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Broadband dielectric spectroscopy on side group liquid crystal polymers

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Broadband dielectric spectroscopy on side group liquid crystal polymers

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Dielectric studies on three liquid-crystalline side group polymers were performed in the temperature range from 100 K to 450 K and in the frequency range from 10^{-1} Hz to 10^{7} Hz. All samples exhibit an α relaxation with a WLF dependence of the activation energy as well as a β relaxation, which are comparable in the glassy state. Their mean relaxation times, their relaxation time distribution, in its asymmetry and half-width, and their activation energies are nearly unaffected by the spacer length, terminal group and/or main chain. These findings are supported by N.M.R. measurements. A third relaxation process occurring close to the clearing point is also observed and assigned to the cooperative rotation of the side group around the main chain.

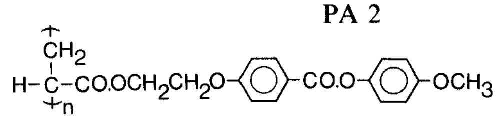
1. Introduction

Since their first synthesis in 1978 [1, 2], thermotropic liquid-crystalline side group polymers have attracted considerable interest. Measurements of the complex dielectric function $\hat{\varepsilon}(\omega)$ over a large frequency range at different temperatures provide a powerful tool with which to detect the molecular dynamics of these compounds since different polar groups are involved in different motions. Hence its relaxations are, in general, well separated on the frequency and temperature scale [3–7, 16]. Zentel *et al* [3] have studied a variety of liquid-crystalline side group polymers and introduced a nomenclature for the relaxation motions. Boeffel *et al.* have studied slightly different polyacrylate and polymethacrylate liquid-crystalline polymers with N.M.R. spectroscopy [8, 9]. In order to make a direct comparison with these results, dielectric measurements on the same samples are presented in this paper.

2. Experimental section

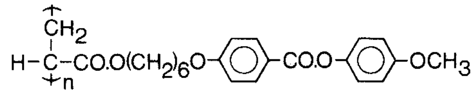
Samples: All three compounds studied contain phenylbenzoate as a mesogenic group. The molecular weights are determined by GPC using polystyrene as a standard. The phase transitions were determined by D.S.C. and polarisation microscopy. The phase characterization was done by X-ray measurements.

PA 2



$M_n = 60{\cdot}000$
g 335 K N 389 K I

PA 6



$M_n = 40{\cdot}000$
g 304 K S 367 K N 394 K I

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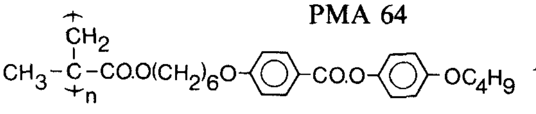
PMA 64



M_n = 250·000
g 307 KS 380 KN 385 KI

The dielectric measurements covered the frequency range from 10^{-1} Hz to 10^7 Hz. For that a Hewlett–Packard impedance analyser (HP 4192A; frequency range: 10 Hz to 10^7 Hz) and a frequency response analyser (Solartron–Schlumberger FRA 1254, frequency range: 10^{-4} Hz to 6×10^4 Hz) were employed. The latter was connected with a high-impedance preamplifier of variable gain [10]. The sample material was kept between two condenser plates (gold plated, brass electrodes, diameter: 40 mm) with a separation of 200 μm which was provided with a silica ring giving a sample area of 706 mm^2. The condenser plates were pressed together by a micrometer screw. The temperature of the whole arrangement was controlled by a stream of nitrogen gas (temperature range: 100 K to 500 K, stability of the temperature adjustment: ± 0·02 K). Both measurement systems are fully computer controlled. The samples were studied in the unaligned state as well as homogeneously and homeotropically aligned states. This alignment was achieved by cooling the samples from the isotropic phase through the liquid-crystalline phases into the glassy state at a rate of 0.5°C/min inside a superconducting N.M.R. magnet (maximum field strength: 7·5 T).

3. Results and discussion

The temperature dependence of the dielectric loss of PA2 at 10 kHz (see figure 1) allows us to distinguish between three relaxation processes. The stronger one occurring at higher temperatures is the α relaxation, i.e. its relaxation rate extrapolated to the glass transition temperature approaches low frequency. This can be seen in figure 2. The temperature dependence of the relaxation rate ν_τ can be described by the WLF equation [11]

$$\log\frac{\nu_\tau}{\nu_0} = \frac{C_1(T - T_g)}{C_2 + T - T_g}, \qquad (1)$$

where T_g is the static glass transition temperature, ν_0 its corresponding relaxation rate and C_1 and C_2 are fitting parameters. A least squares fit yields values for C_1 of 11·4 and C_2 of 32·7. At T_g of 335 K a relaxation rate ν_0 equal to 0·05 Hz is found.

The second relaxation process is strongly broadened. According to Zentel *et al.* [3] it is the β process, which is assigned to the rotational motion of the mesogenic group around its long axis. It is observable dielectrically because of the phenylbenzoate ester group. This relaxation process is strongly asymmetric and so the Havriliak–Negami [12] function

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + (i\omega\tau)^{1-\alpha})^\beta} \qquad (2)$$

is chosen to fit the data. Here ε_∞ and ε_s are the values of the dielectric function on the high frequency and low-frequency side of the relaxation process respectively, τ is the mean relaxation time and a and β are fitting parameters which describe the broadening and the asymmetry of the relaxation time distribution. At low frequencies a further strong temperature dependent contribution to the dielectric loss results from electrical conductivity within the sample. (See figure 3.) Its frequency dependence can

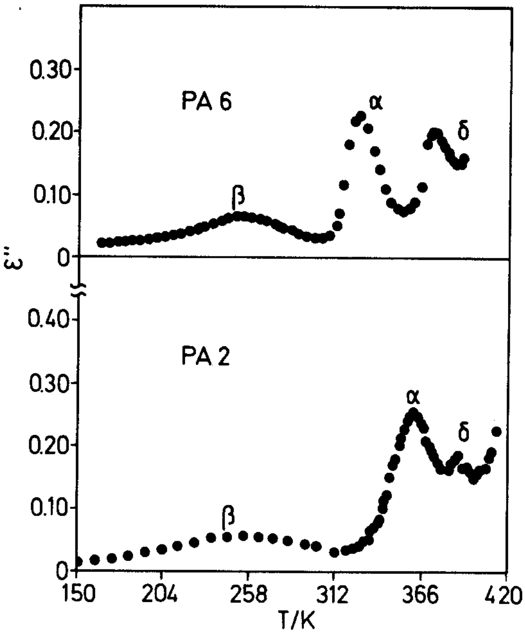


Figure 1. Dielectric loss versus temperature at 10 kHz. Sample: PA2 and PA6 (both unaligned). The error bars in this and the following figures are not larger than the size of the symbols

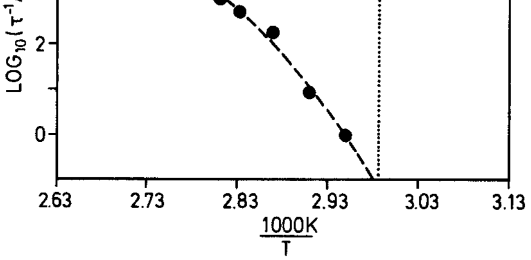


Figure 2. Relaxation rate as determined from the dielectric loss maxima versus inverse temperatures (WLF plot). Sample: unaligned PA2. The dots correspond to the experimental values. The vertical dotted line indicates the static glass transition temperature measured by D.S.C. The dashed line is a fit according to the WLF equation [11].

be fitted using

$$\varepsilon''(\omega) = \frac{\delta_0}{2\pi\varepsilon_0 \nu^s}, \tag{3}$$

where δ_0 and s are fitting parameters [13] and ε_0 is the permittivity of free space. S

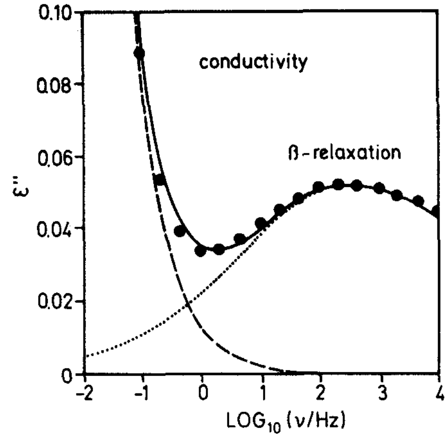


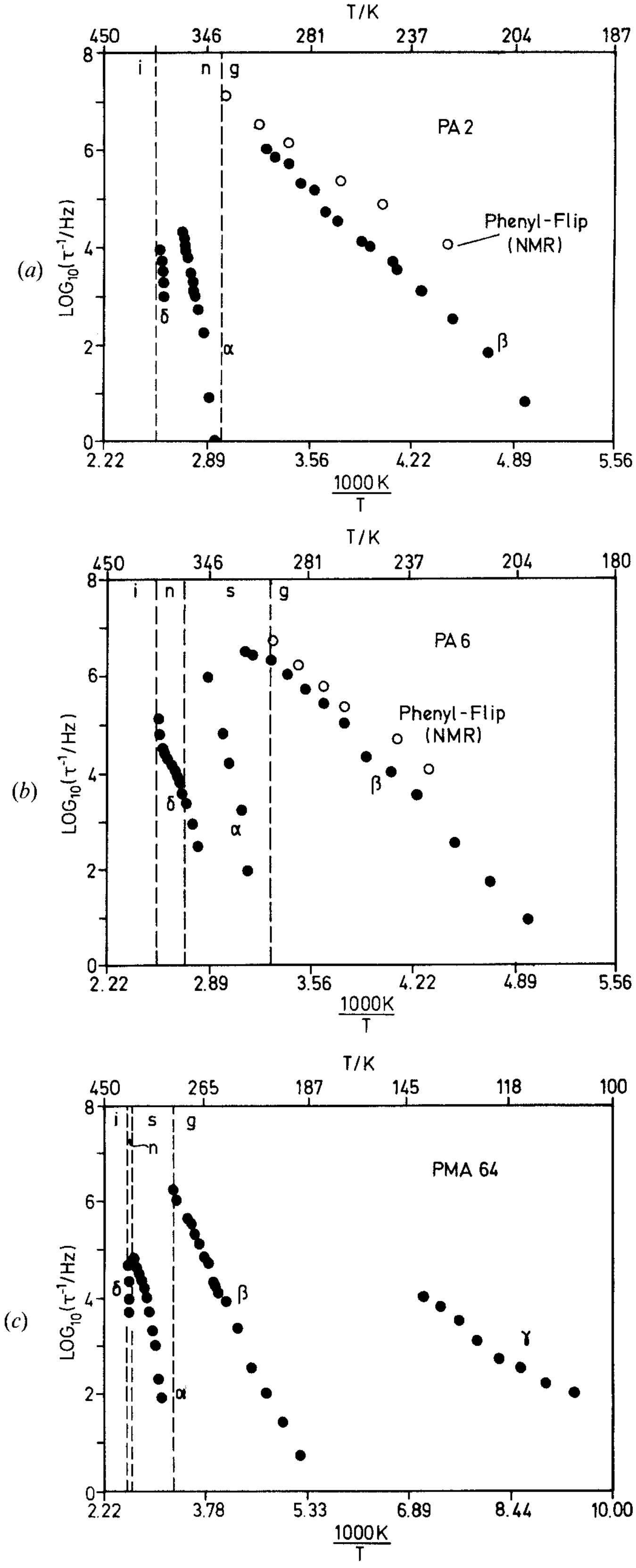
Figure 3. Dielectric loss versus frequency at 214·7 K. Sample: unaligned PA2. The dotted points are experimental values. The solid line is the superposition of a conductivity contribution (dashed line) calculated according to equation (3) and a relaxation term (dotted line) according to equation 2. (Fitting parameters: $\delta_0 = 7 \times 10^{-11}$ 1/Ωcm; $s = 0{\cdot}8$, $\varepsilon_\infty = 4$, $\varepsilon_s = 4{\cdot}495$, $\alpha = 0{\cdot}38$, $\beta = 0{\cdot}39$, $\tau = 5{\cdot}35 \times 10^{-3}$ s).

values of 0·8 are found, indicating that the conductivity originates from the hopping of ions.

Using the Havriliak–Negami function the value and temperature dependence of the mean relaxation time τ and the mean relaxation rate ν_τ ($\equiv 1/\tau$) is deduced. The result, given in figure 4(*a*), shows that the β relaxation has an Arrhenius-like temperature behaviour in the frequency range studied and within the glassy state. The corresponding activation energy is 55 ± 4 kJ/mol. For comparison the N.M.R. data [9, 14] for the 180° phenyl-flip inside the mesogenic group are shown in the same figure, these give an activation energy of 44 ± 3 kJ mol^{-1}. The difference between the dielectric and the N.M.R. results is not surprising in view of the following differences: (i) The molecular probe in the dielectric measurement is the polar ester group (ester flip) and in the N.M.R. measurement the deuterons form the probe (phenyl flip). (ii) the N.M.R. results are sufficiently described by a symmetric gaussian distribution of correlation times with a half-width of 2·2 decades [9], [14]. Dielectrically an asymmetric distribution of relaxation times with a higher half-width of 3·16 decades was measured. (iii) For the N.M.R. measurements one phenyl ring was deuteriated. For the sake of completeness the α-relaxation process shown in figure 2 is also presented in figure 4(*a*).

A further relaxation with a small strength is found above the glass transition. It is assigned to the δ relaxation, i.e. a (presumably collective) rotation of the whole mesogenic group around the polymer main chain [15]. The δ relaxation and the α relaxation are separated on the frequency scale by about 2 decades, for a similar polymer with terminal cyano group the same separation was found [16].

Figure 4. (*a*) Activation plot (relaxation rates versus inverse temperature) for unaligned PA2. ●, dielectric measurements, ○, N.M.R. measurement for 180° phenyl-flip. (*b*) Activation plot (relaxation rate versus inverse temperature) for unaligned PA6. ●, dielectric measurements; ○, N.M.R. data for the 180° phenyl-flip. (*c*) Activation plot (relaxation rate versus inverse temperature) for unaligned PMA 64. ●, dielectric measurements.


(a)
T/K
450
346
281
237
204
187
i
n
g
PA 2
Phenyl-Flip
(NMR)
δ
α
β
$LOG_{10}(\tau^{-1}/Hz)$
8
6
4
2
0
2.22
2.89
3.56
4.22
4.89
5.56
$\frac{1000K}{T}$
(b)
T/K
450
346
281
237
204
180
i
n
s
g
PA 6
Phenyl-Flip
(NMR)
δ
α
β
$LOG_{10}(\tau^{-1}/Hz)$
8
6
4
2
0
2.22
2.89
3.56
4.22
4.89
5.56
$\frac{1000K}{T}$
(c)
T/K
450
265
187
145
118
100
i
s
g
n
PMA 64
δ
α
β
γ
$LOG_{10}(\tau^{-1}/Hz)$
8
6
4
2
0
2.22
3.78
5.33
6.89
8.44
10.00
$\frac{1000K}{T}$

For the second polyacrylate polymer containing six methylene groups as the spacer (PA6) three distinct processes are found (see figure 1) namely β, α and δ relaxation. As for PA2 the α relaxation is connected with the static glass transition-temperature when extrapolated to low frequencies. Above the glass transition δ relaxation occurs and is again assigned to the motion of the whole mesogenic group around the polyacrylate main chain. The decreased relaxational strength in unaligned PA2 for this δ process might be due to the shortening of the spacer length and hence the stronger coupling between the mesogenic group and the polymeric main chain. It should be noted that the δ relaxation has an unusual temperature dependence of the activation energy (see figure 4(*b*)). Presumably the δ relaxation is hindered at low temperatures. Close to the clearing point the viscosity decreases strongly as does the order parameter [8], [14]. The α relaxation and δ relaxation have at 343 K a separation of 4 decades on the frequency scale, for a similar polymer with terminal cyano group 3 decades were measured [16]. Steric hinderance is reduced leading to higher relaxation rates. The β relaxation in PA6 is similar to that in PA2. It is again assigned to the rotational motion of the mesogenic group around its long axis. By analysing it using the Havriliak–Negami function a narrower relaxation time distribution is found (see table). This might be caused by the higher order in the smectic glass of PA6, while in PA2 the β process occurs in a nematic glass. In the glassy state the β relaxation has an Arrhenius like temperature dependence with activation energies of 57 ± 4 kJ/mol (cf. 47 ± 3 kJ/mol for N.M.R. measurements [9, 14]). In the smectic phase its activation energy is smaller, furthermore its relaxation time distribution is broader. At higher temperatures the β and α relaxations overlap and meet in the same frequency and temperature range.

Half-width of the relaxation time distribution of the β process in the glassy state as measured by dielectric spectroscopy and N.M.R.

	Half-width of relaxation time distribution [decades]	
Sample	Dielectric spectroscopy (asymmetric distribution function)	N.M.R. (symmetric gaussian distribution function)
PA2	3·16	2·24
PA6	2·26	2·50

For the third liquid-crystalline side group polymer PMA 64 again the α and the β relaxations are found (see figure 4(*c*)) with the same assignment as for the others. The activation energy for the β relaxation is 54 ± 4 kJ/mol in the glassy state. The half-width of the relaxation time distribution is 2·56 decades. As for PA2 above the glass transition again a δ process is found with decreased relaxational strength. That is reasonable because of the increased stiffness of the polymethacrylate main chain. At temperatures below 150 K a further relaxation process occurs in the glassy state. Its relaxational strength is so small, that it was measurable with sufficient resolution only with our frequency response analyser. It was assigned to the γ relaxation of the terminal butyl group which only exists in the PMA 64 sample. Its activation energy is 17 ± 4 kJ/mol.

The α relaxation process in the three polymers studied is characterized by a temperature dependence of the activation energy in accord with the WLF equation.

It is assigned to micro-brownian motions of main chain segments which are dielectrically observable because of the dipole moment of the ester group. Furthermore motions of the mesogenic group coupled via the spacer may contribute [17, 18]. A more detailed analysis of the observed relaxation processes according to Attard *et al.* [19–21] using aligned samples is in progress.

4. Conclusion

The relaxational movements observed by dielectric spectroscopy (frequency range: 10^{-1}–10^{7} Hz, temperature range: 100 K to 450 K) are presented in figure 5. All three liquid-crystalline side group polymers PA2, PA6 and PMA 64 exhibit an α relaxation with a WLF-like temperature dependence of the activation energy. All three samples have a β relaxation with comparable properties in the glassy state. Their mean relaxation times, their relaxation time distribution, in its asymmetry and half-width, and their activation energies are nearly unaffected by spacer length, main chain and/or terminal groups. This is also supported by N.M.R. measurements. In PA6 a δ process and in PMA 64 a γ process are additionally observed in the unaligned samples. For PA2 and for PMA 64 the δ process has a small relaxational strength.

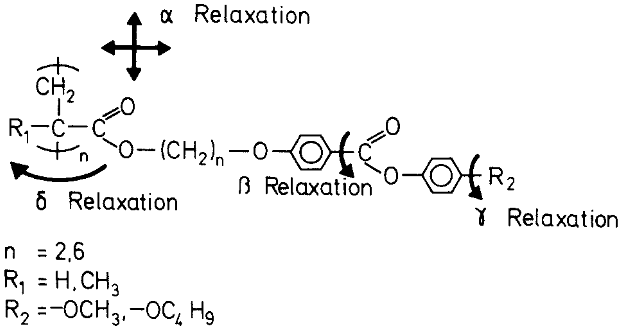


Figure 5. Scheme of the liquid-crystalline side group polymers and the relaxation movements which were observed in the measurements (indicated by arrows).

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