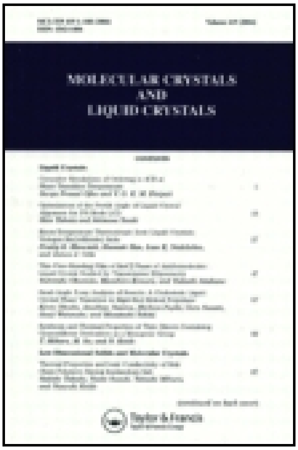

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Molecular Dynamics in Liquid Crystalline Side Chain Polymers

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Molecular Dynamics in Liquid Crystalline Side Chain Polymers†

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The static and dynamic dielectric properties of two liquid crystalline side chain polymers, one with a polychloroacrylate and one with a polyacrylate backbone and mesogenic side groups based on phenylbenzoate cores have been studied. The substitution of the polar chloro group at the main chain was done in order to get more information about the role of the main chain in the molecular dynamic processes.

Dielectric permittivity measurements have been carried out with samples oriented in a magnetic field of 1.2 Tesla, in the frequency range 10 Hz to 10 MHz and a temperature range of −50 °C to +150 °C. A different behaviour is observed for the polyacrylate and the polychloroacrylate.

The polyacrylate shows well resolved δ- and α-relaxations. For the polychloroacrylate the α-relaxation is extremely broad on the temperature and frequency scale. The δ-relaxation is also unusually broad and sets in very near to the clearing point. The dipole strengths of the relaxations are different for the two compounds due to the chloro group. The broadening of the relaxation processes for the polychloroacrylate is explained by a rapid increase of the viscosity below the clearing point.

Keywords: polymeric liquid crystals, dielectric properties, molecular dynamics

INTRODUCTION

Dielectric permittivity measurements in the radio frequency range are a valuable tool to study molecular motions in which polar groups

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are involved.[1] In recent years this method has also been applied to liquid crystalline side chain polymers with acrylate and siloxane backbones and various mesogenic groups.[2–8]

Using the magnetic field orientation techniques developed in our group[9–13] some more specific information can be obtained than with oriented samples.

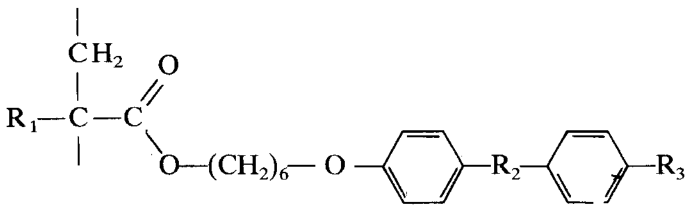
Recently we described the static and dynamic anisotropic dielectric properties of two polyacrylates with $(CH_2)_6$-spacer and different mesogenic moieties, namely phenylbenzoate and biphenyl. Both have the same strongly polar cyano end groups.[13]

In order to get more information about the main chain dynamics we are now interested in the effect of a substitution of a polar group at the main chain. We studied two compounds with very similar mesogenic side chains and different backbones with and without polar chloro groups. The first liquid crystalline polymers with chloroacrylate and methacrylate backbones were studied by Zentel.[2] Whereas for the most compounds, including our own investigations, two main relaxation processes, the so-called δ-process and α-process can be discussed above the glass temperature, for the chloroacrylates and methacrylates only one relaxation was observed which broadened very rapidly with decreasing temperature.

Preliminary results of our oriented measurements of the chloroacrylate where presented in (11). Recently a short report on unoriented dielectric properties of the same chloroacrylate was published by Decobert *et al.*[14]

EXPERIMENTAL

The general structure of the side chain polymers is:



Some properties of the investigated compounds are listed below

R_1	R_2	R_3	name	transition temp.	mol. weight
H	COO	OCH_3	*1*	g 35 s 97 n 123 i	20000
Cl	COO	OC_4H_9	*3*	g 39 s 103 n 113 i	24000

The substances were prepared as described previously.[2] The transition temperatures were determined by DSC (DuPont 990 thermal analyser). The liquid crystalline phases were characterized by polarizing microscopy and X-ray diffraction on oriented samples. The molecular weight distribution was determined by GPC using polystyrol as calibration substance.

Dielectric measurements were done in a shielded plate condensor described previously.[13] The distance between the plates was 150 μ for all the measurements. The cells were first calibrated using air, toluene and chlorobenzene as standards, then the sample was filled in by capillary force. A magnetic field of 1.2 T was usually used for orientation. The quality of alignment was checked by polarizing microscopy and by watching the time development of the dielectric anisotropy.

The two substances exhibit different orientation properties; whilst both align well in the 0.7 mm tubes used for the X-ray measurements, complete alignment could not be achieved for *2* in the dielectric cell. The quality of alignment could be improved by longer exposure times in the magnetic field and by increasing the field strength to 3 Tesla. This caused the dielectric anisotropy to rise from 0.3 D to 1.1 D, but no saturation value was reached, as the polarizing microscope showed.

The measurements at lower frequencies up to 1 kHz were performed using a GenRad 1615 capacitance bridge supplemented with an Ithaco lock-in detector. The higher frequencies were measured with the Hewlett-Packard self-balancing bridge hp4192A.

The data were corrected for the static conductivity and for the high-frequency deviations caused by the inductance and resistance of the cables and connectors.

RESULTS AND DISCUSSION

The X-ray diffraction patterns reveal very narrow meridional spots for both substances. The intermolecular spacing determined from them is 5.2 Å for both. The inner reflections indicate a smectic A phase for *1* with a layer distance of 29 Å. A more complicated X-ray pattern is obtained for *2* (Figure 1). It is similar to that reported in (14), but sharper. We also conclude to a smectic C phase. The tilt angle is 35°, the layer thickness is 51 Å. Comparing this with the molecular length of 27 Å, which was calculated using Dreiding models, one must assume a bilayer structure. This was first discussed by Zentel[2] and later by Decobert *et al.*[14]

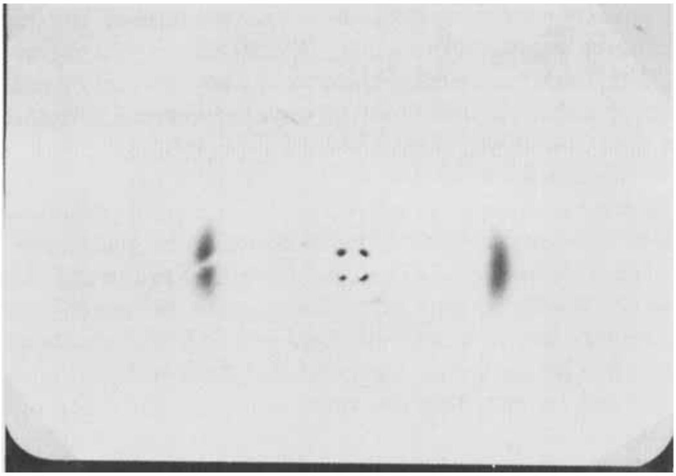
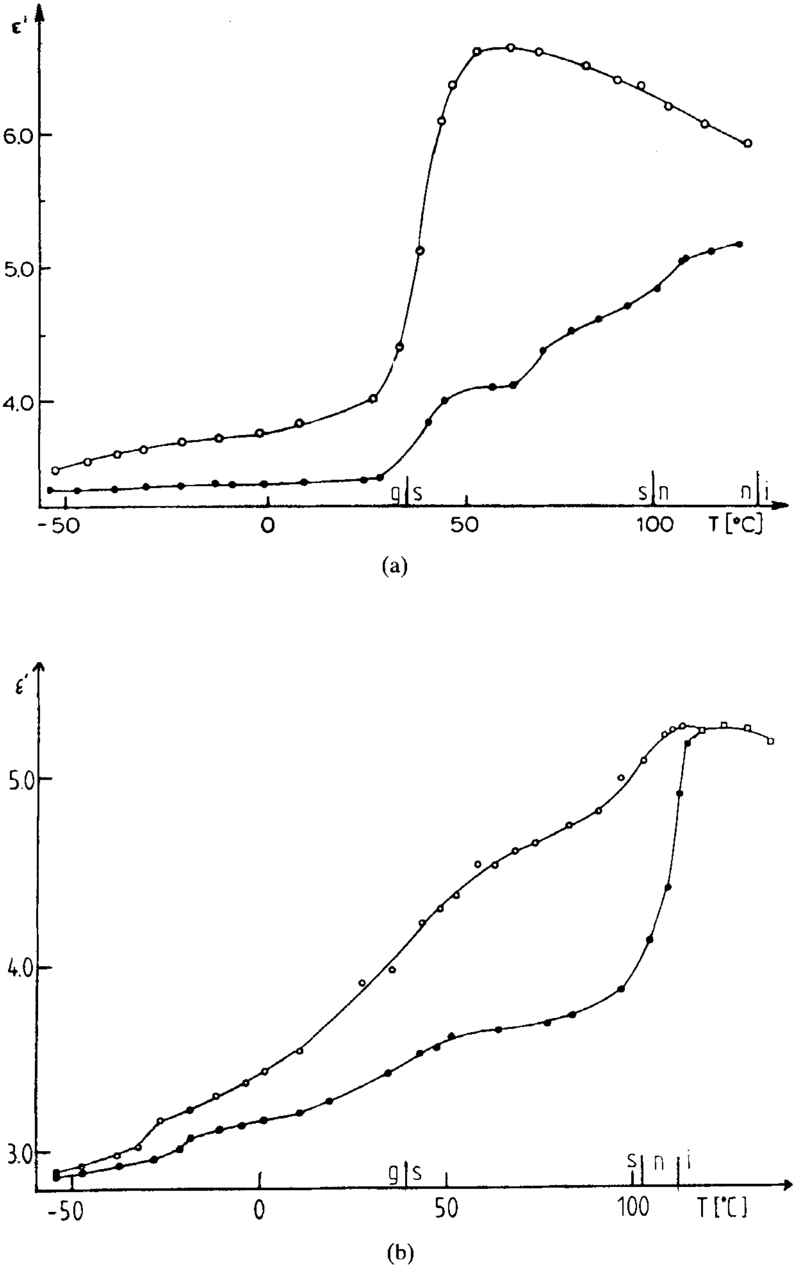


FIGURE 1 X-ray-pattern of *2* at room temperature (oriented sample).

In order to lay a foundation for an interpretation of the dielectric properties let us first shortly discuss the differences in the dipole strengths between the two compounds. We do this in terms of group dipole moments. The monomeric unit is separated in the main chain part and the mesogen. Both parts are separated and decoupled by the spacer. We assume that their orientations are only weakly correlated, so we choose different reference axes for the composed dipole moments. For the mesogen, this is roughly the axis of smallest moment of inertia. According to Klingbiel *et al.*,[15] the overall dipole moment μ_1 along this axis is 0.89 D and the transverse moment μ_t is 2.41 D for both substances.

For the main chain part the reference axis is the C—C bond. The dipole components referred to this axis are $\mu_1 = 0.89$ D and $\mu_t = 1.68$ D for *1* and $\mu_1 = 0.39$ D and $\mu_t = 2.17$ D for *2*. The difference is due to the Cl-group.

Figure 2 shows the temperature dependence of the quasistatic dielectric permittivity. We start the discussion with compound *1* which has a similar behaviour as the previously investigated compound with CN instead of OCH_3.[13] In the following we will refer to this latter compound as *1'*. In contrast to *1'*, *1* is dielectrically negative, which follows directly from the discussion of dipole moments given above. Two steps in ϵ' vs. T are observed, the first one is at lower temperatures in both orientations at ≈40°C, the second one at higher temperature in parallel orientation at ≈70°C. A small jump is found additionally at the S_A/n transition.



(a)

(b)

FIGURE 2 Real part of quasistatic dielectric permittivity (100 Hz) as a function of temperature. Open circles: ⊥; closed circles: ||; rectangles: isotropic. 2a): compound *1* 2b): compound *2*. The lines are guides for the eye.

The first step is caused by the glass relaxation or α-process. The second step indicates the onset of the end-to-end rotation of the mesogenic side chains (δ-process). A comparison between parallel and perpendicular orientation shows that the glass relaxation process is mainly determined by the transverse dipole components, while the parallel relaxation is connected with the longitudinal component. Above the step at ≈40°C, setting in at ≈50°C, the perpendicular component of ϵ' is monotonously decreasing, while the parallel component is increasing above the second step at ≈70°C. These effects are partly explained by the normal decrease of the order parameter with increasing temperature. As to the relatively large increase of $\epsilon'_{\parallel}$ in the smectic phase, we assume an antiparallel correlation between the longitudinal dipole components within the layers, which becomes weaker as the temperature rises and essentially disappears in the nematic phase, where $\epsilon'_{\parallel}$ remains nearly constant. Such behavior has also been described for some related low molecular weight liquid crystals.[16,17]

Regarding the ϵ' vs. T curve for *2* differences with *1* are obvious. The perpendicular component is increasing more or less monotonously over the whole range with a very broad step at the glass transition and another small step at the s_c-n transition. The parallel component exhibits a very small step at the glass transition and a sharp increase around the smectic-nematic transition. In the isotropic phase the permittivity is slightly decreasing. The maximum dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ is 1.1 for *2* but 2.2 for *1* though the dipole moments of the two molecules are equal except for the chloro group.

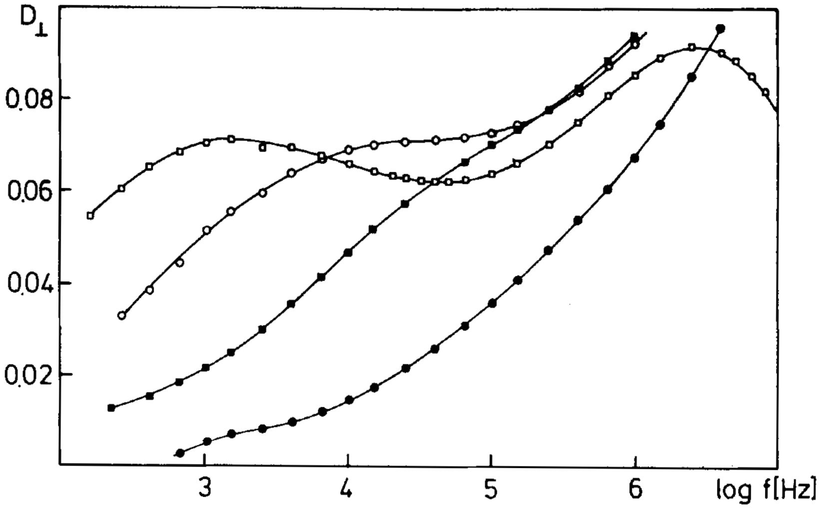
These observations show:

—The steps corresponding to the δ-relaxation and the α-relaxation are also present for *2*, but less distinguished.

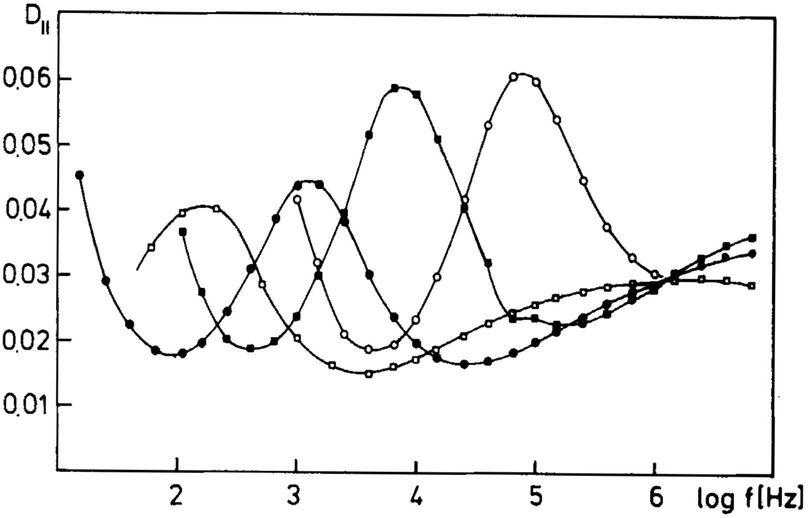
—The step heights are different for *1* and *2*, the α-step being larger for *1* by 2.5 D to 1.5 D and the δ-step being larger for *2* by 1.7 D to 1.2 D. The reasons for this in terms of dipole structure will be discussed later on.

—There is no complete alignment. This is indicated by the small $\Delta\epsilon$-value for *2* as compared to *1* and by the second step near the s_c-n transition, which appears in both orientations in contrast to *1* and all the previously investigated compounds.[9–13,18]

The steps in the static permittivity correspond to maxima in the dielectric loss factor, which is connected with ϵ' and ϵ'' by $D = \epsilon''/\epsilon'$, in a frequency-dependent plot. Figure 3a shows this for *1* in perpendicular orientation. Two maxima are observed; the low-frequency



(a)



(b)

FIGURE 3 Loss factor D vs. log f for *1* at different temperatures.
a) $D_\perp$; ●: T = 80 °C; ■: T = 61 °C; ○: T = 53 °C; □: T = 47 °C
b) $D_\parallel$: ○: T = 118 °C; ■: T = 98 °C; ●: T = 83 °C; □: T = 69 °C

part is the glass- or α-relaxation; the high frequency maximum appearing in the curve for T = 47°C continues far into the glassy state. Therefore it must be a local process. It appears also in parallel orientation, though very weak. Since it is only observed for phenylbenzoate side chains we ascribe it to the ester bridge in the mesogenic moiety. This relaxation is also observed for *2*, though not shown here, and for previously investigated compounds with phenylbenzoate side chains.[9–13,18]

Figure 3b shows the parallel or δ-relaxation for *1*. We note that, at the same temperature, this parallel relaxation lies at much lower frequencies than the glass relaxation.

Compound *2* (Figure 4) is characterized by a broad relaxation in the isotropic phase, which continues into the nematic phases with contributions in both orientations. It disappears around the smectic-nematic transition, probably by broadening. In the liquid crystalline phase the relaxation curves of *2* are very similar in shape and temperature dependence for both orientations. So we conclude that the relaxation process underlying these curves is characteristic of the parallel orientation, corresponding to the large step in $\epsilon_{\parallel}'$ in Figure 2, and that the contribution in perpendicular orientation is due to incomplete alignment.

Around the temperature of the first step in Figure 2, no corre-

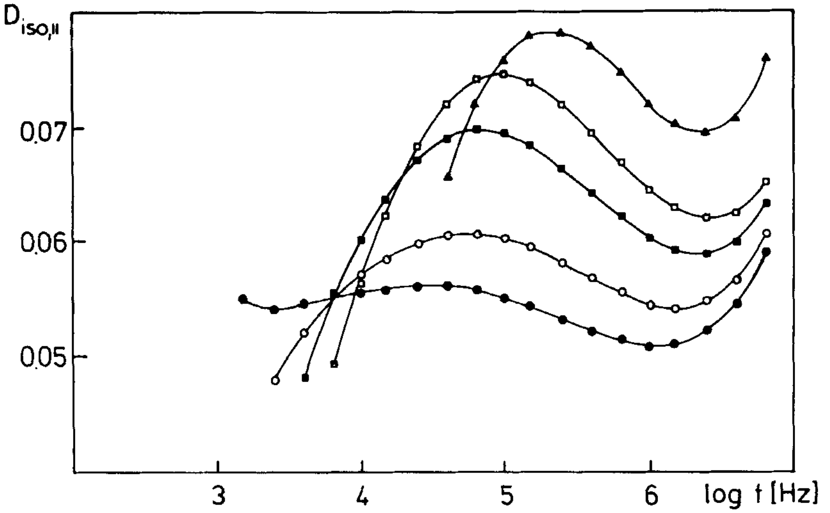
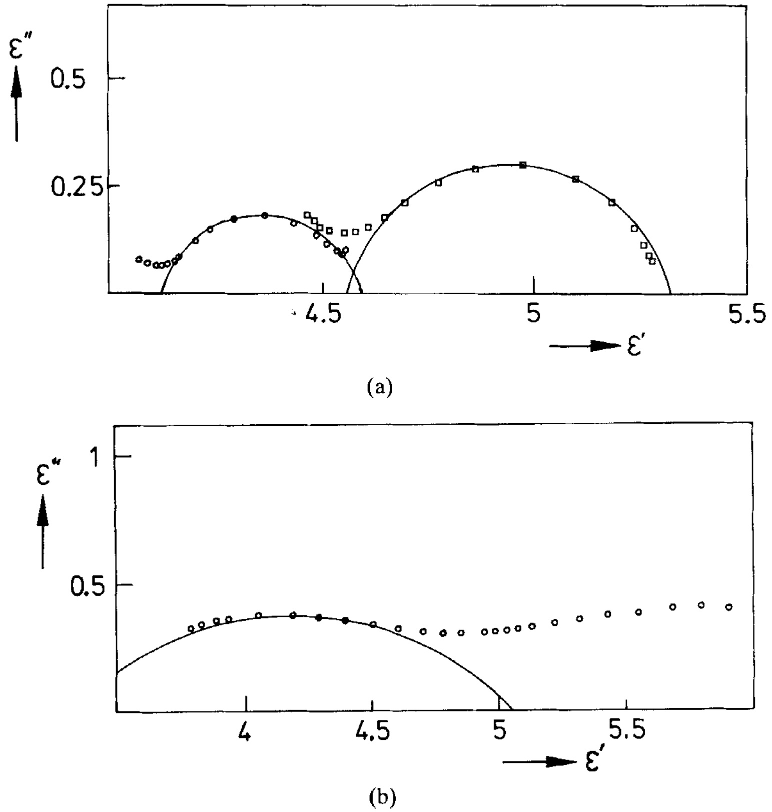


FIGURE 4 Loss factor D vs. log f for *2* for parallel orientation and isotropic ▲: T = 124 °C; □: T = 117 °C; ■: T = 114 °C; ○: T = 112 °C; ●: T = 110 °C

sponding maximum is found in the loss factor curves. This can only be due to a very broad relaxation curve of the α-process for *2*.

The Cole-Cole plots yield further information about the relaxation types. Figure 5a shows nearly semi-circles for the δ-relaxation for *1*, characterizing this relaxation as nearly Debye-like. The relaxation strength (diameter of the circle) increases with temperature and the center of the circles is shifted along the ϵ'-axis. This confirms our conclusions from Figure 2a concerning the dipole correlations. The effective dipole moment of the relaxation increases due to the weakening of the antiparallel coupling between the longitudinal dipole components. The same process causes the shift to larger ϵ'-values at higher temperatures. The glass relaxation (Figure 5b) is characterized



(a)

(b)

FIGURE 5 Cole-Cole plots for *1*.
a) ||; ○: $T=76$ °C, $\alpha=0.22$; □: $T=118$ °C, $\alpha=0.18$
b) ⊥; $T=47$ °C, $\alpha=0.48$ for the drawn circle; a second relaxation is superposed at high ϵ'-values

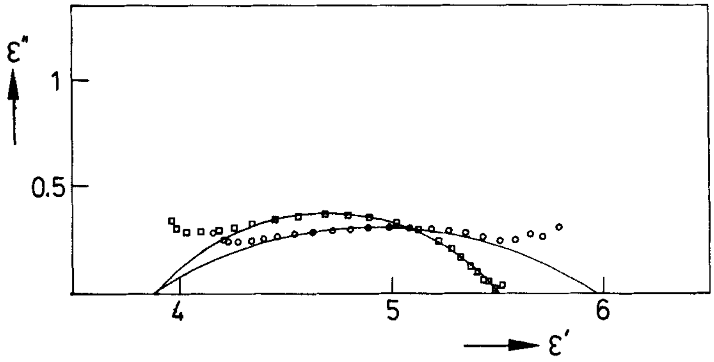


FIGURE 6 Cole-Cole plot for *2*. ○: T = 113 °C, parallel orientation, α = 0.68. □: T = 124 °C, isotropic, α = 0.46

by a shifted semi-circle (large value for the distribution parameter α) which means a broad distribution of relaxation times. This agrees with our previous results.[9–13,18]

In contrast, for *2* the Cole-Cole plot gives relatively large α-values both in the isotropic and in the nematic phase (Figure 6). They increase slightly passing from isotropic to nematic.

The relaxation frequencies f_R were determined from the maxima of the loss factor curves. Their temperature dependence is shown—except the isotropic one for *1*—in Arrhenius plots in Figures 7 and 8. The curves obey the Arrhenius law $f_R = f_o^* \exp(-E_A/kT)$ in the measured range and the activation energies E_A determined thereof are given in Table I; f_o^* and k have the usual meaning. The values for *1* are very similar to those obtained for related compounds for the δ- and α-process.[13]

For *2* the activation diagram shows also linear temperature dependence of the relaxation frequencies, but with different slopes in the isotropic and nematic phase.

The temperature dependence of the local ester (or β –) relaxation discussed above is also given in the activation diagrams. It is linear over the whole range. Its activation energies are nearly the same for both substances.

It should further be noted that the activation energies of the chloroacrylates for the δ-process are significantly larger than for the acrylate *1*.

Finally let us make a comparison between the two present compounds and with the related polyacrylate *1'*.

As to the acrylate *1*, our investigations reveal dielectric properties

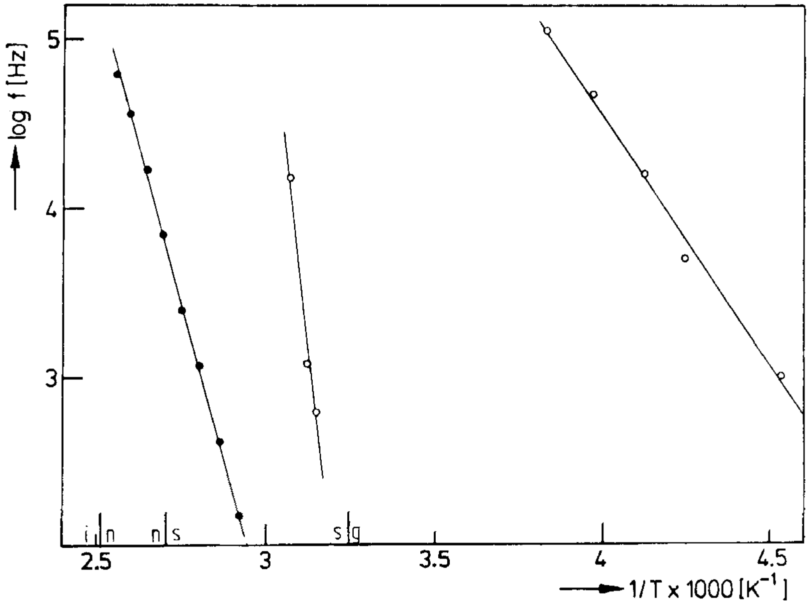


FIGURE 7 Activation diagram for *1*. ○ perpendicular orientation; ● parallel orientation.

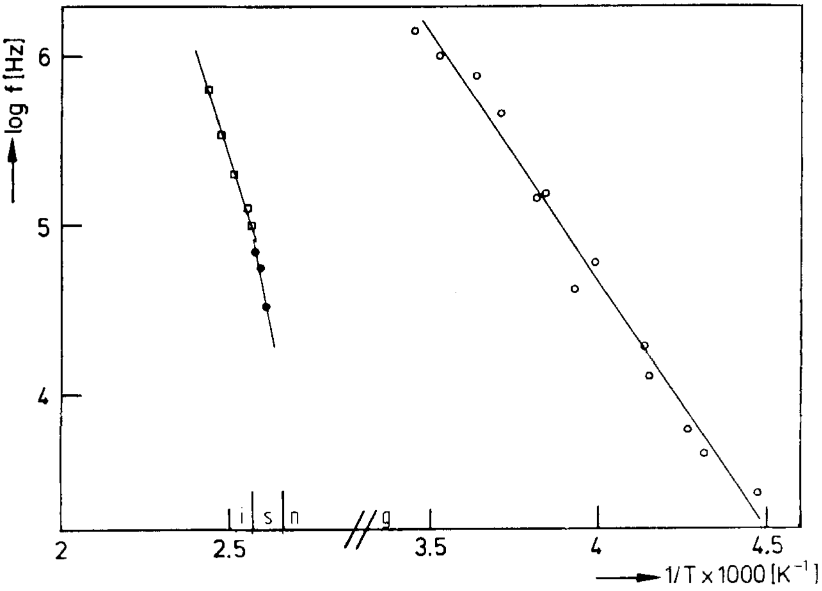


FIGURE 8 Activation diagram for *2*. ○ perpendicular orientation; ● parallel orientation; □ isotropic.

TABLE I

Activation energies (kJ/mole) compounds

phase	process	orientation	1	2
glass	β	perp.	57	56
smectic	α	perp.	330	—
smectic	δ	par.	140	—
nematic	δ	par.	140	220
isotropic	δ		132	175

that agree with *1'*: two well separated relaxations, the δ-process in parallel orientation and the glass process with its major contribution in perpendicular orientation.

The δ-relaxation is much weaker for *1* than for *1'* because the CN-group is missing. Antiparallel dipole correlation in the smectic A phase for *1* leads to an increase of ϵ (Figure 2) and a shift of the relaxation in the Cole-Cole plot which was not observed for *1'*.

The relaxation behavior of *2* differs from that in two ways: First, the α-relaxation is only indicated by a broad step in ϵ' vs T, not by a maximum in the loss-factor; the step height in ϵ' is smaller than for *1*.

Second, the δ-relaxation is much broader than for *1* and can therefore only be measured in a small temperature range; its step height in ϵ' vs T is larger than for *1*.

We discuss these results with regard to the role of the chloro group.

The chloro group gives rise to an additional longitudinal dipole moment. So when the monomeric unit is assumed to reorient as a whole during the δ-process, the dipole strength of the relaxation is increased. This explains the larger δ-step in Figure 2 for *2*.

The influence of the chloro group on the α-relaxation is less obvious. At first sight one expects an enhancement. The opposite happens, as the step heights in Figure 2 show. Therefore we suggest that the dipole moments of the chloro and the ester group at the main chain tend to an antiparallel arrangement leading to a partial cancellation of the transverse dipole moment.

We conclude that the molecular motions that determine the δ-relaxation and the α-relaxation in the *1* are also existent for the chloroacrylate, though with different dipole strength due to the chloro group. The extreme broadening of these relaxations in *2* is a consequence of a sharp increase of the viscosity, which takes place below the clearing point. This latter effect has been measured by Zentel[19] for *2* in the nematic and even more enhanced in the smectic phase.

The reason for this behaviour is unclear. The smectic bilayer structure may be important, since it includes a high degree of order for the main chains, too; however, the increase of viscosity has also been found, though less distinct, for methacrylate main chains.[19] Moreover, a second chloroacrylate side chain polymer, which has recently been measured by us and has only a nematic phase, shows similar dielectric properties as *2*.[20] So we believe that the dominant effect leading to the broadening phenomenon of the chloroacrylates is a stiffening of the main chain by the chloro group.

Acknowledgment

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