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Comparative dielectric investigations of two liquid-crystalline side chain polymers

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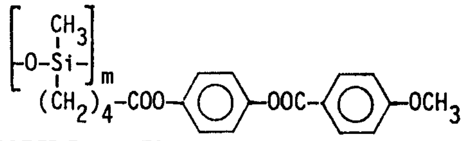
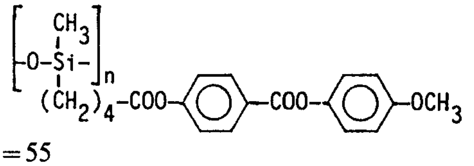
Dielectric relaxation measurements of two isomeric siloxane polymers with opposite direction of the carboxyl group in the liquid crystal part of the side chain were carried out in the frequency and temperature range from 10 Hz to 10 MHz and 150 K to 400 K. For every sample two intensive absorption ranges ($\varepsilon'' > 0\cdot1$) and two dielectric absorptions with lower intensities ($\varepsilon'' < 0\cdot05$) were detected. The first two are interpreted as reorientation processes of the side group as a whole around the short and long molecular axes, respectively. The less intensive absorptions can be observed below the glass temperature. They are discussed with respect to the different structures as the reorientation of the carboxyl electric dipoles in the middle part of the side group and of the terminal methoxy group, respectively.

1. Introduction

Dielectric measurements are a powerful tool with which to study the dynamics in liquid-crystalline polymers [1–10]. About ten years ago the first measurements were carried out in which the interaction of the liquid-crystalline side chains with one another and with the structure of the phase were investigated [1, 2]. Later the influence of the spacer [3–7], the main chain [6–8], the degree of polymerization [9, 10] and of the liquid-crystalline side chain [3, 6] were systematically studied. Relaxation measurements close to the glass transition [4, 5] and theoretical considerations [11, 12] of the different relaxation processes give at the time a relatively complex picture of the motions in liquid-crystalline polymers. Some questions related to local reorientation processes are still open and so the isomeric siloxanes [13]


(I)

g 321 K S_A 395 K N 397 K I, $m = 70$


(II)

g 324 K N 365 K I, $n = 55$

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were investigated. The average degrees of polymerization *n* and *m* were estimated by gel permeations chromatography using a polystyrene standard. The only structural difference between the siloxanes (I) and (II) is the direction of the carboxyl (COO) group between the phenyl groups which should be seen in the mobility of the –COO– and $-OCH_3$ electric dipoles.

2. Experiments and results

Dielectric measurements were performed with the Hewlett–Packard impedance analyser HP 4192 A from 100 Hz to 10 MHz and with the frequency response analyser Solartron Schlumberger FRA 1254 which covers the frequency range from 10^{-4} Hz to 65 kHz. The unaligned sample was kept between two gold plated condensor plates (diameter 15 mm, distance: 50 μm). The temperature stabilization ($\pm$0·02 K) and the measurements were fully computer controlled [14].

A survey of the dielectric absorption ε'' as a function of frequency and temperature of sample **I** is given in figure 1; at least the two absorption ranges 1 and 2 can be detected. Some irregularities occur at lower temperatures and frequencies. The picture of the dielectric loss at different frequencies in figure 2 shows that the absorption range 1 is covered by the conductivity at low frequencies. A very broad relaxation range at 240 K can be separated from the intensive mechanism at 1 kHz. At lower frequencies absorption range 3 is well separated from 2 (see figure 2). The increase of the absorption

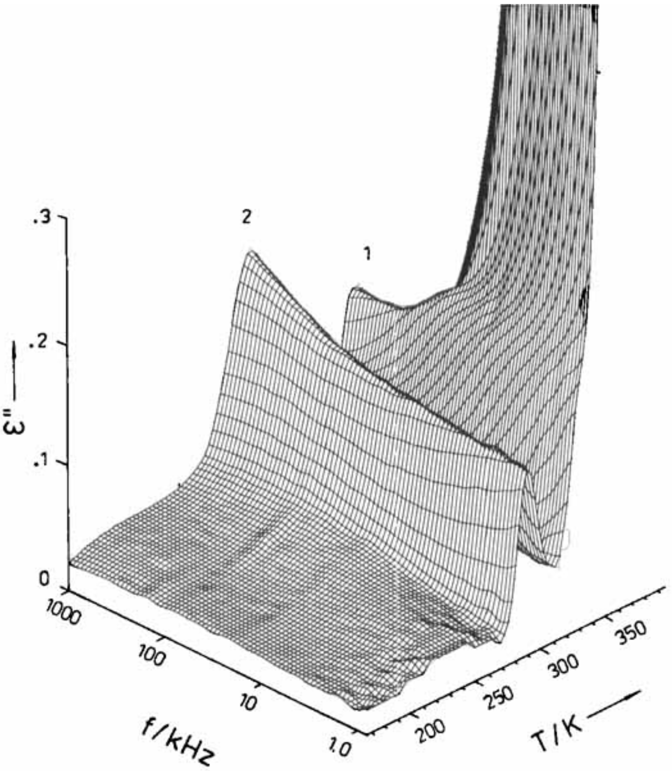

Figure 1. The dielectric loss ε'' of the unoriented sample **I** as a function of the frequency and the temperature (measured using HP 4192 A). The relaxation ranges 1 and 2 are indicated with decreasing temperature.

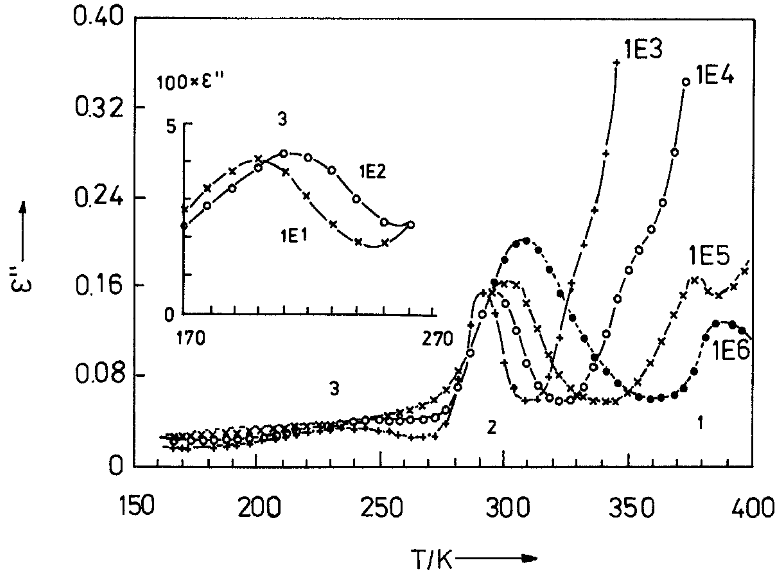

Figure 2. ε'' as a function of temperature according to figure 1. The frequencies are given in Hz: for example 1E3 = 1 kHz. At f = 1 MHz the intensity of 2 is about two times higher than that of 1. Range 3 can be separated at 1 kHz. At $f \geqslant 0{\cdot}1$ MHz relaxation process 3 is covered by process 2. The experimental error is ±5 per cent in ε''. The solid lines connect only points of the same frequency. Insert: The extremely low dielectric loss at low frequencies and temperatures measured with FRA 1254.

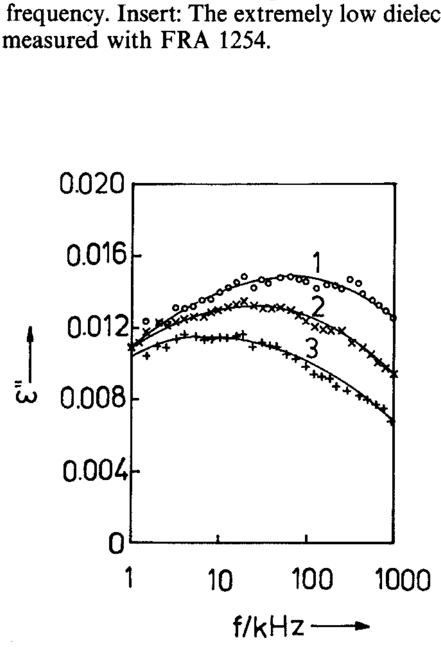

Figure 3. Dielectric absorption curves at different frequencies according to figure 1. $T(1) = 161{\cdot}9$ K, $T(2) = 151{\cdot}3$ K, $T(3) = 141{\cdot}0$ K. The solid line connects the points. Relaxation frequencies: $f_R(1) = 80$ kHz, $f_R(2) = 25$ kHz, $f_R(3) = 9$ kHz.

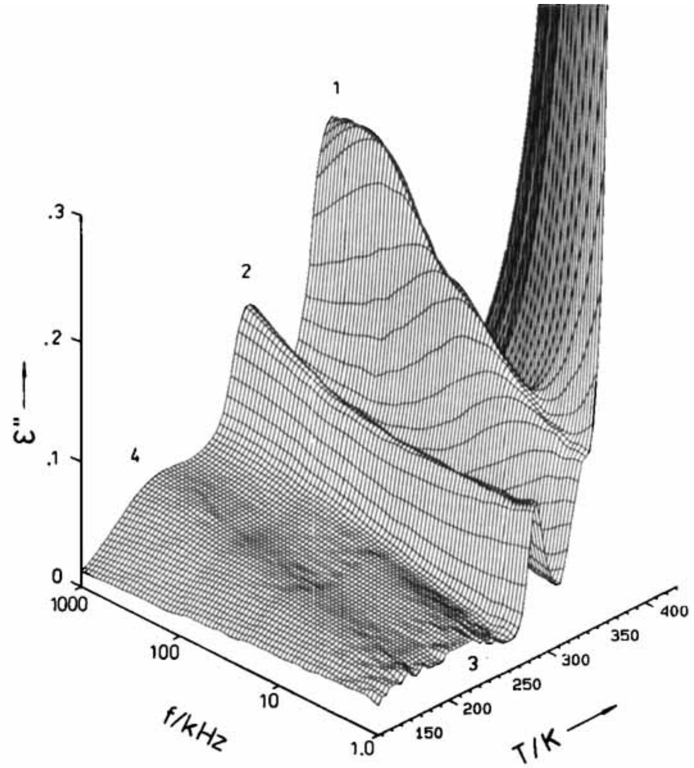

Figure 4. The dielectric loss of the unaligned sample II measured with HP4192 A. The two main relaxation processes 1 and 2 as well as the low intensity absorptions 3 and 4 can be seen.

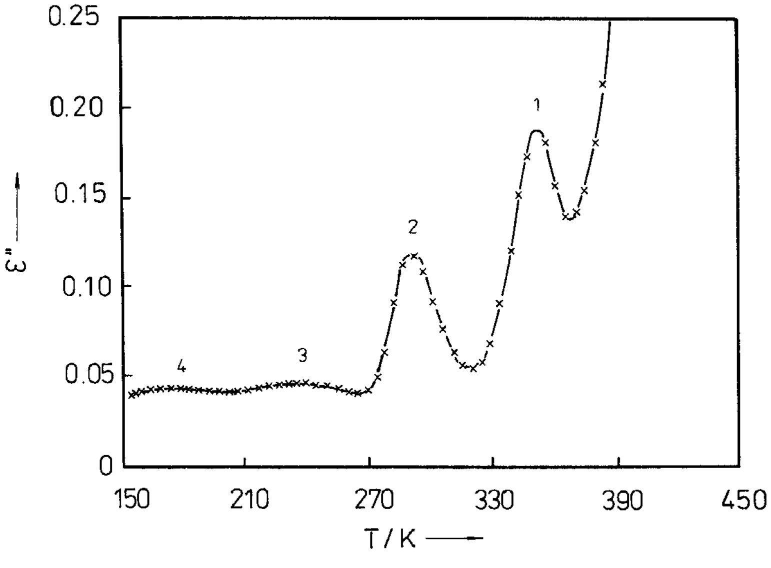

Figure 5. ε'' as function of temperature at 10 kHz according to figure 4. The conductivity dominates at $T > 380$ K.

intensity at low temperatures and high frequencies in figure 2 was the reason to analyse the data in the temperature range from 140 K to 170 K at higher frequencies. Figure 3 shows the very broad dielectric absorption range 4.

Due to the lower conductivity the main relaxation processes of substance **II** is better separated from the strong increase of ε'' at low frequencies. From the general picture in figure 4 we can conclude that there are again four relaxation processes. At 10 kHz the low frequency process (observed at about 350 K) has a higher intensity than process 2 (see figure 5); the processes 3 and 4 are clearly separated.

3. Discussion

The conductivity part [7]

$$\varepsilon'' = \frac{\sigma_0}{2\pi\varepsilon_0 f}, \tag{1}$$

where σ_0 is a fitting parameter and ε_0 is the permittivity of the free space, was separated from the low frequency relaxation process using the Cole–Cole equation [15]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (if/f_R)^\alpha}. \tag{2}$$

Here ε_S and ε_∞ are the dielectric constants on the low and high frequency sides of the relaxation process, respectively, f_R is the relaxation frequency and α is a fitting parameter. For sample **I** only a few values of f_R could be obtained close to the clearing temperature. For substance **II** relaxation frequencies of both the isotropic and the nematic phase could be calculated. For all of the other absorption ranges, the frequency of the respective maximum of ε'' was taken as the relaxation frequency. The data are summarized in figure 6 and the table. The high activation energies of processes 1 and 2 in the liquid-crystalline phases indicate the influence of the vicinity of the glass transition. Furthermore a jump in the molecular mobility at the phase transition from the nematic to the isotropic phase could be found for mechanism 1. The activation energy of the isotropic state is much lower than that of the nematic phase. By comparing these results with former experiments [1, 3] we can conclude that

Activation energies E_A, correlation coefficients K of the linear fit, number of points X used for the fit for the relaxation ranges 1–4.

Range	1	2	3	4
Substance **I**		Smectic A		
E_A/kJ mol^{-1}	—	317	53	35
K	—	−0·999	−0·998	−0·89
X	—	8	10	6
Substance **II**		Nematic		
E_A/kJ mol^{-1}	139†	410	54	40
K	−0·993	−0·989	−0·999	−0·99
X	10	8	7	3

† In the isotropic phase: $E_A = 50\,\mathrm{kJ\,mol^{-1}}$; $K = -0{\cdot}99$; $X = 3$.

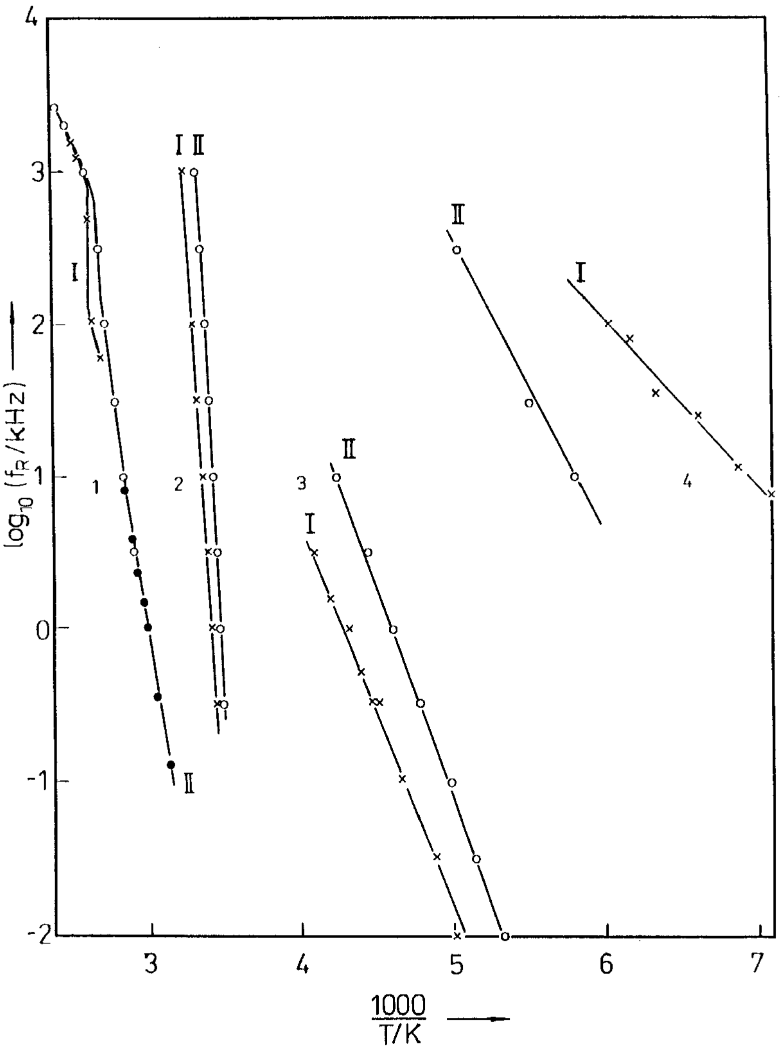

Figure 6. Dielectric relaxation ranges 1 to 4 of the samples **I** and **II**. The data of **II** 1 (●) were partially measured using a Sawyer–Tower bridge [1].

mechanism 1 is the reorientation of the longitudinal dipole of the liquid-crystalline side group.

The second mechanism has an activation energy of $E_A > 300\,\mathrm{kJ\,mol^{-1}}$. From a comparison with data on oriented samples [12] and measurements of low molecular weight liquid crystals with a high glass transition temperature [16] it follows that relaxation range 2 is the reorientation of the liquid-crystalline side group as a whole around the molecular long axis. Both processes, 1 and 2, seem to be limited for each substance by the respective glass processes.

The relaxation processes 3 and 4 have a low intensity, a strong broadening of the absorption curves with respect to the Debye absorption [15] and low activation energies. Both can be detected at $T < T_g$ and therefore, mechanisms 3 and 4 are local motions. A comparison of **I** and **II** shows that the different directions of the COO dipoles result in strong differences of the relaxation frequencies. Therefore, processes 3 and 4 should be related to motions of the –COO– and $-OCH_3$ groups, respectively. From the experimental results it follows that

(i) mechanism 3 splits up from a common relaxation process with mechanism 2 (see figure 5) and
(ii) the activation energy of 3 is in good agreement with that of the flip-flop of the phenyl ring [7].

We can conclude that process 3 is caused by a local reorientation of the COO groups surrounded on both sides by phenyl rings. The fastest process 4 must be the rotation of the terminal $-OCH_3$ group.

Summarizing the experimental data of both polymers we can conclude that

(i) the two main mechanisms 1 and 2 are not so strongly influenced by the chemical variations. Here it seems to be more important that both glass transition temperatures are quite near to each other and
(ii) the relaxation frequency of process 3 of **II** is decreased in relation to sample **I** whereas process 4 is faster.

It may be that the higher stability of the liquid-crystalline phase of **I** is a result of a stronger decoupling of the local reorientation processes 3 and 4.

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