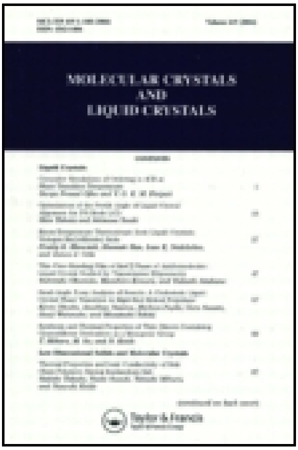

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 13 Dec 2006.

To cite this article: Franz-Josef Bormuth & Wolfgang Haase (1987): Molecular Dynamics of Liquid Crystalline Side Chain Polymers of Different Types, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 153:1, 207-216

To link to this article: http://dx.doi.org/10.1080/00268948708074537

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 207-216
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Printed in the United States of America

MOLECULAR DYNAMICS OF LIQUID CRYSTALLINE SIDE CHAIN POLYMERS OF DIFFERENT TYPES

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Abstract We present a dielectric spectroscopic study of a newly synthesized liquid crystalline side chain polymer with a methacrylate main chain. By a comparison with analogous compounds where only the α-substituent at the main chain is varied we examine the influence of the polymer backbone on the relaxation processes in the different orientations. The main results are: the δ-relaxation has a non-Arrhenius-like temperature-dependence of the relaxation-frequencies; its relaxation time distribution is broadened in the sequence acrylate-methacrylate-chloroacrylate; the activation energy increases in the same sense; the main chain substituent has no effect on the relaxation strength, which is only determined by the longitudinal dipole moment; the α-relaxation for the methacrylate shows a nearly temperature-independent relaxation frequency near the clearing point and a splitting at lower temperatures - both effects have not been observed so clearly for other side chain polymers. Some molecular interpretations for these phenomena will be discussed.

INTRODUCTION

A large number of dielectric relaxation studies of end-fixed l.c. polymers have been undertaken in the last years (1-13). Shortly summarized these investigations led to the following common results:

There are two relaxation regimes in the isotropic and l.c. state; The low frequency relaxation shows a narrow absorption curve very similar to the absorptions that are associated with the rotation around the short molecular axis known from low molecular weight (lmw) liquid crystals; however, its activation energy is larger and the typical relaxation times are slowed down by a factor of 10^3 compared with lmw analogues. Oriented measurements show that this so-called δ-relaxation is only observable in homeotropic alignment and that its temperature dependence is essentially nonlinear in the Arrhenius-plot.

The most discussed model for the δ-relaxation assumes that it is caused by cooperative 180°-rotations of the side groups . This model is supported by the large relaxation strength and its dependence on the longitudinal dipole component.

The high-frequency relaxation, often called α-relaxation, shows a very broad absorption curve. Its main contribution is in homogenous orientation, but it is also weakly observed in homeotropic orientation. Its relaxation strength depends on the strength of the transverse dipole components. The temperature dependence is nonlinear in the Arrhenius-plot. The α-relaxation can probably not be described by a single molecular motion, but is composed of both segmental motions of the main chain (polymeric glass relaxation) and transverse rotations of the side chains.

Our recently published work on a polychloroacrylate system (10) as well as Zentel's extensive work (1-3) indicated that the main chain has a considerable influence on both main relaxations. However, the chloroacrylate data were difficult to interpret because of incomplete alignment. Therefore we turned to the present methacrylate, which has the advantages of good alignment properties combined with a strong dipole moment.

EXPERIMENTAL

Figure 1 shows the principal structure of end-fixed l.c. side chain polymers

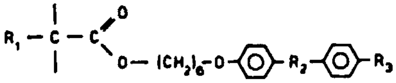

FIGURE 1. Principal structure of l.c. side chain polymers.

Comp.	R_1	R_2	R_3	trans.temp.	Ref.
1	CH_3	COO	CN	g 35 s 93 n 102 i	this work
2	H	COO	CN	g 36 n 133 i	(8)
3	Cl	COO	OC_4H_9	g 39 s 103 n 113 i	(10)
4	CH_3/H*	COO	CN	g 32 n 110 i	(18)

*: Copolymer with 50% of 1 and 50% of 2

In this work, we report mainly on measurements of compound 1 with a methacrylate main chain. For comparison we use the previously investigated compounds 2 and 3 with acrylate and chloroacrylate main chains. Some preliminary data of a copolymer series between 1 and 2 will also be referred to. Compound 1 was kindly supplied by Röhm GmbH, Darmstadt, and was dried 24 hours before use to remove residual solute. The transition temperatures were measured by DSC and polarization microscopy. The structure was manifested by x-ray-diffraction.

The dielectric measurements at higher frequencies were carried out with the apparatus already described (8-10). For the lowest frequencies (below 1 Hz) we used an evaluation of Lissajou figures obtained by recording the voltage and current through the sample. The principle of this method is described in (14). This method gave an absolute error of 0.01 in th loss-factor.

The samples were aligned by a magnetic field, as described previously (8-10). Quality of alignment was checked by recording the absorption curves during alignment to see if they reached saturation. After cooling to the glass-state the orientation was controlled by polarization microscopy.

RESULTS AND DISCUSSION

Anisotropic dielectric function

A description of the dielectric spectrum of oriented liquid crystals is given by the dynamical extension of the Maier-Meier-equations:

$$(1a)\quad \epsilon_{\parallel}(\omega) = \epsilon_{\parallel}^{\infty}+G/3kT(\mu_{\ell}^{2}(1+2S)F_{\parallel}^{1}(\omega)+\mu_{t}^{2}(1-S)F_{\parallel}^{t}(\omega))$$

$$(1b)\quad \epsilon_{\perp}(\omega) = \epsilon_{\perp}^{\infty}+G/3kT(\mu_{t}^{2}(1-S)F_{\perp}^{1}(\omega)+\mu_{t}^{2}(1+S/2)F_{\perp}^{t}(\omega))$$

where $\epsilon_{\parallel,\perp}$ is the complex dielectric constant, μ_1 and μ_t means the dipole components parallel and perpendicular to the long axis of the mesogenic molecule, $F_{\parallel,\perp}$ are frequency-dependent relaxation functions for the different dipole components.

The first term in 1a describes a end-to-end rotation around the short molecular axis, the second term in 1a and 1b means rotation around the long molecular axis, while the first term in 1b describes a stochastic reorientation of the molecules about the director.

For polymeric liquid crystals, equations 1 should be augmented by a term that accounts for relaxations of the main chain, especially the glass process known for amorphous polymers (15). It will contribute in both orientations. Moreover, the polymer backbone has a considerable specific influence on each of the four relaxation functions $F^{l,t}(\ )$.

Static dielectric permittivity

Figure 2 shows the behaviour of the quasistatic ϵ' at 110 Hz.

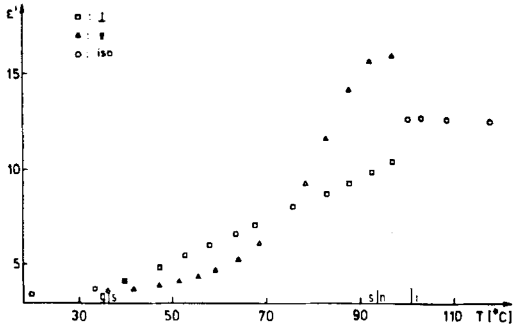

FIGURE 2. Real part of dielectric constant at 110 Hz.

The homeotropic component starts to rise at ≈50 °C and increases monotonically over a temperature range of ≈50 °C to a value of ≈16. This is different from the l.c. polyacrylate 2 or l.c. polysiloxanes (9), where we observed two marked steps in ϵ' according to two different relaxation types. The lower temperature step is missing or very weak, similar to the chloroacrylate 3. The homogenous component begins to increase around the glass transition, but exhibits no marked step with a plateau as 2. It is rising more or less monotonically, much like 3.

These observations indicate that the relaxation usually causing the low temperature step has a very broad distribution on the temperature and frequency scale for 1

DYNAMIC PERMITTIVITY

In order to extract reproducible parameters from the experimental data we performed least-square fits of the $\epsilon''(\omega)$-values with theoretical absorption curves of the Fuoss-Kirkwood type (16):

$$(2) \qquad \epsilon''(\omega) = \frac{\epsilon''_m}{(\omega/\omega_r)^{\beta} + (\omega/\omega_r)^{-\beta}}$$

Here, ϵ_m'' is the maximum of the absorption curve, $\omega_r = 2\pi\nu_r$ is the relaxation frequency and β is the distribution parameter, $\beta=1$ for an ideal Debye-relaxation.

The Fuoss-Kirkwood curves have the advantage of giving a rather simple expression for ϵ''. Their main supposition is the symmetry of the distribution function. The homeotropic data were fitted with one function of type (2), for the homogenous data we used a superposition of two Fuoss-Kirkwood curves.

Homeotropic alignment

The absorption curves are shown in figure 3.

The fitted curves form a good approximation to the experimental points. Some striking features are:

- The distribution parameter β lies far below the Debye-value $\beta=1$ and is nearly temperature-independent. This means that the relaxation time distribution for the homeotropic relaxation of 1 is much broader than for the acrylate 2, where $\beta=0.9$; Yet, it is smaller than for the chloroacrylate ($\beta=0.4$).
- The relaxation strength $\epsilon_0-\epsilon_\infty$ is nearly the same as that of the acrylate 2.

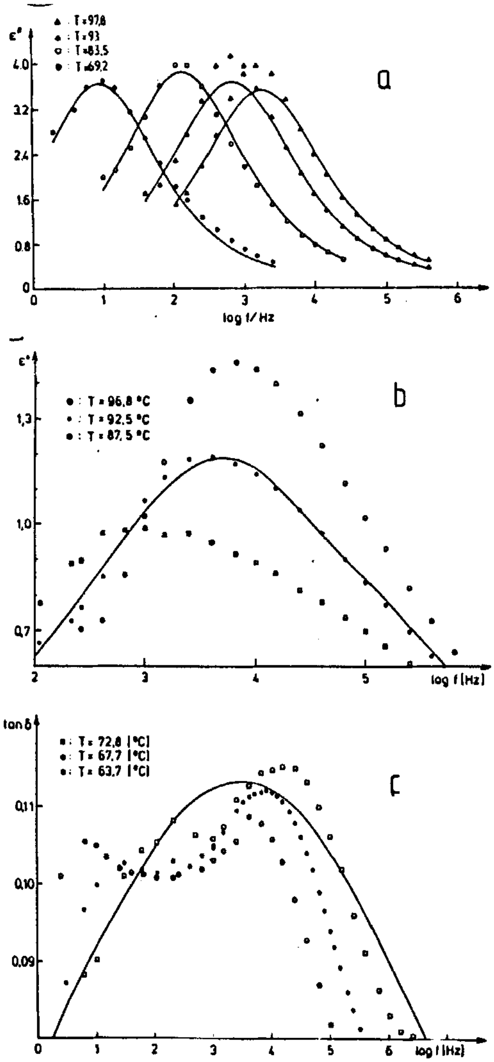

FIGURE 3. Experimental absorption curves for homeotropic (3a) and homogenous alignment (3b,c). The full lines are fitted curves. In figure c the loss-factor is directly represented to demonstrate the splitting.

So we note that variations of the main chain have little influence on the relaxation strength (which means the number of dipoles being relaxed in a specific process), but strong influence on the relaxation time distribution in the case of the δ-relaxation.

Homogenous alignment

The absorption curves are represented in figures 3b,c. One line fits gave sufficient approximations only for the highest temperatures (3b). For lower tempratures we tried 2-line-fits, but the results are rather poor (3c). We believe that we have more than two separate absorptions in the experimental curve and/or the F.K.-function (2) does not exactly describe the physical behaviour. So for these temperatures no accurate relaxation parameters could be determined. Only the relaxation frequencies could be estimated from the separate maxima in the loss-factor curves.

The high-frequency-curves yield an extremely broad distribution. They remain at nearly the same position over a wide temperature range. Both properties are similar to 3.

The nature of the low-frequency absorption which is separated in figure 3c is unclear. Its relaxation frequencies are near to those of homeotropic alignment, so one could assign it to incomplete alignment leading to a contribution of the δ-relaxation in homogenous alignment. However, different orientation times did not influence the peak height of this absorption. Another possibility is that there is a separation between main chain and side chain motions. Further investigations are necessary to elucidate this problem. First results of a copolymer series acrylate/methacrylate showed a similar behaviour (18).

Activation diagram

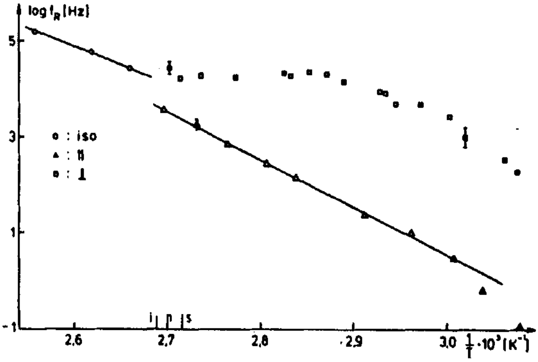

FIGURE 4. Activation diagram.

Homeotropic alignment

The relaxation frequencies obey a function of the WLF-type (15) like other l.c. side chain polymers (10-13). For the higher temperatures an Arrhenius-law can also be used, with an activation energy of (185kJ/mol), which is relatively large compared with 2, but smaller than for 3. In the isotropic phase, this activation energy decreases to 145 kJ/mol.

Homogenous alignment

The relaxation frequencies are determined from the high frequency maxima in figure 3c. They remain nearly constant over some temperature range, then decrease almost parallel with the homeotropic values. The retardation near the clearing point has been observed for an acrylate polymer with cyanobiphenyl side group (8) and for the chloroacrylate 3, while the partial parallelity with the δ-relaxation seems to be typical for l.c. acrylates, but not for siloxanes (9).

TABLE I Relaxation parameters of 1 and related compounds

Comp.	ϵ'_{max} at 100 Hz		$\epsilon_0-\epsilon_\infty$		β		E_a(kJ/mol)		
	∥	⊥	∥	⊥	∥	⊥	∥	⊥	iso
1	16	10.4	13.5	≈7	0.57	≈0.25	185	≈180	145
2	19	9	12.5	5.6	0.88	0.37	143	≈140	104
3	-	-	2.1	-	0.27	≈0.2	220	-	175
4	17.4	10.5	13.5	≈5.5	0.78	≈0.3	165	≈160	138

Conclusions

Some important relaxation parameters for the methacrylate 1 are listed in table I, opposed with the corresponding parameters for the related compounds with different main chains. On the basis of these data we come to the following conclusions:

- For homeotropic orientation the relaxation mechanism is analogous with the δ-relaxation described above. Its broadening as compared to 2 is probably due to a different conformation of the main chain, which leads to a wider spectrum of local relaxation times. It is well known that polyacrylate an polymethacrylate have different conformations in their crystalline state (17) and that this effects the frequency position of side chain relaxations (19).
- For the homogenous relaxation we propose a composition of segmental motions of the main chain (analogous to the polymeric glass process) and motions of the side group according to eq. 1b. The nature of the splitting remains an open question. The high frequncy maximum seems to be analogous to the α-relaxation described for other l.c.polymers. Its redardation near the clearing point is certainly an affect of the substituent at the main chain, as in the chloroacrylate 3.

We thank Dr. Rau from Otto Röhm GmbH for supplying us with substances This work was supported by Deutsche Forschungsgemeinschaft.

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