

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Molecular dynamics in liquid-crystalline side chain polymers studied by dielectric relaxation spectroscopy: A comparative study

F. J. Bormuth^a; W. Haase^a

^a Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt, F. R. Germany

To cite this Article Bormuth, F. J. and Haase, W.(1989) 'Molecular dynamics in liquid-crystalline side chain polymers studied by dielectric relaxation spectroscopy: A comparative study', *Liquid Crystals*, 5: 6, 1849 – 1860

To link to this Article: DOI: 10.1080/02678298908045693

URL: <http://dx.doi.org/10.1080/02678298908045693>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Molecular dynamics in liquid-crystalline side chain polymers studied by dielectric relaxation spectroscopy: a comparative study

by F. J. BORMUTH and W. HAASE

Institut für Physikalische Chemie, Technische Hochschule Darmstadt,
Petersenstraße 20, 6100 Darmstadt, F.R. Germany

A series of liquid-crystalline side chain copolymers with different main chains have been studied by the dielectric method in a maximum frequency range of 9 decades. Oriented samples were used throughout. The data were analysed in terms of the Havriliak-Negami and Fuoss-Kirkwood formulae for the relaxation functions. Two well separated dispersion regions with their strengths depending strongly on the macroscopic orientation were found. The low frequency or δ -relaxation shows a marked change in its curve form and width with different main chain structure, its strength being determined by the longitudinal dipole moment of the mesogenic unit. The high frequency relaxation shows a more complicated dependence of its characteristic parameters on the molecular structure. In some cases a decomposition into two underlying relaxations was successfully attempted. We discuss the models for molecular motions developed for low molecular weight liquid crystals and for amorphous polymers, in order to explain the behaviour of the different dispersions found.

1. Introduction

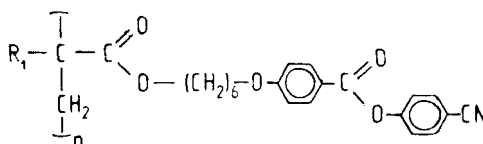
Dielectric spectroscopy of side chain polymeric liquid crystals has revealed that two basic relaxation regimes determine the spectra up to MHz range above the glass transition temperature. The higher frequency process, known as δ -relaxation, is microscopically comparable with the reorientation around the short axis known from low molecular weight liquid crystals. The lower frequency process, often called α -relaxation, which is associated with the glass transition, is best characterized as a mixture of several molecular motions [1], including reorientations of the side groups about their long axis as well as segmental motion of the main chains.

In polymeric liquid crystals however, these relaxation processes, especially the δ -relaxation, require conformation changes in the spacer and main chain. This should lead to a certain degree of dynamic coupling between neighbouring side chains, depending for example on the length of the spacer [3] or the specific main chain structure. The purpose of this work was to study the influence that the main chain structure has on the coupling strength on a more quantitative level than before.

We used a series of copolymers with different compositions of methacrylate and acrylate monomers, where the mesogenic side groups are identical. For linear polymers it is well known that introduction of the voluminous α -methyl group into acrylate chains reduces the chain flexibility [4], leading for example to a significant shift of the glass relaxation. The dielectric properties of the corresponding homopolymers have already been reported [1, 2]. They are analysed again and used for comparison.

In order to obtain more quantitative data from the usually very broad relaxation curves we carefully approximated the experimental values by using symmetric and asymmetric theoretical relaxation functions as well as superposition of relaxation functions.

2. Experiment



Fractions of monomers

$R_1 = H$	$R_1 = CH_3$	Transition temperatures/ $^{\circ}C$	Molecular weight	Name
0	100	G 27 S _A 94 N 102 I	28 000	MAPB
10	90	G 30 S _A 109 N 118 I	40 000	A1MA9
50	50	G 32 N 110 I	30 500	A5MA5
90	10	G 26 N 120 I	21 000	A9MA1

The copolymers, as shown above, are composed of cyanophenylbenzoate mesogenic groups, connected by a hexyloxy-group to the main chain, which may be an acrylester or a methacrylester. Three different compositions of the two monomer units are investigated.

The samples were prepared for us by Dr. Omeis from Otto Röhm G.m.b.H., Darmstadt, by radical copolymerization. The correct composition was checked later by determining the remaining unpolymerized monomer in the product and also by pyrolysis and subsequent analytical gas phase chromatography (G.P.C.).

Due to the larger reactivity of the methacrylate units, the chains formed at the beginning of the reaction will have a higher methacrylate content than those formed later, when the methacrylate monomer concentration has decreased. So we in effect have a mixture of chains with different compositions; this must be taken into account in the interpretation of physical properties.

The molecular weights were determined by analytical G.P.C. The transition temperatures were determined by differential scanning calorimetry (D.S.C.) and polarization microscopy. For the phase characterization we used X-ray diffraction on oriented samples.

For the dielectric measurements the same cell structure was used as described previously. Three different experimental techniques were applied to cover the whole frequency range, from 10^{-2} to 10^7 Hz. Their principles are described in [5, 6].

3. Results

3.1. X-ray measurements

For the copolymer A1MA9, as for the homopolymer MAPB, a smectic phase is present below a very small nematic phase. From its small angle reflexes we determined a layer thickness of 34.5 \AA (by photodensitometry), which is very close to the value for pure MAPB (33.5 \AA). It is in any case larger than the theoretical length of the monomer (25 \AA) in its stretched conformation, indicating partial overlapping. From the diffuse outer equatorial haloes a value of 5.1 \AA is derived for the mean intermolecular distance, which holds for all of the copolymers.

In addition to the inner and outer reflections we found another diffuse maximum at intermediate angles, which depends only weakly on the orientation. It is assigned to the backbone structure, although no definite explanation can be given.

The other copolymers (A9MA1 and A5MA5) show only nematic phase. We must note here that we found a weak smectic Bragg-reflex also in A5MA5, described as nematic earlier. This is assigned to a certain content of smectic regions, formed by the methacrylate-rich chains, as explained earlier. By comparison of the intensity of the smectic peak of A5MA5 and pure MAPB we could estimate this content as being smaller than 10 per cent.

We also made X-ray diffractograms of fibres oriented by drawing from the melt. For A1MA9 these measurements showed a preferred orientation of the side chains perpendicular to the direction of draw, as was found for MAPB [2]. For the other copolymers a tendency to parallel alignment with respect to the draw is observed. If we assume that drawing aligns the main chains, this means that the side chains tend to parallel alignment with the main chains for A9MA1 and A5MA5, but to perpendicular alignment for A1MA9. This result is consistent with other works [7] and may be correlated with the smectic phase for A1MA9.

3.2. Dielectric measurements

In figure 1 we show some representative spectra of ϵ'' versus frequency for the three compounds in homeotropic orientation (\parallel). One spectrum is given for each copolymer, all at roughly the same reduced temperature $T - T_g$, where T_g is the glass transition temperature. The dominant absorption seen is the usual δ -relaxation. Also represented are the fitted curves, which were calculated using the symmetric Fuoss-Kirkwood (F.K.) function

$$\epsilon''(\omega) = 2\epsilon''/\cosh[\alpha \ln(\omega/\omega_0)]. \quad (1)$$

The fit parameters are f_r , the relaxation frequency, α , the distribution parameter and ϵ''_m , the maximum of ϵ'' . In table 1 some of the parameters calculated for the three

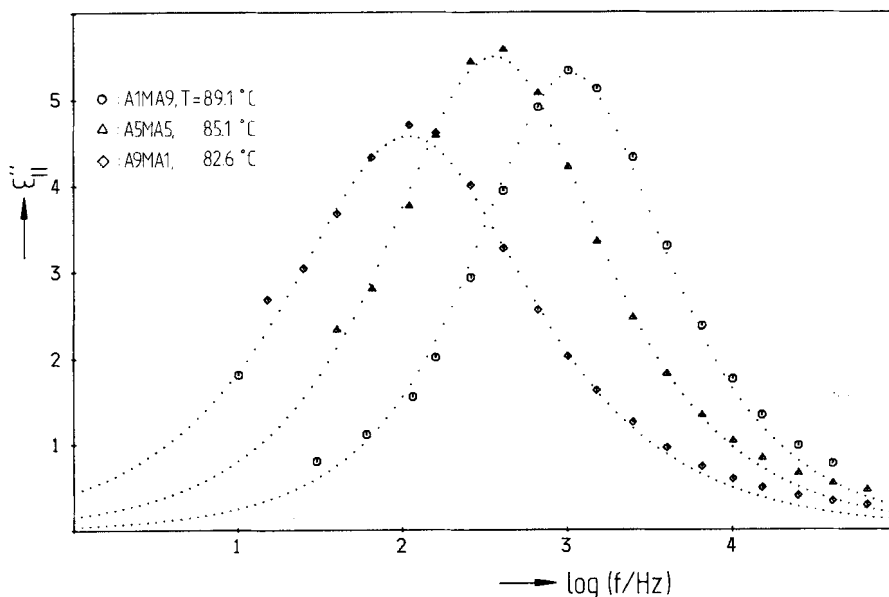


Figure 1. Absorption curve ϵ'' at comparable temperatures for the three copolymers; the dotted lines are the fits according to the F.K. function (equation (1)).

Table 1. Fit parameters of $\varepsilon''(\omega)$ ($\mathbf{E} \parallel \mathbf{n}$) approximated by the F.K. function (equation (1)). $d(x_i)$ is defined as $[|x_{\text{exp}} - x_{\text{calc}}|^{1/2}/(n - 1)]/x$, where x_{exp} and x_{calc} are the experimental and calculated values, and x is the average value. $d(x_i)$ gives a normalized measure for the quality of the fits. The uncertainty of the parameters is always in the last decimal, if not specifically noted.

T/K	f_r/kHz	ε_m	β	$\varepsilon_0 - \varepsilon_\infty$	$d(x_i)$
A9MA1					
104.4	13.9	4.88	0.79	12.4	0.038
92.5	4.3	5.13	0.76	13.5	0.060
82.6	1.12	5.29	0.81	13.1	0.031
69.4	0.104	5.01	0.78	12.8	0.027
A5MA5					
103.6	5.8	4.88	0.71	13.2	0.044
94.9	1.7	5.17	0.73	14.2	0.041
85.1	0.36	5.49	0.73	15.0	0.028
75.3	0.066	5.72	0.70	16.3	0.045
A1MA9					
111.2	3.1	4.89	0.72	13.6	0.045
101.5	0.74	4.64	0.68	13.6	0.038
89.1	0.11	4.57	0.65	14.1	0.031
71.7	0.0045	4.17	0.60	13.9	0.015

compounds are compared. It is also obvious from figure 1 that the relaxation is shifted to lower frequencies with increasing content of methacrylate units. In the same sense the distribution parameter α tends to decrease, which means that the width of the curve increases. The relaxation strength $\varepsilon_0 - \varepsilon_\infty$, which is calculated from $\varepsilon_0 - \varepsilon_\infty = 2\varepsilon_m''/\alpha$ is highest for A5MA5, but does not differ much between the three compounds. It always increases with decreasing temperature.

Since the fits by F.K. functions deteriorate by a deviation from the experimental points at higher frequencies, we also tried to approximate the δ -relaxation by the asymmetric Havriliak–Negami (H.N.) function

$$\varepsilon^*(\omega) = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty)/(1 + i\omega\tau_r)^{1-\alpha})^\beta. \quad (2)$$

In this function β describes the asymmetry, α the symmetric broadening ($\beta = 1$ leads back to the symmetric Cole–Cole function). The H.N.-fits have also the advantage that both parts of the complex ε^* are evaluated for the approximation.

The results of some of these fits are shown as complex plane plots in figure 2 and the parameters determined for them are listed in table 2. Figure 2 shows that the curves can be well approximated by the asymmetric relaxation function. The asymmetry parameter β decreases from A9MA1 to A1MA9 and MAPB, which means that the relaxation becomes more asymmetric with increasing methacrylate content. The physical implications of such asymmetry will be discussed later. The parameter α shows no systematic changes.

The relaxation frequencies determined by F.K. approximation have been used for the Arrhenius diagram (see figure 3). The δ -relaxation in this diagram shows a linear dependence on $1/T$ at higher temperatures. From the slopes we determined the activation energies as tabulated in table 3. These increase from A9MA1 to A1MA9, for the isotropic as well as the liquid crystal phase. No difference in activation energies could be found between nematic and smectic A phase for A1MA9. At lower

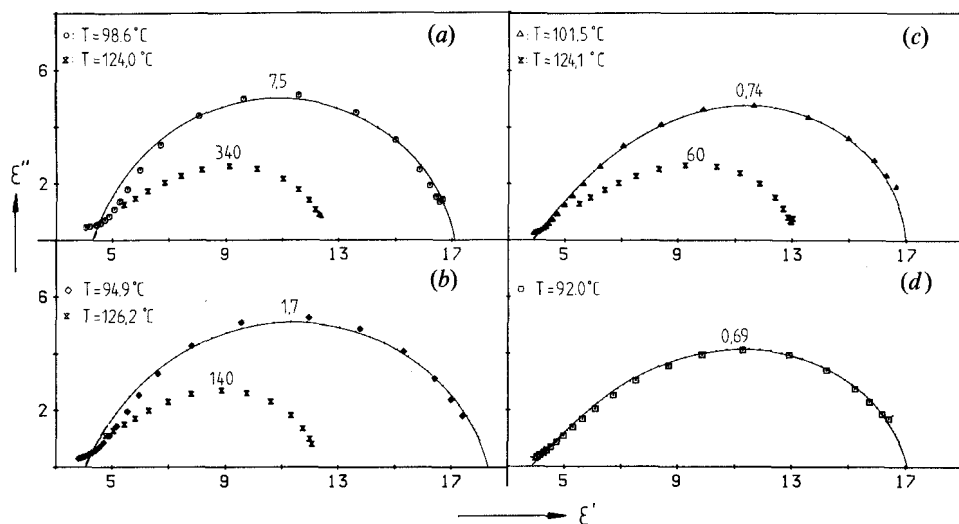


Figure 2. Complex plane plots for (a) A9MA1, (b) A5MA5, (c) AIMA9 and (d) MAPB. Fits by the H.N. equation (equation (2)). The curves with point symbol (x) are in the isotropic phase. Numbers above the curves indicate the frequency (in kHz) at the maximum.

Table 2. Fit parameters obtained by approximation of the H.N. function (equation (2)) for ϵ' and ϵ'' ($\mathbf{E} \parallel \mathbf{n}$). Average values from both components are given. $d(x_i)$ is defined as in table 1.

T/K	f_r /kHz	β	$1 - \alpha$	$\epsilon_0 - \epsilon_\infty$	ϵ_∞	$d(x_i)$
A9MA1						
104.4	11.3	0.83	0.90	12.2	4.30	0.025
92.5	7.0	0.92	0.87	12.7	4.33	0.019
82.6	1.04	0.94	0.87	13.2	4.42	0.026
A5MA5						
103.6	3.1	0.62	0.92	12.7	3.89	0.025
94.9	1.6	0.92	0.82	14.1	4.03	0.033
85.1	0.31	0.85	0.84	14.8	3.95	0.030
AIMA9						
111.2	2.0	0.67	0.91	13.5	3.99	0.022
101.5	0.45	0.62	0.94	13.1	3.86	0.017
89.1	0.08	0.75	0.88	13.2	3.86	0.017
71.7	0.0033	0.73	0.79	13.1	3.82	0.025
MAPB						
92.0	0.49	0.68	0.80	13.2	3.86	0.022
87.6	0.20	0.64	0.83	13.1	3.76	0.020
78.5	0.045	0.68	0.79	12.9	3.77	0.020
68.6	0.005	0.57	0.84	12.4	3.68	0.018

temperatures a deviation from the linear behaviour occurs for all compounds. This shows that the temperature dependence of the δ -relaxation must actually be described by the W.L.F. equation or the Vogel-Fulcher equation [8] as used for cooperative relaxations in glass-forming liquids. This non-linearity indicates that the relaxation rate of the δ -relaxation is governed by the redistribution of the free volume.

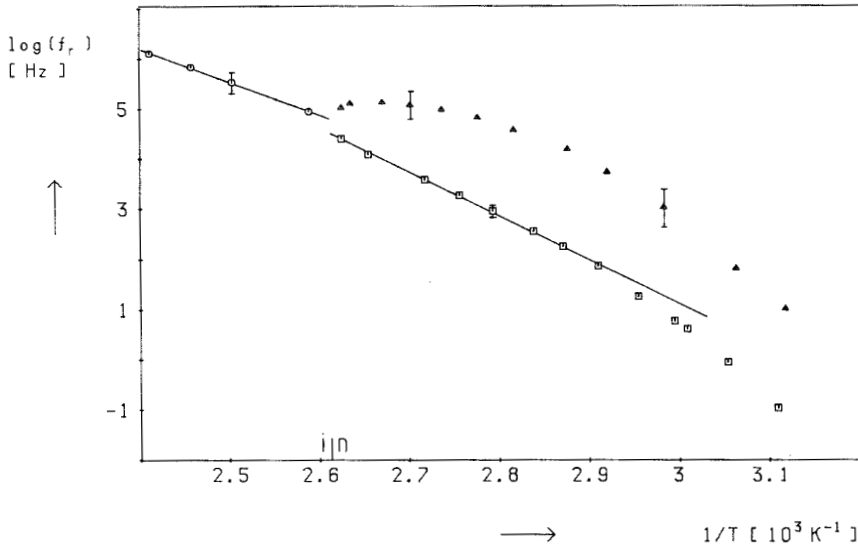


Figure 3. Activation diagram for A5MA5; (□) ||-orientation, (Δ) ⊥-orientation and (○) isotropic.

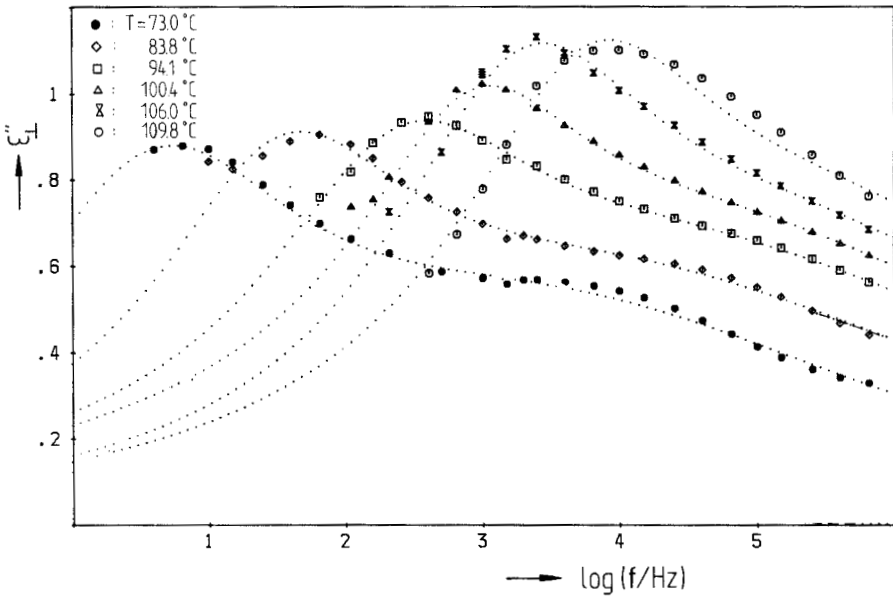


Figure 4. Absorption curves ϵ'' for A1MA9 (\perp -orientation); dotted curves are fits obtained by superposition of two F.K. functions.

We now come to the spectra in homogeneous (\perp) orientation. In figure 4 they are shown for A1MA9, for which their typical features can best be demonstrated. A broad maximum is found, which becomes smaller when the clearing point is approached. Simultaneously the shift of the average relaxation frequency with temperature becomes smaller and practically zero. These properties are also obtained by performing fits to the curves using a single F.K. function (see the fit parameters in table 4). On going to lower temperatures such single-line fits grow continuously worse.

Table 3. Activation energies in kJ mol^{-1} for the δ -relaxation.

Compound	S _A phase	N phase	Isotropic
A9MA1	–	135	95
A5MA5	–	164	124
A1MA9	174	–	151
MAPB	189	–	152

Table 4. Fit parameters for $\epsilon''(\omega)$ ($\mathbf{E} \perp \mathbf{n}$) approximated by one F.K. function (columns 2–5) or two superimposed F.K. functions (columns 6–9 give parameters for the second line). $d(x_i)$ and errors as defined in table 1. Note that for some temperatures the parameters of one-line fit and two-line fit are both given. For the other temperatures only the two-line fits are listed. Parameters in parentheses have been fixed in the fitting procedure.

T/K	f_τ/kHz	ϵ_m	β_1	$\epsilon_0 - \epsilon_\infty$	f_τ/kHz	ϵ_m	β_2	$\epsilon_0 - \epsilon_\infty$	$d(x_i)$
A9MA1									
112.0	350 ₂₀	1.37	0.45	6.1	–	–	–	–	0.047
99.6	270 ₂₀	1.09	0.36	6.1	–	–	–	–	0.053
85.5	97	0.90	0.24	7.5	–	–	–	–	0.019
70.6	13	0.81	0.23	6.8	–	–	–	–	0.023
A5MA5									
106.5	30	0.83	0.65	2.6	290 ₇₀	0.78	0.27	5.8	0.011
106.5	66	1.43	0.39	7.3	–	–	–	–	0.050
97.2	13	0.53	0.65	1.6	190 ₅₀	0.75	0.28	5.4	0.018
97.2	55	1.11	0.33	6.7	–	–	–	–	0.074
87.2	3.8	0.59	0.52	2.3	140 ₃₀	0.60	0.31	3.9	0.025
74.7	0.06	0.33	0.44	1.5	4.3 ₁	0.70	0.25	5.6	0.013
A1MA9									
115.5	(15)	1.00	0.66	3.0	600 ₁₅₀	0.74	(0.24)	6.7	0.020
115.5	41	1.48	0.38	7.8	–	–	–	–	0.035
109.8	(6)	0.61	0.54	2.3	280 ₅₀	0.69	(0.22)	6.5	0.012
109.8	25	1.07	0.26	8.2	–	–	–	–	0.029
106	2.0	0.59	0.57	2.0	122 ₁₅	0.68	(0.19)	7.2	0.015
106	6.3	1.00	0.20	10	–	–	–	–	0.029
100.4	0.86	0.43	0.66	1.3	33	0.70	(0.19)	7.4	0.014
94.1	0.32	0.35	0.64	1.1	11	0.68	(0.19)	7.2	0.005
88.9	0.10	0.52	0.55	1.9	22	0.59	(0.19)	6.3	0.006
83.8	0.035	0.53	0.53	2.0	10	0.57	(0.19)	6.2	0.008
77.8	0.010	0.58	0.50	2.3	5.3	0.53	(0.19)	5.6	0.012
73.0	0.004	0.60	0.60	2.4	2.8	0.51	(0.19)	5.4	0.013
70.2	0.002	0.6	0.9	1.0	0.83	0.56	(0.19)	5.9	0.011

The absorption is not simply broadened, but is obviously split up into two underlying relaxations. A fit by a linear superposition of two F.K. functions describes the spectra very well (see table 4). The low frequency contribution (α_1) is narrower and has a smaller relaxation strength than the high frequency contribution. The temperature dependence of the relaxation strengths is opposite for the two contributions, as is demonstrated in figure 5. For α_1 $\epsilon_0 - \epsilon_\infty$ increases with the temperature, whereas $\epsilon_0 - \epsilon_\infty$ of α_2 is slightly decreasing. This is also true for pure MAPB, where the splitting is also observed very clearly [2]. However, the relative strengths of α_1 and α_2 are different for these two compounds (see figure 6). For the other two copolymers A9MA1 and A5MA5 splitting of the \perp -relaxation was not such obvious as for

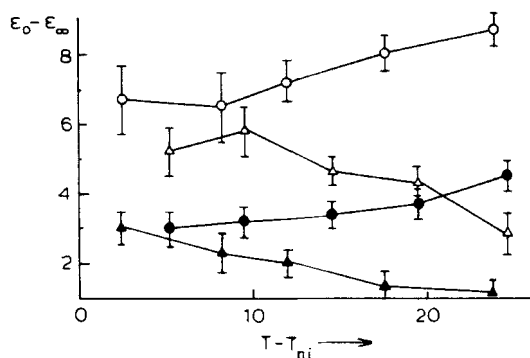


Figure 5. Relaxation strengths $\epsilon_0 - \epsilon_\infty$ for the subrelaxations in \perp -alignment. (Δ) α_1 for MAPB, (\bullet) α_2 for MAPB, (\blacktriangle) α_1 for A1MA9 and (\circ) α_2 for A1MA9.

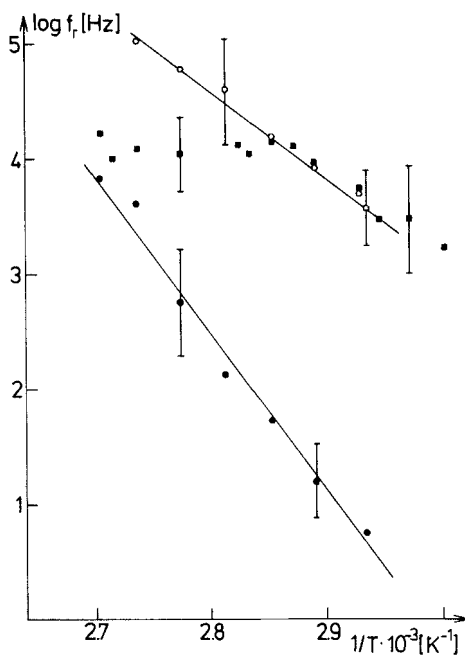


Figure 6. Relaxation frequencies for MAPB in \perp -orientation (α -relaxation) as obtained by (\blacksquare) one-line fit and (\bullet) α_1 and (\circ) α_2 two-line fit.

A1MA9. In any case two-line fits gave better approximation for the \perp -spectra of these compounds too, although the fit parameters were less reproducible. In table 4 the parameters and qualities of the two-line fits and one-line fits are compared.

A principal feature of the \perp -relaxation for all the copolymers as well as the homopolymers is the retardation of the relaxation frequencies near the clearing point, accompanied by a narrowing of the whole absorption curve. This behaviour is readily explained by the decomposition in two subrelaxations. Since the low frequency relaxation increases in relaxation strength when approaching the clearing point, the average relaxation frequency (as obtained by a one-line fit) is shifted to lower frequencies. The relationship between this retardation and the behaviour of the

subrelaxations α_1 and α_2 is shown in figure 6 for MAPB only, since this compound shows the most marked effect.

4. Discussion

The first question that may be answered by studying copolymers is to what extent the molecular reorientation associated with the δ -relaxation is a single particle process, i.e. whether the monomer unit moves independently of the neighbouring chain elements or whether it is a predominantly collective process. This was checked by calculating theoretical relaxation curves under the following assumptions: (a) that the monomers reorient with different relaxation times, which differ by the same ratio as the relaxation times of the corresponding homopolymers, and (b) that the relaxation strength that each monomer species contributes is proportional to its percentage in the composition.

The theoretical relaxation curves are shown in figure 7, together with the comparable experimental data. We tried to approximate these superposed curves again by a single F.K. function. The distribution parameter and relaxation frequencies determined this way are represented in figure 8 for homopolymers and copolymers and opposed to the experimental parameters. It is obvious that there is an essential difference between the two. For a single particle motion we would expect a bimodal relaxation curve or at least a maximum in curve width in the middle of the concentration range (at equal composition). This is not observed, the distribution parameter decreasing monotonically from acrylate to methacrylate. The relaxation frequency is not determined by the excess partner of the copolymer, as would be the case for single particle motion, but changes significantly even on addition of only small amounts of comonomer.

We conclude therefore that the δ -relaxation curves are homogeneously broadened for the copolymers as well as the homopolymers. This broadening is asymmetric, as our H.N. analysis shows, and the asymmetry increases with the methacrylate content. The presence of correlation is also in agreement with the existence of only one average relaxation frequency for the copolymers, which has been shown earlier.

In order to achieve a quantitative understanding of the δ -relaxation, a theoretical model would be needed. This should start from well developed theories for cooperative motions in linear polymers and take into account the specific molecular dynamic process which is responsible for the δ -relaxation. In a forthcoming publication [11] we will try to elaborate such a simple model.

Our analysis of the \perp -spectra showed that the so-called α -relaxation can be separated into independent subrelaxations, and that this separation is a possible explanation for the effects of temperature dependent curve shapes and retardation of the average relaxation frequency near the clearing point. It is important to note that these latter effects have been found to be quite marked in all of the liquid-crystalline side chain polymers with strong longitudinal dipole moment of the mesogenic groups [1–3], but not for those with stronger transverse dipole moment [5]. For these the low frequency contribution (α_1) seems to be missing, and the overall relaxation behaves similar to the high frequency component of the resolved spectra [5]. One conclusion which can be drawn from this comparison is that α_1 is caused by the longitudinal dipole moment. If we take the expression for $\epsilon_{\perp}(\omega)$ derived from the Nordio–Rigatti–Segré model, adding a term accounting for the main chain motions (for details see [2, 3]):

$$\epsilon^*(\omega) \approx \mu_l^2(1 - S)A_{10}(\omega) + \mu_l^2(1 + \frac{1}{2}S)A_{11}(\omega) + \mu_h^2 f(S)A_h(\omega), \quad (3)$$

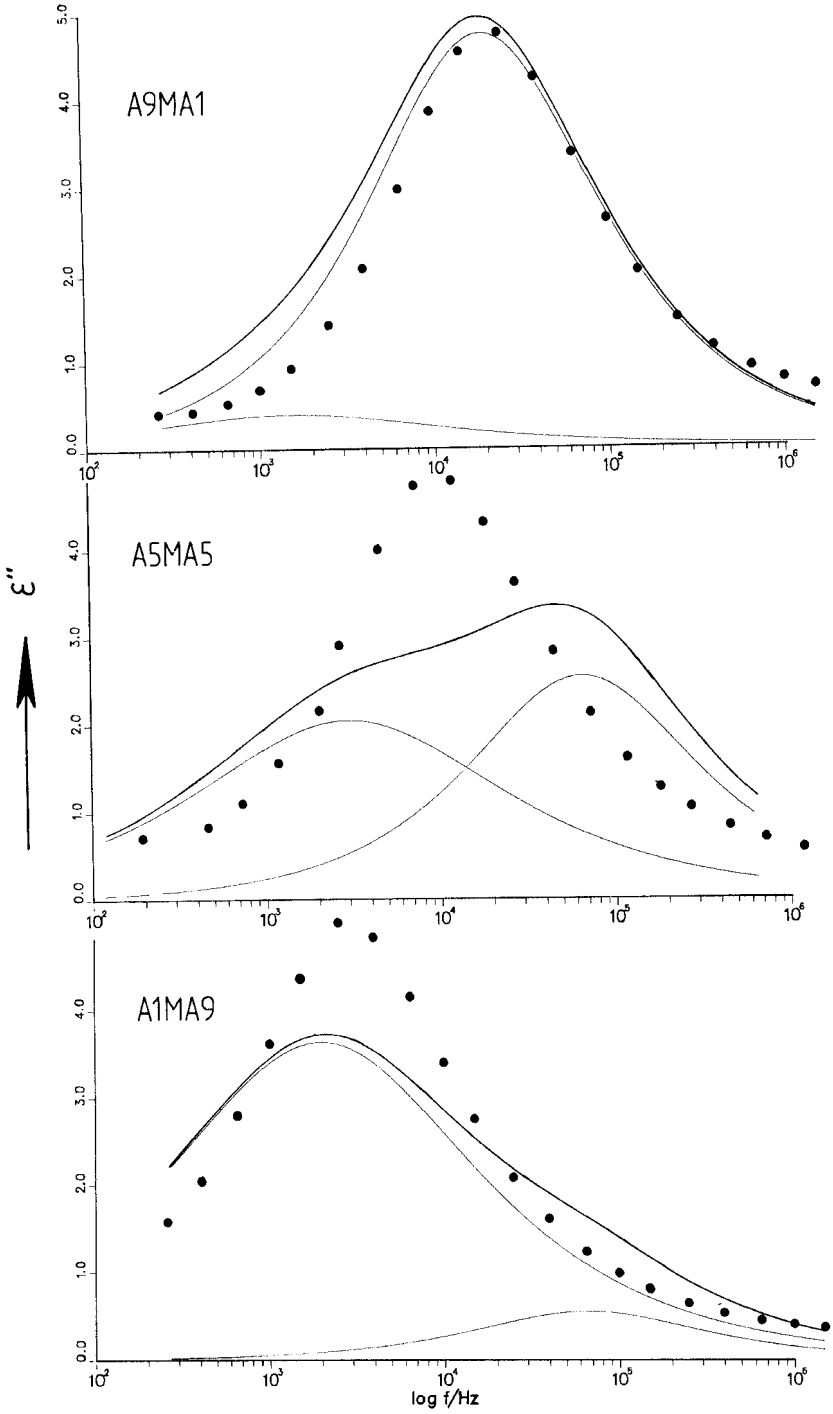


Figure 7. Theoretical superimposed relaxation curves (—) and experimental values. See text.

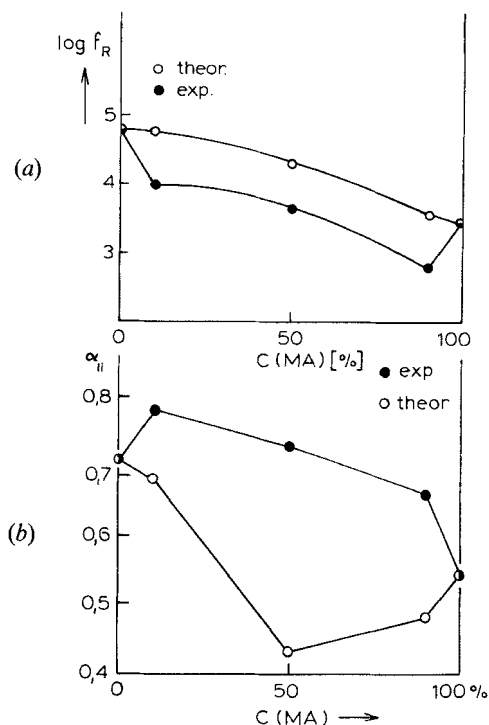


Figure 8. Parameters determined by fitting one F.K. function to the theoretical curves of figure 6. (a) Relaxation frequency and (b) distribution parameter α .

we find that the first term, which describes a kind of precessional rotation around the director, would fulfil this requirement. It would also be consistent with the dependence of the degree of order for α_1 (see figure 6). However, we cannot completely exclude the possibility that the α_1 -contribution is caused by an admixture of the δ -relaxation due to incomplete alignment, since the relaxation frequencies of α_1 are very close to those for δ . However, we point out that, if it were an admixture of δ , such an admixture due to incomplete alignment would have been present for all of the side chain polymers investigated, since all show the same typical effects.

The high frequency contribution α_2 must mainly contain the last two terms in equation (3), if α_1 is identified with the first term. As the interpretation for α_1 is uncertain, the same uncertainty holds for α_2 . We hope that new and more accurate data will help to give a more detailed interpretation of the two or more contributions to the \perp -spectrum.

This work was supported by the Deutsche Forschungsgemeinschaft.

References

- [1] HAASE, W., PRANOTO, H., and BORMUTH, F. J., 1985, *Ber. Bunsenges. phys. Chem.*, **89**, 1229.
- [2] BORMUTH, F. J., and HAASE, W., 1987, *Molec. Crystals liq. Crystals*, **153**, 207.
- [3] BORMUTH, F. J., BIRADAR, A., QUOTSCHALLA, U., and HAASE, W., 1989, *Liq. Crystals*, **5**, 1549.
- [4] HÉDVIK, P., 1977, *Dielectric Spectroscopy of Polymers* (Hilger), p. 207.
- [5] PRANOTO, H., BORMUTH, F. J., HAASE, W., KIECHLE, U., and FINKELMANN, H., 1986, *Makromolek. Chem.*, **187**, 2453.

- [6] BORMUTH, F. J., HAASE, W., and ZENTEL, R., 1987, *Molec. Crystals liq. Crystals*, **148**, 1.
- [7] BOEFFEL, CH., and SPIEB, H. W., 1989, *Side Chain Liquid Crystals*, edited by C. B. McArdle (Blackie).
- [8] MCCRUM, N. G., READ, B. E., and WILLIAMS, G., 1967, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley).
- [9] YOSHIHARA, M., and WORK, R. N., 1980, *J. chem. Phys.*, **72**, 5909.
- [10] MASHIMO, S., NOZAKI, R., YOGIHARA, S., and TAKEISHI, S., 1982, *J. chem. Phys.*, **77**, 6259.
- [11] BORMUTH, F. J., and HAASE, W., *Coll. Polym. Sci.* (to be published).