 9. The field polarity was reversed at time $t = 50$ μs. The first 10 spectra ($0 < t < 50$ μs) of these series coincide with the static spectra at positive polarity and the last to the static spectra at negative polarity. The relative intensity changes versus time for bands corresponding to the mesogenic unit, spacer and backbone are presented in figure 10. The intensities of the 1608, 1499 and 1261 cm^{-1} bands decrease, whereas those for the 2924, 2855 and 1765 cm^{-1} bands increase when the polarity of the electric field is inverted. This behaviour is expected according to the previously described model. The reorientation process starts immediately after inversion of the field polarity ($t = 50$ μs). Reorientation to the second stabilized state takes approximately 300 μs under the given experimental conditions. It can also be derived from these data that all molecular segments take part in the reorientation process. For a qualitative comparison of the orientation rates of different molecular segments we used the normalized intensity A_N which is calculated as:

$$A_N = (A(t) - A_M)/(A_0 - A_M) \qquad (3)$$

where $A(t)$ is the band peak absorbance at time t; A_0 is the value before inversion of the polarity, and A_M is the corresponding absorbance after completion of reorientation. The results are presented in figure 11. They show that under the given experimental conditions and within the experimental accuracy (that is ±0·001 in absorption units) the normalized time-profiles for the selected bands are similar. This means that the reorientation rates of the molecular segments corresponding to these bands

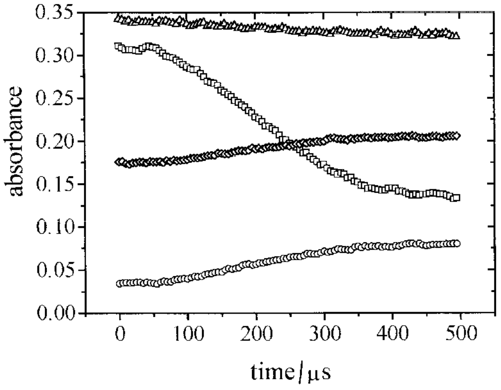

Figure 10. Time-dependence of absorbance changes for the 1499 cm^{-1} (□), 1765 cm^{-1} (○), 2924 cm^{-1} (◇) and 1261 cm^{-1} (△) bands.

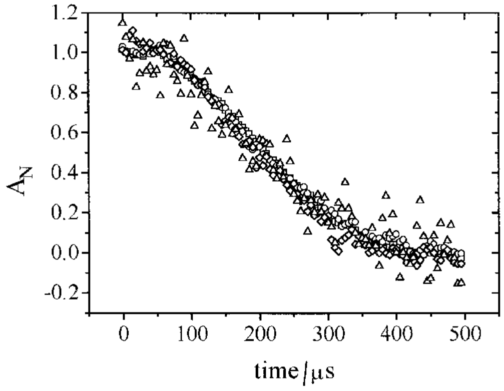

Figure 11. Normalized absorbance versus time for the 1499 cm^{-1} (□), 1765 cm^{-1} (○), 2924 cm^{-1} (◇) and 1261 cm^{-1} (△) bands.

are close to each other. The similarity in time-resolved band profiles is also confirmed by other time-resolved studies of polymeric [12, 13] and non-polymeric [8–10] LC ferroelectrics and non-polymeric nematics [17, 22]. In contrast to these results, some authors have reported for LC nematics [16, 23, 24] and ferroelectrics [25, 26] that the time-resolved profile of bands due to the mesogenic unit and the flexible part may be different. As was shown recently for LC nematics [22], this difference can appear under certain experimental conditions and can be related to the dependence of the reorientational properties of the local director and its orientation relative to the laboratory coordinate system. In the case of ferroelectric LCs (where the orientation is not uniaxial), the apparent time lag for different bands may arise as a result of differences in the orientation distribution of corresponding moieties around the director [26]. Apparently under the given experimental conditions, the observed pronounced differences in orientational distribution functions for molecular moieties of the FLCP studied in this work do not lead to differences in time-resolved band profiles.

These preliminary results reveal the great potential of time-resolved spectroscopy for studying the fast reorientational motion in ferroelectrics. To build up a dynamic model of segmental motion in ferroelectric liquid crystals, the time-resolved experiments must be carried out for different polarization angles ω. This work is in progress.

4. Conclusions

The analysis of the mutual arrangements of different molecular segments for a ferroelectric liquid crystalline polymer molecule was done on the basis of IR spectroscopy data. It was directly shown that the averaged spacer axis and the mesogenic axis do not coincide with each other. This result is consistent with the ‘zigzag’ model of molecular conformation. The rotation of the carbonyl group was confirmed to be biased. The maximum of the orientation distribution function lies out of a plane perpendicular to the smectic layers.

Time-resolved step–scan FTIR spectroscopy enabled us to follow the intra- and inter-molecular responses of the FLCP to an external electric field with a time resolution of 5 µs. It was detected that mesogenic unit, spacer and backbone take part in the reorientation process. The time responses of these different molecular segments are similar on the time scale of a few hundred microseconds.

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