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Infrared-spectroscopic investigations of molecular order in liquid crystalline side chain polymers

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Summary

Infrared dichroism was used to determine the order parameters of liquid crystalline side chain polymers. By this the order parameters of the main chain, of the spacer and of the mesogenic group can be obtained separately. Therefore spectra of two liquid crystalline polyacrylates were recorded with polarized light at different temperatures. In a poly(acrylate) with 6 CH_2 groups in the spacer a high order parameter was found not only for the mesogenic group, but also for the spacer and the main chain. The orientation of the poly(acrylate) with a spacer of only 2 CH_2 groups is lower due to the stronger interaction of main chain and mesogenic group.

1. Introduction

Liquid crystalline side chain polymers became more and more interesting during the last years. They show an electro-optical behaviour like low molecular weight liquid crystals, combined with freezing of the molecular motion at the glass transition. Therefore they are discussed for use in future optical display or storage devices (1,2).

Macromolecules of this class of substances contain three molecular units: The mesogenic group, the spacer and the main chain . The mesogenic group is usually formed by two para-substituted benzene rings; it can be considered as a rigid rod. The spacer is typically an alkane chain containing 2 - 11 CH_2-groups (3,4). Via the spacer, the mesogenic groups are linked to the main chain. The main chain be an organic polymer molecule or a SiO chain molecule. In lc polymers two substances are chemically linked which have a principally different phase behaviour. The mesogenic group together with the aliphatic spacer normally undergoes a liquid crystalline mesophase. This partially ordered state is present in a temperature range between the crystalline state and the isotropic phase (melt). The main chain can be considered as a usual polymer: if there is no crystallisation it shows only a glass transition. There is no long range order evident in non crystalline polymers, except when they are oriented by external strain. The composed system shows liquid crystalline ordering, and, at the clearing point T_c, a phase transition where it becomes isotropic. To lower temperatures it passes a glass transition, where the liquid crystalline order freezes (2).

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Because of the interaction between the main chain and the mesogenic group via the flexible spacer, an ordering of the main chain below T_c is possible. On the other hand the ordering of the mesogenic groups can be influenced by the main chain. While the ordering of the mesogenic groups is known to be comparable with that of low moleculer weight liquid crystals, only little is known about the main chain and the spacer. Former measurements by NMR and IR-dichroism show that the orientation of these parts of the lc polymer is very low (3,4). For these experiments the liquid crystalline polymers have been oriented by a magnetic field or mechanical strain, respectively.

This paper reports on studies of molecular order of two liquid crystalline side chain polymers. Here, the orientation of the molecules is provided by surface effects (see chapt.2). IR spectra showing characteristic dichroism for several absorption bands are recorded as a function of temperature.

Order parameters of different parts of the molecules are calculated from the linear dichroism of characteristic absorption bands. Using this method no labeling of the molecules is necessary like in NMR.

2. Samples and Preparation

Two polyacrylates and a low molecular weight liquid crystal with a chemical structure similar to the side groups of the polymers were studied. The chemical structures of the polymers are the same except the length of the spacer (see fig.1). The polymers where synthesized by R. Zentel at the University of Mainz (5). The three substances show a liquid crystalline mesophase of the nematic type. The transition temperatures and molecular weights are listed in table 1. According to (5) the abreviations P/H/6/CN, P/H/2/CN and L/7/CN are used to identify the samples. P and L stand for the Polymer and for the Low molecular weight liquid crystal, respectively; H means the hydrogen atom at the main chain next to the mesogenic group, the figure gives the length of the aliphatic side chain and CN denotes the cyano end group.

In order to measure the IR-dichroism it is necessary to prepare a thin film of the samples with a well known direction of orientation. Therefore two KBr-plates where coated with a thin polyimide film and then rubbed by a rotating wheel of foamed polystyrene. Between these plates the polymers, heated to the isotropic state, where pressed to a film of about 10μm in thickness. Annealing this film at a temperature only a few degrees below the clearing point leeds to a sample which is homogenous oriented with the mesogenic groups directed parallel to the direction of rubbing (6). This method is well known for the orientation of low molecular weight liquid crystals. By this process the latter are aligned in a relatively short time, whereas the polymers need many hours of annealing to form a homogenous film (7).

Table 1:

Sample	M_n	phase transitions
P/H/6/CN	20000	g 33°C n 133°C i
P/H/2/CN	18000	g 75°C n 110°C i
L/7/CN	321	k 45°C n 55°C i

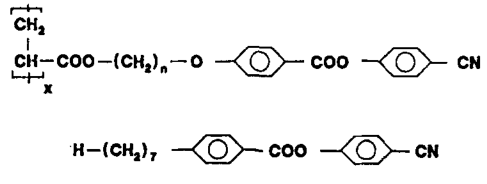

Fig. 1:
Chemical structure
of the samples

3. Dichroism and Orientation

Macroscopic orientation of a sample leads to different absorption of IR radiation depending on the state of polarisation. A transition moment absorbs only the electric field component of the incident radiation which is parallel to its own direction. In the mid infrared region, the transition moment is caused by a molecular vibration, which, in many cases, is localized within few chemical bonds. Thus, by measuring the dichroism of the different absorption bands at special wavelengths information on the ordering of special groups, e.g. mesogenic group, spacer and main chain can be obtained. Here we describe how the order parameter is calculated from the measured dichroism.

In the nematic phase the rod-like mesogenic groups are oriented in one main direction. There is no positional long range order. In uniaxially ordered systems, the state of order is expressed in terms of the order parameter:

$$S = (3\langle\cos^2\theta\rangle-1)/2 \qquad (1)$$

θ is the angle between the molecular axis of an individual molecule and the director $\vec{n}$ which is parallel to the optical axis. The nematic order is completely described by the distribution of θ. S is the second moment of the Legendre expansion of this distribution. Dichroism and birefringence measurements give only a value of S and no further information about the distribution function.

The dichroism is measured in terms of the dichroitic ratio R, i.e. the ratio of the absorbance of radiation with the electricl field parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the optical axis, which is given by the direction of rubbing:

$$R = A_\parallel/A_\perp \qquad (2)$$

This ratio and the order parameter are related by the well known formula (8):

$$S= \frac{1}{(3\cos^2\delta-1)/2}\;\frac{R-1}{R+2} \qquad (3)$$

δ is the angle between the molecular axis and the transition moment. Because δ is not known, in many cases, an optical order parameter is defined which depends only on the measured absorption values:

$$S_{OPT} = \frac{R-1}{R+2} \qquad (4)$$

In order to registrate the dichroism of an absorption band as a function of temperature it is recommended to relate the measured value $A_\parallel$ or $A_\perp$, respectively, to the absorption of unpolarized light, A_{ISO}, at the same wavelength. Introducing

$$N_\parallel = A_\parallel/A_{ISO}\ ,\quad N_\perp = A_\perp/A_{ISO} \qquad (5a,b)$$

the optical order parameters are then calculated (9) by :

$$S_{OPT} = 1 - N_\perp \text{ and } S_{OPT} = (N_\parallel+1)/2, \qquad (6,7)$$

respectively.

The influence of the internal field is taken into account by applying an expression given by Vuks (10). This leads to a correction factor

for the dichroitic ratio in eq.6, so that $(n_\perp/n_{iso})N_\perp$ must be used instead of $N_\perp$ (12).
If the order parameter is known, the refractive index can be calculated by:

$$n_\perp = n_{iso} - 1/3 \{S\, \Delta n(T=0K)\} \qquad (8)$$

$\Delta n(T=0K)$ is the difference of the refractive indices $n_\parallel - n_\perp$ extrapolated to 0 K. This leads to a correction of the order parameter:

$$S_{OPT} = (1 - N_\perp) \left[1 - \frac{1}{3S_\delta} \frac{\Delta n(T=0K)}{n_{iso}} N_\perp \right]^{-1} \qquad (9)$$

with $$S_\delta = (3\cos^2\delta - 1)/2 \qquad (10)$$

4. Experimental

MIR spectra of the three substances at different temperatures in the nematic and the isotropic phase were recorded with a Perkin-Elmer PE-283 spectrometer. The IR beam was polarized by a wire grid on an AgCl substrate (Perkin-Elmer). With the slit program used the resolution was better than 2 cm^{-1} in the examined wavenumber range.
Additionally the change of transmission with temperature was measured at a fixed wavenumber. With this method the temperature dependance of the C≡N stetching absorption and its dichroism was registrated continuously. These measurements must be carried out with very low heating rates (0.1 - 0.5 K/min) to keep the samples, especially the polymers, in equilibrium. The samples were heated with temperature controlled silicon oil, flowing through two ring channels around the KBr plates. A Pt-100-resist was placed in a hole in one of the KBr plates to measure the temperature of the sample.

5. Results and discussion

As expected, the spectra recorded from the samples in the nematic phase show a strong dichroism (fig.2). It decreases with temperature and finally drops to zero at the transition temperature nematic-isotropic. Depending on the angle δ between the molecular axis of the mesogenic group and the transition moment, some bands are more intense when the electric field is parallel to the optical axis of the sample, some other bands show the opposite behaviour.
In the fig.3-5 three wavenumber regions are shown as examples for anisotropic absorption of the substances under study. These spectra

P/H/6/CN

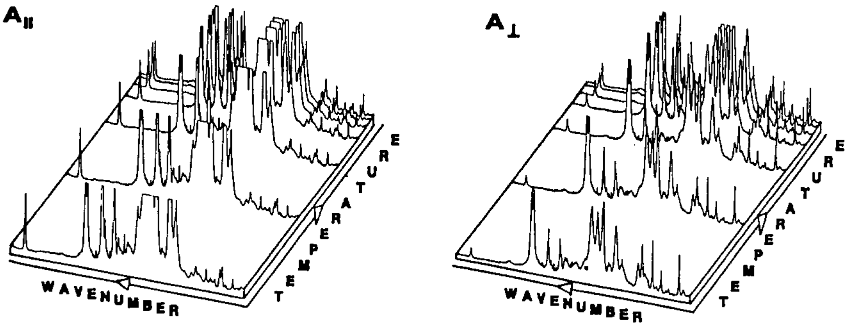

Fig. 2: Temperature dependance of the spectra of P/H/6/CN
Wavenumber range 2350 cm^{-1} - 400 cm-1
Temperature range 50°C - 135°C

Table 2: Band assignments

Wavenumber	Vibration	δ
2235 cm^{-1}	C≡N-stretching	≈ 0°
1420 cm^{-1}	CH_2-bending	
1410 cm^{-1}	CH_2-bending	
1020 cm^{-1}	C-C-stretching	
880 cm^{-1}	Φ-H-bending (A_2)	≈ 90°
690 cm^{-1}	Φ-H-bending (B_1)	≈ 90°
540 cm^{-1}	C≡N-bending	≈ 90°

were recorded at a certain temperature within the nematic range to have a high degree of order. In table 2 the assignments of a few bands are given, which are selected for further considerations. Bands that appear in the spectra of the polymers but not in the monomer L/7/CN where assigned to vibrations of the spacer or those of the main chain. The assignment to the spacer must be taken into account because of the oxygen atoms at both sides of the spacer. This possibly leads to a frequency shift of the CH_2 vibrations compared with L/7/CN. The bands assigned to the spacer and the main chain can also be observed in the spectrum of poly(butyl acrylate) (11) which represents the polymeric samples without the mesogenic groups.

The optical order parameters S_{OPT} of the bands assigned in table 2 are shown in fig.6 and 7. They were calculated from the band intensities using eq.4. The order parameters evaluated by this method are calculated from the transmission peak intensities and are within an error range of 10 - 50 %. This is caused by the uncertainity of the base lines due to band overlapping. Therefore no internal field correction is necessary. To get the molecular order parameters from S_{OPT} the values of the angle δ in eq.3 must be known.

As an example we look at two vibrations of the mesogenic group: the CN-stretching vibration at 2235 cm^{-1} with $\delta \approx 0°$, and the out-of-plane bending vibration of the hydrogen atoms of the benzene ring (880 cm^{-1}, $\delta \approx 90°$). The calculated values S_{OPT} are depicted in

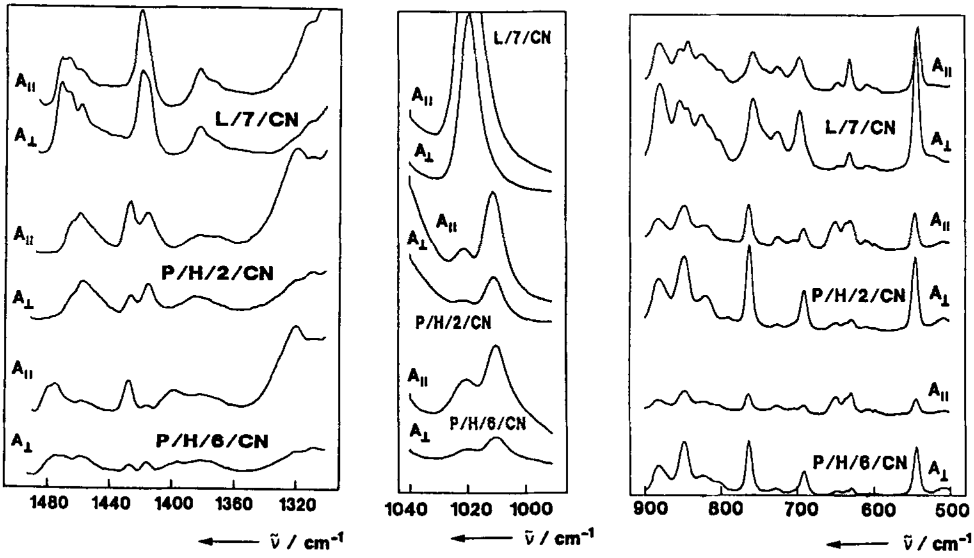

Fig 3-5: Three wavenumber sections of the spectra recorded at a temperature of the nematic range

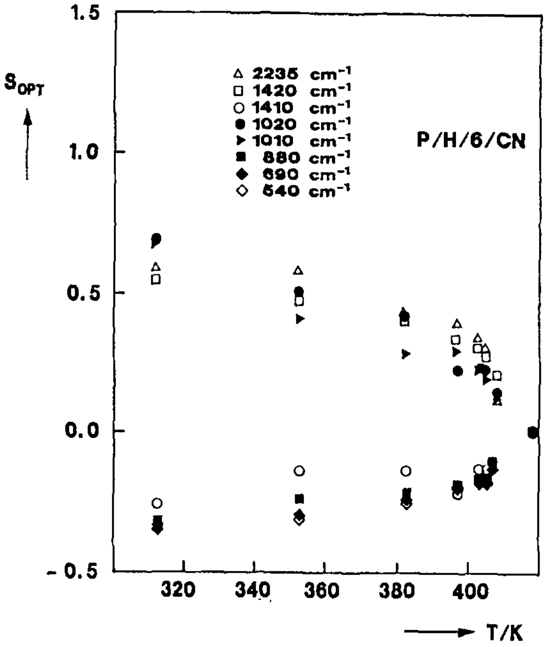

Fig 6:
Optical order parameters calculated from several absorption bands of P/H/6/CN

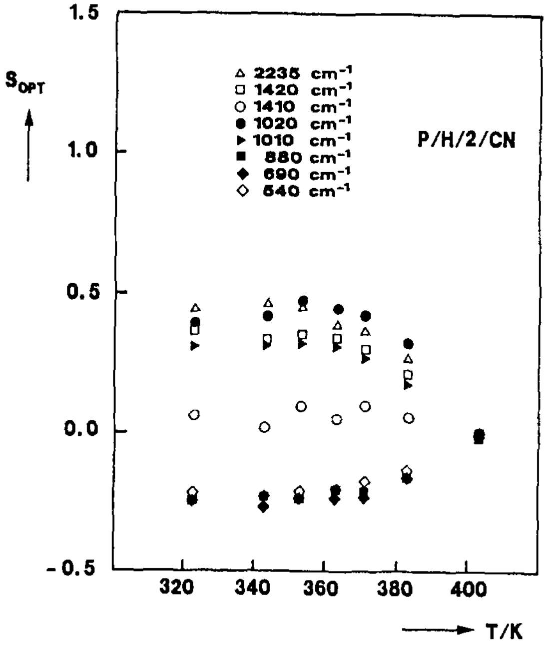

Fig 7:
Optical order parameters calculated from several absorption bands of P/H/2/CN

fig.6. Taking into account the corresponding values for δ leads to identical values for S describing the orientation of the whole mesogenic group. The temperature behaviour of S_{OPT} in fig.6 agrees with that of low molecular weight liquid crystals like L/7/CN.

Fig.6 shows that the bands assigned to vibrations of the spacer or those of the main chain of P/H/6/CN show the same behaviour as one of the two bands mentioned above. If angles of $\delta \approx 0^\circ$ for the bands with positiv optical order parameters are assumed, and $\delta \approx 90^\circ$ for the others, it can be seen that the order parameters of the spacer, the main chain and the mesogenic group are the same. Other angles would lead to order parameters that are higher or negative and are therefore not possible.
In P/H/2/CN the 1420 m^{-1} band leads to very small values of S_{OPT} (fig.7). Obviously parts of the spacer or the main chain are disordered. Because this is a CH-vibration it can't be assigned precisely to a special CH-group of the molecule. Therefore no more detailed conclusions can be drawn from the dichroism of this band.

The CN stretching vibrational band.

The order parameter of the mesogenic group can be determined very exactly with the isolated absorption band of the C≡N-stretching vibration. The transition moment of this vibration is known to be parallel to the CN-group. This axis and the axis through the centers of gravity of the two benzene rings include an angle of a few degrees. This means that the optical order parameter is lower than the molecular order parameter by a factor S_δ (eq 10). This was neglected in the considerations up to now. The factor is the same for the two polymers and the low moleculer weight liquid crystal L/7/CN. Therefore we can compare molecular ordering by comparing optical order parameters.
We measured the transmission at the center of this band while heating the samples very slowly through the whole nematic range up to the isotropic state. We used IR radiation polarized parallel and perpendicular to the optical axis of the liquid crystal. With eq.6 and 7, respectively, both lead to identical values of the order parameter. However, using the $A_\perp$ values the error tolerances of S are the better ones. The isotropic absorption was calculated from the transmission in the isotropic phase. The influence of the internal field was corrected using eq.9 . The values of the refractive indices in eq.9 were measured with an optical microscope (12), or taken from (13) (see table 3). The value n_{ISO} of P/H/2/CN was assumed to be the same

Table 3: Refractive indices

	P/H/6/CN	P/H/2/CN	L/7/CN
n_{ISO}	1.57 (13)	-	1.546 (13)
$\Delta n(T=0K)$	0.19 (12)	0.39 (12)	0.41 (12)

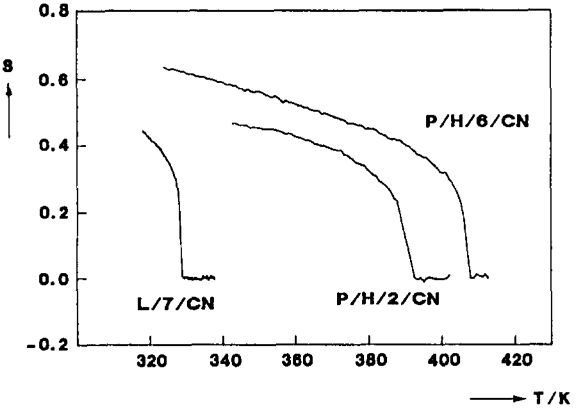

Fig 8:
Optical order parameters calculated from the CN stretching absorption bands (continously measured)

as of P/H/6/CN. For the correction δ was taken 0°.
The temperature dependence of S_{OPT} is shown in fig.8 for the three substances.
For a more detailed comparision of the curves we used an empirical equation for the temperature dependance of S_{OPT} (14):

$$S_{OPT} = SS_{\delta} = S_0 \, (1-T/T_{NI})^{\alpha} \qquad (11)$$

Using a logarithmic regression procedure S_0 and the exponent α can be calculated from the measured S_{OPT} values (see table 4). Since S is known to become 1 at 0 K for low molecular weight liquid crystals, the obtained value of S_0 must be the same as S_{δ}. With S_{δ} = 0.84 (L/7/CN) the angle δ is calculated to be 19°. If there is an additional disorder due to interaction of the mesogenic group and the main chain, S_0 will be smaller then S_{δ}, this must be the reason why S_0 is only 0.77 (see table 4) for P/H/2/CN.

Table 4:
Results of linear regression procedure

	P/H/6/CN	P/H/2/CN	L/7/CN
S_0	0.86	0.77	0.84
α	0.24	0.23	0.20

Conclusions

The results of this study show that in lc side chain polymers the order of the mesogenic groups can be transformed to the main chain. On the other hand the arrangement of the mesogenic groups is influenced by the main chain, if there is a strong interaction between these parts given by a short spacer.

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