Reorientation of Nematic Liquid-Crystals and Liquid-Crystalline Polymers in an Electric Field Studied by FT-IR Time-Resolved Spectroscopy and 2D-Correlation Analysis

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Fourier-transform infared (FT-IR) time-resolved spectroscopy was used to study the segmental mobility of two low molecular weight nematic liquid-crystals (*p*-cyanophenyl *p*-(*n*-hexyl)benzoate, 6CPB, *p*-cyanophenyl *p*-(*n*-heptyl)benzoate, 7CPB) and a nematic liquid crystalline polymer (poly[*p*-(*n*-hexyl)(*p*-(cyanophenyl)-benzoate) acrylate], NLCP), which has a 6CPB unit in the side chain. Of particular interest was the comparison between the reorientation of free 6CPB and 6CPB integrated in the side chain of the polymer. The samples were studied under different experimental conditions of temperature, voltage, and prealignment. To accentuate and derive more useful information from the original time-resolved spectra, we applied 2D-correlation analysis. It has been shown that molecules of 6CPB and 7CPB reorient as rigid units. In the case of NLCP only the mesogen and a small part of the spacer, directly attached to the mesogen, participate in the reorientational movement; the rest of the spacer and the main chain do not move under the influence of the electric field. The temperature, in a narrow range, and the prealignment do not have a noticeable effect on the rate of reorientation of the nematic low molecular weight liquid-crystals, whereas increasing temperature and prealignment significantly shorten the relaxation times of the NLCP.

Introduction

An understanding of the dynamics of liquid-crystals (LCs) and liquid-crystalline polymers in external electric and magnetic fields is of particular importance for their widespread use in display devices and for optical information storage. In most cases, LC molecules consist of a rigid core (mesogen) and a flexible chain attached to the core. The mesogen moves like a rigid rod, whereas the flexible part has some freedom for internal motion. In side-chain LC polymers the core is often attached to the main chain via a flexible spacer. An electric-field-induced reorientation of LC molecules is due to their dielectric anisotropy.[1] As it is assumed that the dielectric anisotropy comes mostly from the mesogen, one can expect a different response of the rigid and the flexible parts of the LC molecules in an external electric field. However, it has been commonly accepted that the LC molecules reorient as rigid units, and there is no difference in the movement of the mesogen and the flexible part.[2−4] Intensity changes in the course of the reorientation of LC molecules in external fields are too fast to be monitored by conventional FT-IR spectroscopy. Thus, introduction of step-scan FT-IR spectroscopy a few years ago[5−7] was a turning point in the field of time-resolved studies of the reorientation of LCs. By monitoring different IR bands the method can provide insight into simultaneous movement of different functionalities of the LC molecules during the reorientation process.

The last reports from various research groups have revealed that the mechanism of the reorientation of LC molecules may be different from that commonly accepted. It has been observed that the motion of the pentyl chain of 5CB (4-(*n*-pentyl)-4′-cyanobiphenyl) precedes that of the core in the course of reorientation.[8−11] Other authors reported that the core of 5CB

and other LCs responds more sensitively to the electric field than the flexible part.[12−14] On the other hand, no differences were found for 5CB and other LCs;[15−17] the possible explanation for this disagreement was given elsewhere.[18] In the case of ferroelectric liquid-crystalline polymer, it was proposed that not only the mesogen but also the spacer and at least part of the backbone participate in the reorientation process;[19] however, 2D-correlation analysis for the same sample did not support this conclusion.[18] It has been reported for both low molecular weight nematic LCs[20] and polymeric nematic LCs[18] that the reorientation rate increases as the temperature is raised; the changes are attributed to a viscosity decrease at elevated temperatures. For ferroelectric liquid-crystals (FLC) the situation is not so clear because the tilt angle and the sign of spontaneous polarization (P_s) are temperature dependent.[17,21] It was found for 5CB that the relaxation time of the rise and decay processes decreased with increasing field strength.[12] The same effect was observed for FLC in the region of negative P_s,[17] whereas for $P_s > 0$ there is a very weak influence of the field strength on the rate of reorientation.[17,21]

Significant progress in the understanding of the electric-field-induced structural changes of LCs was made by introduction of two-dimensional (2D) correlation analysis to the infrared spectra by Noda.[22−24] At first, the method was applied in studies of polymers subjected to a small amplitude sinusoidal mechanical perturbation.[22,23] Recently, a general mathematical formalism has been developed to obtain 2D-correlation spectra from any time-resolved spectra having an arbitrary waveform.[24] The method has proved to be especially useful in emphasizing spectral features not readily observable in conventional one-dimensional spectra, as it has the capability of resolving spatial and temporal correlation of reorientational motions of different segmental units. A combination of FT-IR time-resolved spectroscopy with 2D-correlation analysis is the most powerful tool to study time-dependent spectral intensity changes induced

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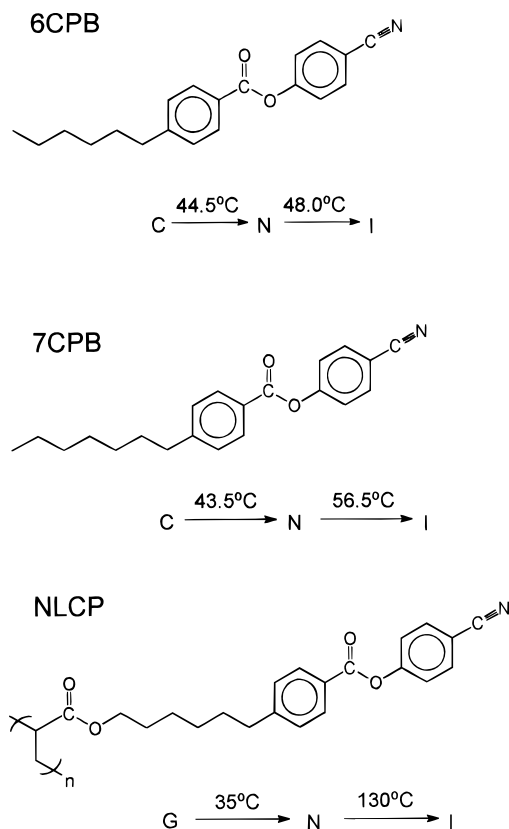
Figure 1. Chemical structures and transitions temperatures of 6CPB, 7CPB, and NLCP. The nematic phase of 6CPB is retained during cooling down to 7 °C below the crystal−nematic transition.

by an external perturbation and can provide many details on the movement of particular molecular segments. Since the first application of the 2D-correlation analysis to time-resolved spectra of a liquid crystal (5CB),[8] numerous similar studies from different laboratories have been reported.[11,25,26] However, to our best knowledge, this is the first example of using the general 2D formalism[24] to investigate the electric-field-induced reorientation of LCs.

In this paper, we report FT-IR time-resolved studies of the electric-field-induced orientation and subsequent relaxation of two nematic LCs (6CPB, 7CPB) and a nematic liquid-crystalline side-chain polymer (NLCP). For a better understanding of the mechanism of reorientation the samples were studied under different experimental conditions such as temperature, voltage, and prealignment. Of particular interest will be the comparison between the mobility of the free 6CPB and the 6CPB-analogue in a side chain of the NLCP. Such a confrontation is made for the first time, and it gave us an opportunity to draw important conclusions concerning the mechanism of the reorientation of liquid-crystalline polymers. To extract more useful information from the time-resolved spectra, in addition to conventional one-dimensional studies, we employed the general 2D-correlation formalism. The preliminary results have been published recently,[18] but some of the basic questions remained open, due to a lack of consistency between the classical one-dimensional investigations and the 2D-correlation analysis. Thus, we undertook more detailed studies to solve this problem.

Experimental Section

The chemical structures of the investigated LCs, together with their transition temperatures, are shown in Figure 1. The samples of 6CPB and 7CPB were supplied by Roche (Basel, Switzerland) and used without further purification. The NLCP was synthesized by the method described elsewhere.[27]

TABLE 1: Vibrational Band Assignments of 6CPB, 7CPB, and NLCP in the 1400−3100 cm^{-1} Range

sample	$\nu(C{=}C)_{ar1}$	$\nu(C{=}C)_{ar2}$	$\nu(C{=}O)$	$\nu(C{\equiv}N)$	$\nu_s(CH_2)$	$\nu_{as}(CH_2)$
6CPB	1509	1612	1746	2235	2862	2934
7CPB	1509	1612	1746	2235	2862	2934
NLCP	1515	1607	1741	2235	2867	2949

The time-resolved spectra were measured on a Bruker IFS-88 FT-IR spectrometer, which can operate in the rapid-scan and step-scan mode. The maximum time resolution in the rapid-scan mode is about 50 ms, and this technique was applied to monitor the movement of NLCP, which has reorientation times from minutes to seconds. The appropriate time resolution was selected individually for the different experimental conditions. To study the reorientational dynamics of 6CPB and 7CPB in the sub-millisecond range, the step-scan technique was utilized. In the employed acquisition procedure 1000 spectra with a time resolution of 0.05 ms were processed. To improve the signal-to-noise ratio, each 10 spectra recorded within a 0.5 ms range were averaged. As a result, 100 spectra with a time resolution of 0.5 ms were finally obtained. All the spectra were recorded at a spectral resolution of 8 cm^{-1}.

For the construction of the measurement cell two germanium plates were used, which served both as windows and as electrodes. They were separated by a polycarbonate spacer of 7 μm thickness. A homogeneous alignment of the LC molecules was induced by covering the inner surfaces of the windows with a thin layer of polyimide, which was rubbed with a cloth in a preferential direction. In the assembled cell the long axes of the LC molecules were then predominantly oriented along the rubbing direction. The LC samples were heated above the nematic−isotropic transition temperature and then introduced in the cell by capillary forces. Upon cooling, the long axes of the LC molecules aligned predominantly along the rubbing direction. A temperature stability of ±0.1 °C was ensured for the cell by a homemade thermocontroller unit.

Under the influence of an electric field the LC molecules undergo a transition from a homogeneous (parallel to the rubbing direction; $E = 0$) to a homeotropic orientation (perpendicular to the rubbing direction; $E > 0$). During this movement spectral changes observed with IR radiation polarized parallel to the rubbing direction appear only for bands with a transition moment component parallel to this direction. Thus, all the time-resolved measurements have been carried out with IR radiation polarized parallel to the prealignment direction. A very detailed description of the experimental conditions is given in a recent review paper.[18]

All calculations were performed using MATLAB software (The Math Works Inc.); for the calculations of the 2D-correlation spectra for each of the data series an average spectrum was taken as a reference.

Results and Discussion

One-Dimensional Analysis. Our studies were restricted to the 1400−3100 cm^{-1} region, although all the spectra were recorded in the 400−4000 cm^{-1} range. In this limited region there appear strong and nonoverlapped spectral features, which can be clearly assigned, to both the mesogen and flexible part of the LC molecule (Table 1). Moreover, most of the absorbances in this region were less than 2, with the exception of the $\nu(C{=}O)$ band, which was not used for calculation of the relaxation time. To characterize the motion of the mesogen, we utilized two $\nu(C{=}C)_{ar}$ bands and the $\nu(C{\equiv}N)$ band; the movement of the hydrocarbon chain was monitored by using the $\nu_{as}(CH_2)$ band. For a quantitative comparison of the
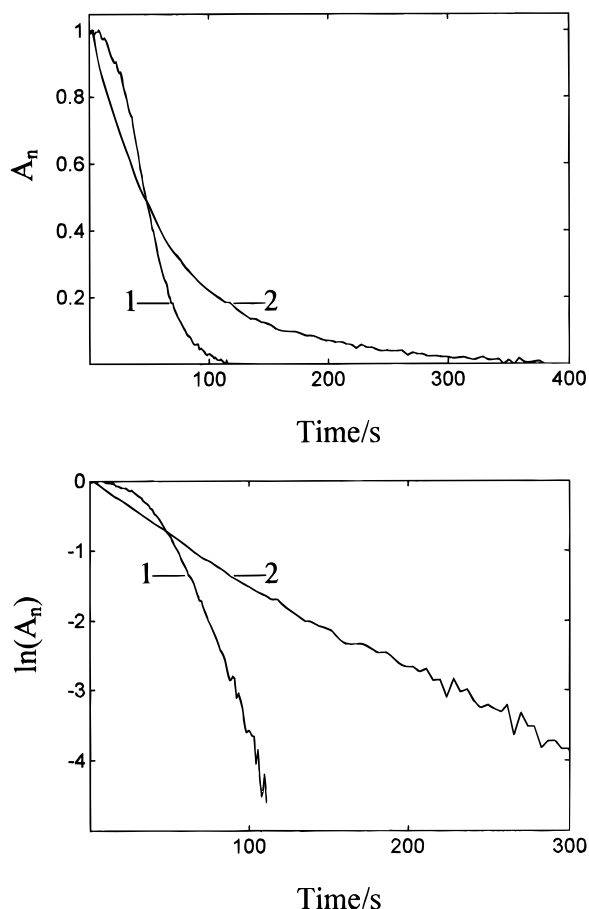
Figure 2. A_n (top) and $\ln(A_n)$ (bottom) plots of prealigned NLCP at 80 °C taken during the orientation (1) and the relaxation (2) for the $\nu(C\equiv N)$ band (2235 cm^{-1}).

reorientational rate a normalized absorbance (A_n) was calculated as follows:

$$A_n = (A_\infty - A(t))/(A_\infty - A_0) \qquad (1)$$

where $A(t)$ is the peak absorbance at time t, A_0 is the value before application of the electric field (the first spectrum), and A_∞ is the corresponding absorbance value when the reorientation is completed (the last spectrum). A_n is always equal to 1 for $t = 0$ and then decays to 0 for the last data point. Figure 2 (top) shows the change of A_n in the course of orientation and relaxation for a prealigned NLCP at 81 °C. As can be seen, the changes for both processes have different character; the same behavior of A_n was observed for the other samples under examination. The relaxation seems to be a simple exponential decay, and it starts immediately after the electric field is turned off, whereas the orientation has a more complex form and it requires an induction period. Such an induction period is well described in the literature[28] and was observed both for nematic LCs[9,10,16,20,29] and for FLC.[17] In Figure 2 (bottom) the $\ln(A_n)$ is plotted versus time; according to our expectation, we get a straight line for the relaxation, whereas a curve is obtained for the orientation process. An exponentially decaying spectrum of normalized absorbance is expressed in the form

$$A_n = e^{-\tau t} \qquad (2)$$

where τ is the characteristic rate constant of the decay process; this value represents the time after which A_n has decayed to $1/e$. From the plot of $\ln(A_n)$ versus t, by using the least squares method, we calculated τ taking the first 20 points; as $A(t)$

TABLE 2: Effect of Field Strength on the Orientation Times (for the First 20 Time-Resolved Spectra; in [s]) of NLCP at 110 °C for Four Selected Bands (No Prealignment)

voltage [V]	$\nu(C=C)_{ar1}$	$\nu(C=C)_{ar2}$	$\nu(C\equiv N)$	$\nu_{as}(CH_2)$
10	4.0	4.7	3.8	4.3
15	2.4	2.6	2.0	2.4
20	0.48	0.52	0.49	0.51

TABLE 3: Relaxation Times (τ) of 6CPB, 7CPB, and NLCP for Four Selected Bands; P, Prealignment; NP, No Prealignment; n, Not Determined

| sample	T [°C]	units	$\nu(C=C)_{ar1}$	$\nu(C=C)_{ar2}$	$\nu(C\equiv N)$	$\nu_{as}(CH_2)$
6CPB, P	35−45	ms	3.9	4.1	4.0	3.9
6CPB, NP	37−47	ms	4.0	4.1	4.1	4.0
7CPB, P	46−50	ms	4.3	4.2	4.1	4.4
7CPB, NP	39−48	ms	4.4	4.1	4.3	4.5
NLCP, P	80	s	98	96	100	n
	100	s	29	27	34	33
	120	s	6.0	6.1	7.5	8.6
NLCP, NP	80	s	303	286	341	384
	100	s	100	95	99	98
	120	s	9.3	9.7	11.8	11.9

approaches A_∞, the values of $\ln(A_n)$ become more scattered and cannot be utilized for quantitative calculations. The relaxation times were determined at a few different wavenumbers across the band, and an average value for each particular band was taken. It makes the values of τ more reliable than the relaxation times calculated at one wavenumber only; however, they are more scattered. Assuming that the reorientation is completed when A_n reaches 0.01−0.02, one can roughly estimate the time needed to finish the reorientation (from eq 2): $\tau_R \approx 4\tau$. All the above considerations deal with the relaxation process, which has an exponential form; in the case of the orientation process τ is not constant and its value changes with time. However, for comparison we estimated τ for the first 20 time-resolved spectra (Table 2). In Table 3 we collected the relaxation times (τ) of all studied samples for four selected bands. They provide information about the rate of relaxation of particular segments of the studied LC molecules. 6CPB and 7CPB form nematic phases in very narrow temperature ranges (see Figure 1), and we did not observe significant changes of τ with temperature; thus, in Table 2 are shown average values of τ. On the basis of the results presented in Tables 2 and 3 we came to the following conclusions.

(a) Both prealigned and non-prealigned samples of 6CPB and 7CPB have the same values of τ; the prealigned sample of NLCP relaxes 3 times faster than the non-prealigned one (at temperatures close to the N→I transition τ for prealigned and non-prealigned NLCP are closer).

(b) 6CPB and 7CPB have similar rates of reorientation regardless of alignment; however, for 6CPB τ is a somewhat smaller. We suppose that this is caused by the slightly smaller moment of inertia of the 6CPB.
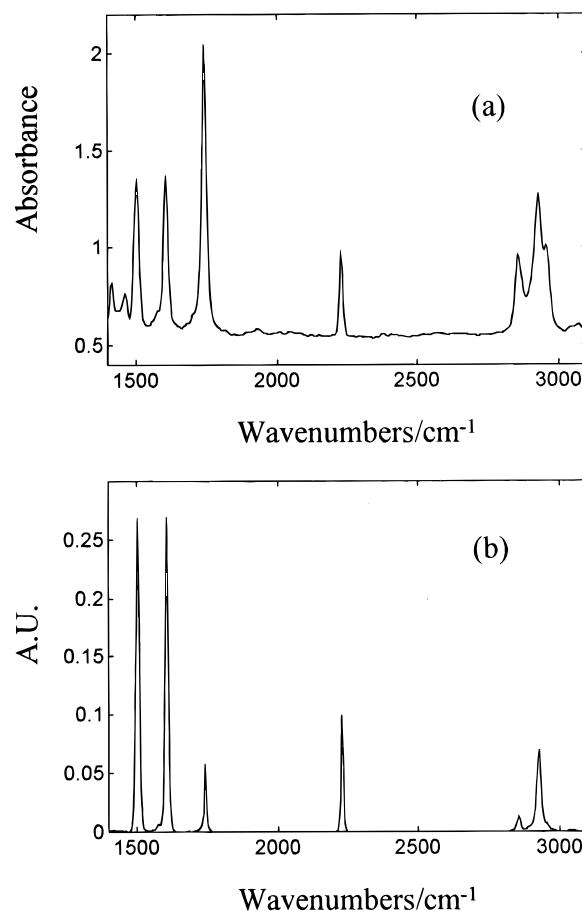
(c) For all studied samples we did not observe any regular changes in the rate of relaxation (and orientation) between the mesogen and the spacer; this means that the whole molecules of 6CPB and 7CPB reorient as rigid units. For NLCP we do not have a separated absorption band to monitor the movement of the main chain; the bands due to the backbone of the polymer are heavily overlapped by the bands due to the spacer, which are weaker than the latter (the spacer contains six methylene groups, whereas the main chain has only two aliphatic units). Hence, we may state that only the mesogen and the spacer of NLCP move at similar rates and we cannot say anything about the motion of the backbone of the polymer.

(d) For NLCP τ decreased with increasing temperature and field strength.

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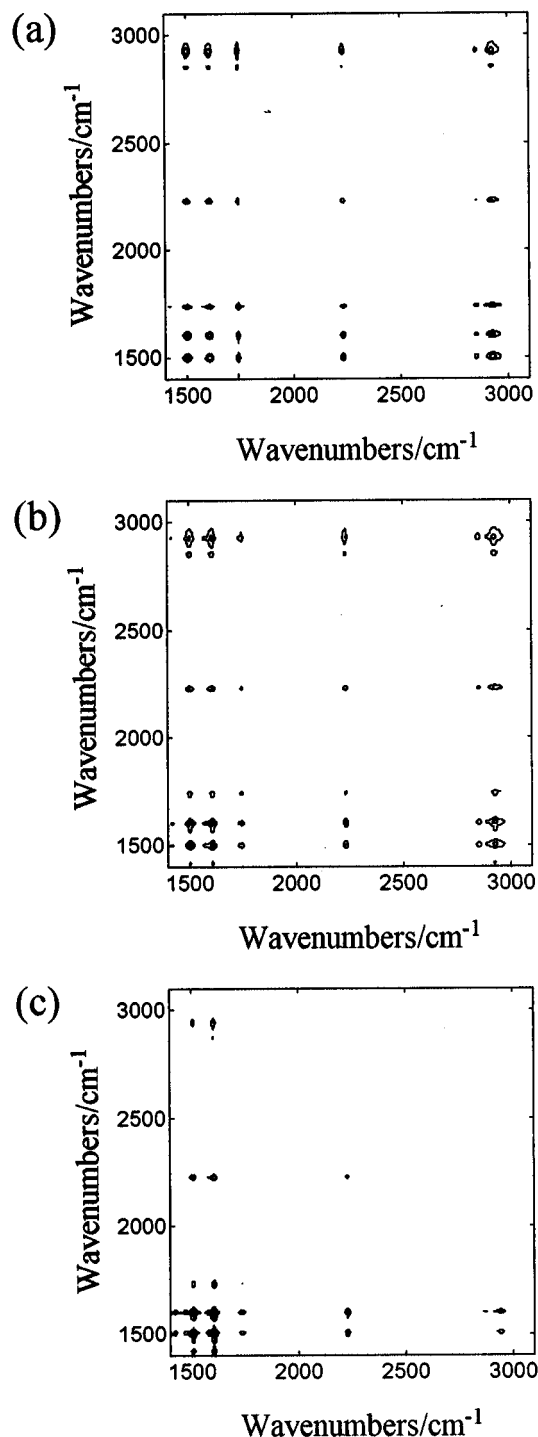
Figure 3. Synchronous 2D-correlation spectra of the relaxation process of prealigned 6CPB at 45 °C (a), 7CPB at 48 °C (b), and NLCP at 100 °C (c).

Figure 4. Average spectrum (a) and a power spectrum (b) of prealigned 6CPB at 45 °C.

The deviations from the average values of τ are as follows: $\pm 5-10\%$ for the $\nu(C{=}C)$ ring bands and the $\nu(C{\equiv}N)$ band (6CPB, 7CPB, NLCP), $\pm 10-15\%$ for the $\nu_{as}(CH_2)$ band (6CPB, 7CPB), and $\pm 20-30\%$ for the $\nu_{as}(CH_2)$ band (NLCP). Since the $\nu_{as}(CH_2)$ band is overlapped by other CH bands, the corresponding relaxation times are more scattered than for the mesogen bands, which are well separated from the other spectral features. A fairly large deviation for the $\nu_{as}(CH_2)$ band of NLCP is due to small intensity changes for this band. Although the values of τ are not strictly identical, they are within experimental error, which is delimited by the level of noise. To confirm the validity of the conclusions drawn from the

relaxation times, 2D-correlation analysis of the dynamic spectra was undertaken.

2D-Correlation Analysis. In Figure 3 the 2D-correlation synchronous spectra for the relaxation process of prealigned 6CPB, 7CPB, and NLCP are shown. As expected, the spectra for the low molecular weight analogues are very similar. The most characteristic feature of the spectra is a strong correlation between all bands that appear in this region. Synchronous peaks between the bands that belong to different parts of the mesogen indicate that the mesogen reorients as a rigid rod. More important, one can also observe a clear correlation between the $\nu(CH_2)$ bands and the bands due to the mesogen. At the same time there is no appreciable asynchronicity in this region.[30] Hence, we may conclude that the molecules of 6CPB and 7CPB reorient as rigid units. This conclusion agrees very well with the results of the conventional analysis described in the previous section. For NLCP one can notice distinct synchronous peaks between different mesogen bands. Correlation between mesogen and spacer absorptions exist as well; however, it seems to be less significant compared to 6CPB and 7CPB. Simultaneously, no considerable asynchronicity in this region was observed. Thus, we deduce that the mesogen and spacer move in phase; however, the intensity changes for the spacer are rather small (for example, the autopeak of the $\nu_{as}(CH_2)$ band, at this scale, does not appear in the synchronous spectrum; Figure 3c).
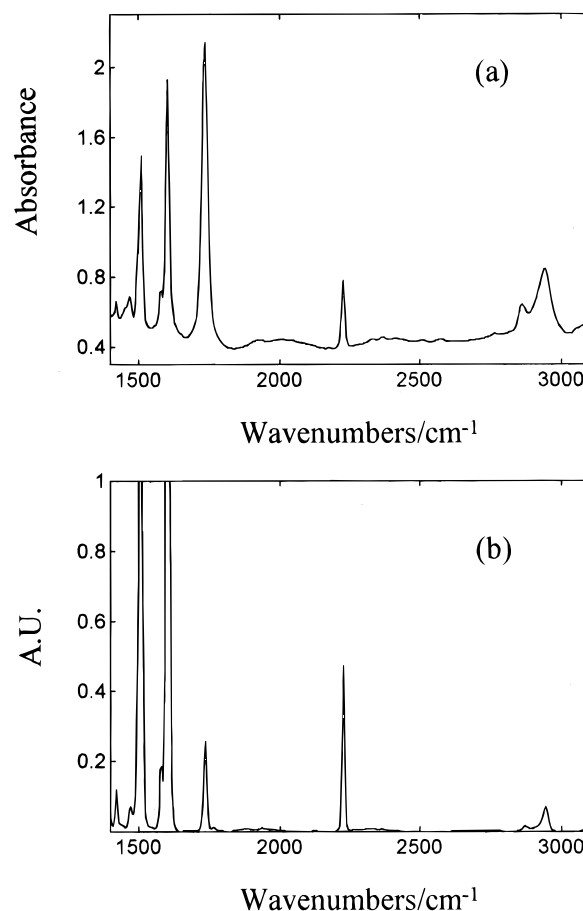
As we mentioned earlier, the bands of NLCP due to the spacer and the backbone of the polymer appear in the same wavenumber region, and the latter are much weaker. As a consequence, we cannot extract any reliable information about the motion of the main chain from the synchronous spectrum. Since the flexible spacer effectively separates the movement of the mesogen from that of the polymer backbone, a different behavior
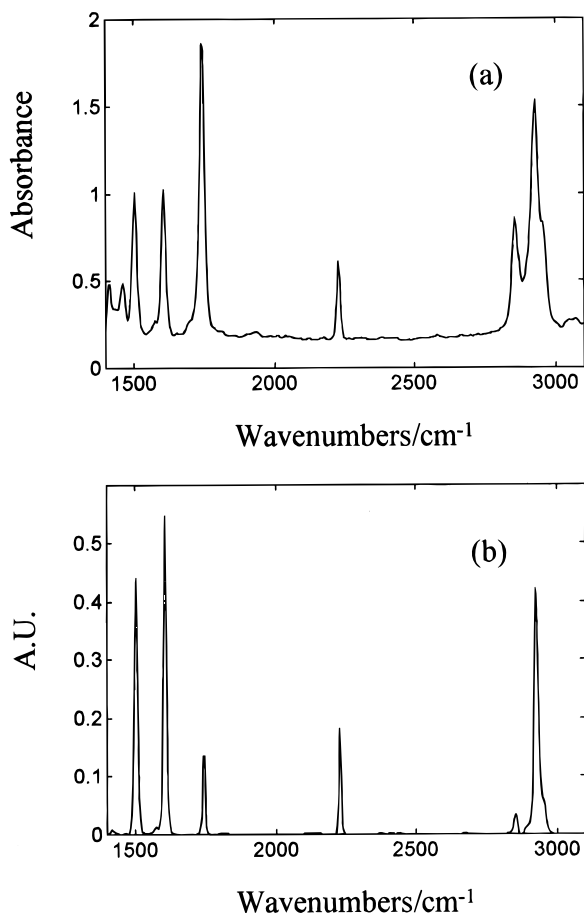
Figure 5. Average spectrum (a) and a power spectrum (b) of prealigned 7CPB at 48 °C.

Figure 6. Average spectrum (a) and a power spectrum (b) of prealigned NLCP at 100 °C.

NLCP

Figure 7. Schematic represenation of the segmental motions of the NLCP during application of an electric field.

of the mesogen and the main chain can be expected in the course of the reorientation. It seems reasonable to assume that the possible movement of the main chain will be partially shifted in phase with respect to the reorientation of the mesogen. If there is any difference in the rate of reorientation between the mesogen or the spacer and the main chain, we should observe clear peaks in the asynchronous spectrum. A detailed inspection of the asynchronous spectrum did not show any peaks of physical meaning. Thus, we conclude that the backbone of NLCP does not participate in the reorientation.

Figures 4−6 show average spectra alongside the corresponding power spectra[31] of 6CPB, 7CPB, and NLCP, respectively. Let us compare the intensity of the $\nu(C\equiv N)$ and $\nu_{as}(CH_2)$ bands in the average spectra with the intensities of power spectra for all studied samples. As can be seen, the intensities of 6CPB are similar both in the average and in the power spectra (Figure 4); in the case of 7CPB the $\nu_{as}(CH_2)$ band is more intense than the $\nu(C\equiv N)$ band, as 7CPB has one methylene unit more than 6CPB (Figure 5). For NLCP both the $\nu(C\equiv N)$ band and the $\nu_{as}(CH_2)$ absorption have comparable intensities in the average spectrum, whereas one can observe a significant intensity reduction of the $\nu_{as}(CH_2)$ band in the power spectrum (Figure 6). This means that the motion of the hydrocarbon chains of the polymer is strongly restricted, as compared to the hydrocarbon chains of 6CPB and 7CPB. Thus, it seems sensible to assume that only a small part of the spacer directly attached to the mesogen, takes part in the reorientational motion, whereas the rest of the spacer does not participate in the motion. As a consequence, the backbone of the polymer also does not reorient, because the spacer does not transfer the reorientational movement to the main chain (Figure 7). The same result was obtained
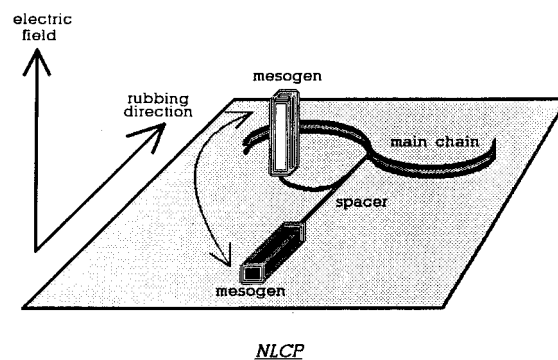
for a ferroelectric liquid-crystalline polymer (FLCP) from 2D-correlation analysis of the time-resolved FT-IR step-scan spectra.[18]

It is very likely that also other side-chain LC polymers, which consist of a mesogen attached to the main chain by a flexible spacer, behave in the same way in external electric fields; only the mesogen and a small part of the spacer move, whereas the rest of the spacer and the backbone of the polymer do not participate in the reorientation. In low molecular weight LCs the hydrocarbon chain is completely free, whereas in polymers the chain (spacer) bonded to the backbone is strongly restricted; it may be regarded as a free chain of infinite length. It sounds very likely that there exists a certain length at which the chain does not move as a unit. At this length the energy of interaction of the dielectric anisotropy of the LC molecule becomes higher than the energy of the conformational changes in the methylene sequence. Measuring a series of samples of different chain

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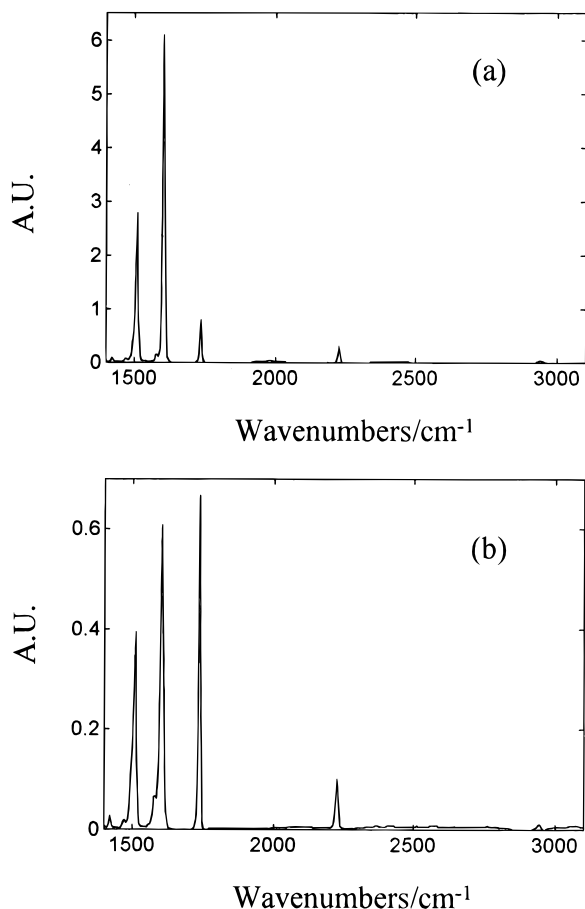
Figure 8. Power spectra for prealigned (a) and non-prealigned (b) NLCP at 120 °C.

Figure 9. Power spectra of prealigned NLCP at 80 °C (a) and 100 °C (b).

length, with the same mesogen, it would be possible to find the "critical" chain length. Unfortunately, however, not all molecules of such a series are still liquid-crystals.

The fact that mesogen and spacer move in phase does not necessarily imply that the spacer reorients as a rigid rod, as was assumed on the basis of the classical one-dimensional analysis.[18,19] The energy between the *gauche* and *trans* conformation for a methylene chain is not high ($\sim$500 cal·mol^{-1}); it is not expected that the methylene sequence will maintain the planar zigzag conformation. In fact, it has been observed that at elevated temperatures the hydrocarbon chain of FLC becomes flexible.[32] Urano and Hamaguchi assumed that the pentyl chain and the cyanobiphenyl core of 5CB move distinctly through the internal rotation around the C(biphenyl)−C(pentyl) bond.[9,10] To explain the behavior of the spacer during the reorientation, it is enough to assume that only a part of it moves in phase with the mesogen and the rest of the spacer is stable. Of course, this fact implies a conformational change of the spacer. It appears very probable that this change occurs only for one C−C bond, whereas the rest of the bonds will still have the *trans* conformation. We can expect that the effect of the conformational change may be clearly observed only for very short chains, because the change in the intensity ratio for *gauche/ trans* will be difficult to observe for longer chains.

Let us compare two power spectra of prealigned and nonprealigned NLCP (Figure 8) recorded at similar experimental conditions (100 °C, 10 V). One can easily notice (see *Y*-axis units) that the intensity variations for the prealigned sample are approximately 10 times higher than for the non-prealigned sample. The same effect occurs for 6CPB and 7CPB, although they have the same relaxation times regardless of the alignment. This means that for low molecular weight nematic LCs the
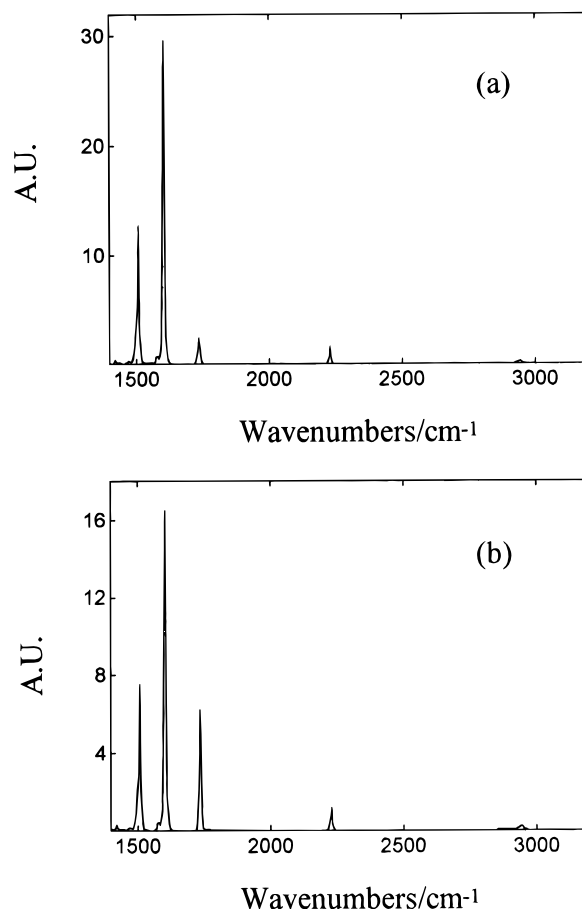
prealignment does not influence the phase of the intensity change but its amplitude, to a great extent.

Figure 9 shows the power spectra of prealigned NLCP at 80 and 100 °C. One can observe that the band intensities at 80 °C are nearly twice as strong as at 100 °C. This effect may be attributed to a decreasing order parameter with increasing temperature.

Finally, from an inspection of Figures 4−6 one can easily notice a considerable reduction of the intensity due to the ν(C=O) band in the power spectra, as was already reported for FLC samples.[13,15,21] However, the band was too intense in the time-resolved spectra ($A > 2$), and thus, we will not interpret this effect.

Conclusions

On the basis of both the classical one-dimensional and 2Dcorrelation analysis we conclude that low molecular weight nematic liquid-crystals (6CPB, 7CPB) reorient as rigid units. The prealignment and the temperature (in a small range) do not effect much the rate of relaxation. As concerns the nematic liquid-crystalline polymer (NLCP), only the mesogen and the small part of the spacer directly attached to the mesogen reorient with the same phase, whereas the rest of the spacer and the main chain of the polymer do not participate in the movement. When the temperature and the field strength increase, the reorientation rate of NLCP increases; the prealigned sample reorients about 3 times faster than a non-prealigned specimen.

At the end, we would like to stress that all above conclusions refer to the given experimental time resolution. If there are any conformational changes in the studied LC molecules, which

are much faster than the time resolution we applied for the measurements, they cannot be detected by our experimental setup.

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(30) The peaks in 2D-correlation spectra that develop before the noise peaks appear are considered as significant. In 2D-correlation asynchronous spectra of all studied samples no significant peaks were found. Thus, the spectra are not presented in this paper because they do not contain any important information.

(31) A diagonal of the synchronous spectrum is called a power spectrum and yields information about the total intensity changes at a given wavenumber.

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