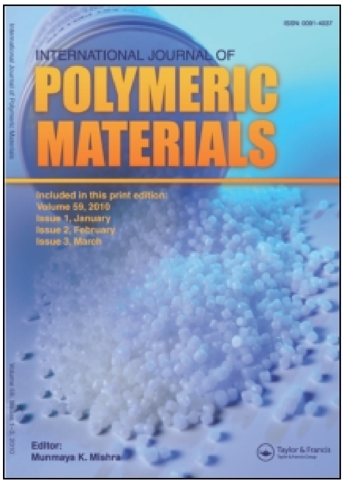

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Dielectric Properties of Thermotropic Polymer Liquid Crystals

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Dielectric Properties of Thermotropic Polymer Liquid Crystals

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Dielectric relaxation spectrometry is a useful tool to study molecular dynamics of macromolecular systems. Theoretical principles as well as experimental techniques are analyzed from the point of view of their capabilities. Results are reported for PET/xPHB, where PET = poly(ethylene terephthalate), PHB = *p*-hydroxybenzoic acid (the liquid crystalline component) and x is the mole fraction of PHB in the copolymers.

Keywords: Polymer liquid crystals; PLCs; dielectric relaxation; macromolecular dynamics; poly(ethylene terephthalate); *p*-hydroxybenzoic acid

1. INTRODUCTION

It has been proved by numerous studies [1] that dielectric relaxation spectroscopy is a useful tool to study the molecular dynamics of macromolecular systems. On the one side, this method provides direct information about the molecular dynamics of dipole moments related to the polymer chain or parts of it. So the molecular motions in the different states of the polymeric system for instance in the glassy or the rubbery state can be investigated in detail [1]. On the other side, information on structure or micromorphology of the system under investigation can be indirectly extracted because the motional processes depend on it. In that case the motion of dipoles is taken as a probe for structure.

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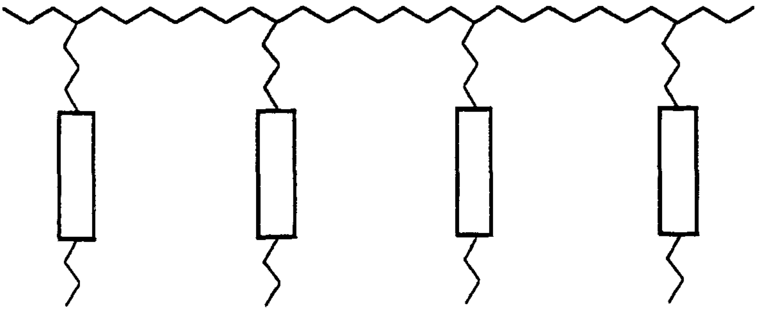
These considerations are absolutely true also for polymeric liquid crystals, which have received much attention since there first synthesis [2, 3] as advanced materials for various applications because of their multifunctional character. First of all, due to the polar nature of the mesogenic units dielectric spectroscopy is a potential analytic method to study the motion of these units in polymeric systems. As it is known for low molecular mass liquid crystal systems the shape of the units which form mesophases can be rod or disk like. But in contrast to low molecular mass liquid crystals polymeric ones can be synthesized in two different basic forms [4] (see Fig. 1). In side chain polymeric liquid crystals (SCPLC) the mesogenic unit is located in a side chain of the polymer backbone. Moreover for rod like mesogenic moieties the coupling with regard to the space groups can be parallel or perpendicular. It is expected that such materials can be applied as active components for



Mesophase forming unit in side chains (one-comb)

Mesophase forming unit in main chain (logitudinal)

FIGURE 1 Basic structures of some mesophase forming polymer chains.

optical data storage, holographic applications and electro-optical devices. This was demonstrated in Ref. [5] for the first time. In these materials molecular dynamic – which can be explored by dielectric spectroscopy – is contemporary and important for their application because the storage of information is connected to a reorientation of molecules or parts of it.

The other basic type of polymeric liquid crystals are main chain polymeric liquid crystals (MCPLC). In those systems the mesogenic moiety is a part of the polymeric backbone. Due to the spontaeous selforganization which leads to nanoscalic structure these materials exhibit enhanced mechanical properties. Information about their dynamical behavior and their phase morphology can be obtained using dielectric spectroscopy [6–8]. Furthermore the data measured give also insight into molecular processes which are responsible for other properties, such as viscoelastic relaxations which are directly related to technological processing parameters like viscosity. However it has to be stated that in comparison to numerous dielectric studies on SCPLC investigations on MCPLC are very rare and limited mainly to ester systems [6]. Recently dielectric studies on liquid crystalline main chain polyethers have been reported [9]. Also some additional references on relaxation studies on MCPLC can be found in [9]. Moreover there are also some studies on combined main chian-side chain liquid crystal polymers (see for instance [10, 11]).

Dielectric spectroscopy on liquid crystal polymers was pioneered by Kresse and coworkers [12–14] followed by the extensive work of Haase and collaborators [15, 16], Williams and his group [17] and Kremer *et al.* [18] and many, many others. Several reviews are also available [19–21] where the most extensive one is Moscicki's work [20]. Due to recent developments in both synthesis and experimental technique there is a growing number of papers which (i) document the dielectric behavior of liquid crystalline polymeric systems over a large rage of frequency and temperature, (ii) interrelate dielectric, mechanical, NMR [22, 23] and other relaxation processes to other qualities like optical properties of these polymers (see for instance [24–26]) and (iii) compare the experimental behavior with the results of theories to obtain insights into the molecular factors which are responsible for the observed dielectric relaxation.

The present paper is not intended to be complete either in the treated topics or in the quoted references. Rather it is a personal account of the authors on their understanding of the dielectric relaxation processes in bulk liquid crystal polymeric systems mainly based on own experimental results. It concentrates mainly on thermotropic SCPLC[1] but also the dielectric relaxation behavior of MCPLC is discussed at one example. The dielectric behavior of lyotropic systems is omitted for seek of space.

2. DIELECTRIC RELAXATION SPECTROSCOPY

2.1. Dipole Moments in Polymers and Basic Relations

Dielectric spectroscopy deals with the influence of an alternating electric field $\vec{E}(\omega)$ on matter (ω – angular frequency, f – frequency, $f = 2\pi\omega$). Application of $\vec{E}$ results in a polarization $\vec{P}$ of the medium. For small electric field strengths a linear relationship holds between

$$\vec{P}(\omega) = (\varepsilon^*(\omega) - 1)\varepsilon_{\mathrm{Vac}}\,\vec{E}(\omega) \quad \text{with} \quad \varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \tag{1}$$

where $\varepsilon_{\mathrm{Vac}}$ denotes the permittivity in vacuum. The quantity ε^*, called the complex dielectric function (ε'-real part, ε''-imaginary or loss part, $i = \sqrt{-1}$), is a material property depending on frequency, tem- perature, pressure and structure. For anisotropic compounds ε^* is a tensor. The consequences for the dielectric spectra of polymeric liquid crystalline systems will be discussed later on.

By the theory of dielectric relaxation ε^* is related to the correlation function $\Phi(t)$ of the polarization fluctuations [27, 28]

$$\begin{gathered}\frac{\varepsilon^*(\omega) - \varepsilon_\infty}{\varepsilon_{\mathrm{Sta}} - \varepsilon_\infty} = \int_0^\infty \left[\frac{-d\Phi(t)}{dt}\right] \exp(-i\omega t)dt \quad \text{with} \\ \Phi(t) = \frac{\langle \Delta P(t)\Delta P(0)\rangle}{\langle \Delta P(0)^2\rangle},\end{gathered} \tag{2}$$

where ΔP denotes a fluctuation of the polarization around its equilibrium value. The brackets denote the averaging over an ensemble or time t. The quantities ε_∞ and $\varepsilon_{\mathrm{Sta}}$ are the permittivities at very high (relaxed permittivity) and at quasistatic (unrelaxed permittivity) frequencies, respectively.

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[1] The dielectric behavior of ferroelectric liquid crystalline polymers is also omitted because recent reviews are available (see for instance [18]).

From a microscopic point of view of macroscopic observable polarization P is related to the dipole density of N permanent molecular dipoles μ_i in a volume V. For a simple low molecular weight molecule in the isotropic state the dipole moment can be well represented by a single rigid vector [27, 29]. For polymeric materials the situation is even more complex because there may be different molecular dipole vectors which have different geometric possibilities for their orientation with respect to the polymer backbone. A nomenclature for it was given by Stockmayer [30] for the first time. So in general the net dipole moment per unit volume (polarization) of a polymer system is given as a vector summation over all molecular dipole types in the repeating unit, the polymer chain, and over all chains in the system[2]:

$$\vec{P} = \frac{1}{V} \sum_{\text{all chains}} \sum_{\text{chain}} \sum_{\text{repeating unit}} \vec{\mu}_i. \tag{3}$$

Because the molecular motions in dense polymer systems are controlled by very different time and length scales, firstly, different parts of the net dipole moment can be reoriented by different motional processes. This will be discussed in detail for SCPLC in the next parts of this article. Secondly, from the experimental point of view, a broadband dielectric equipment is needed to explore the dynamics of polymeric systems in general. To this see Section 2.2.

Each molecular reorientation, if a change of the dipole moment is involved, corresponds to a dielectric active relaxation process where a relaxation region is indicated by a peak in ε'' and a steplike decrease in ε' *versus* frequency at a fixed temperature[3] (Fig. 2). So in general the

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[2] For phase separated or microphase separated systems we have further to sum up over all phases or microphases. This will be also of importance for polymeric liquid crystalline systems especially for MCPLC.

[3] The dielectric relaxation behavior can be also measured isochronally at a fixed frequency *versus* temperature. These measurements also exhibit a loss peak, at a temperature depending on the selected frequency, and a steplike increase in ε' with increasing temperature. But it should be noted that isochronal data in the temperature domain are difficult to analyze quantitatively, because the relaxation strength and the distribution of relaxation time are generally dependent on temperature [32]. Moreover for systems in which phase transitions can take place – like in liquid crystals – the interpretation and evaluation of temperature dependent isochronal dielectric measurements is much more complicated and can lead to wrong conclusions.

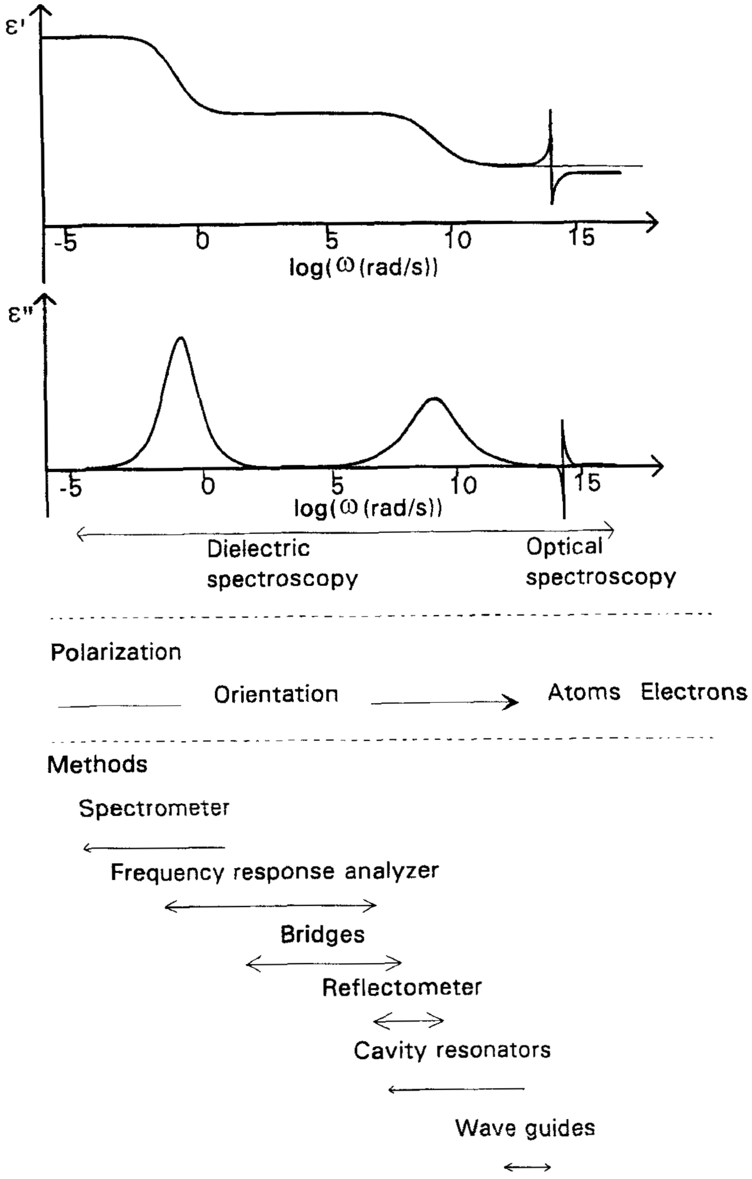

FIGURE 2 Schematic behavior of the complex dielectric function *vs.* logarithm of frequency and measurement methods for the different frequency ranges. The peaks and steps correspond to relaxation regions of the polarization due to movements of molecules or part of it.

dielectric spectrum of a polymeric system shows a multiple relaxation pattern which is of course also true for both MCPLC and SCPLC. Each relaxation process can be described by at least four parameters [31]. The frequency of maximal loss f_p corresponds to a characteristic relaxation time τ of the process by $\tau = 1/2\pi f_p$. The dielectric relaxation strength $\Delta\varepsilon$ which can be estimated either form step of ε' *via* $\Delta\varepsilon = \varepsilon'(f \ll f_p) - \varepsilon'(f \gg f_p)$ or from the area under the loss peak by $\Delta\varepsilon = 2/\pi \int_{\mathrm{Peak}} \varepsilon''(\omega)\, d \ln \omega$ is related to dipole moment μ

$$\Delta\varepsilon = F_{\mathrm{Onsager}}\, g \frac{N\mu^2}{3k_B T} \tag{4}$$

by the theory of Onsager, Fröhlich and Kirkwood (see for instance [27]). $F_{\mathrm{Onsager}} \approx 1$ is an internal field factor, T the temperature, k_B the Boltzmanns constant and N is the number of contributing dipoles. The Kirkwood correlation factor g was introduced to describe local, static correlation of dipoles which may be of importance for liquid crystalline systems [33].

The third feature of the loss peak is its shape which has been attributed either to a distribution of relaxation times [27] caused by spatial inhomogeneities or to molecular details of the underlying relaxation process [34, 35]. Evaluation methods to extract f_p, $\Delta\varepsilon$ and the shape of the loss peak and to separate different relaxation processes will be discussed in Section 2.3.

It should be mentioned that also the method of Cole–Cole-plots [27] (some times also called complex-plane plot method) this means plots of ε'' *versus* ε' are often used to analyze the dielectric data for liquid crystalline polymers.

An example for a dielectric measurement is given in Figure 3 where the dielectric loss is plotted *versus* frequency and temperature for a side group liquid crystalline polymer (see Tab. I sample P4). Several relaxation process are visible.

2.2. Experimental Techniques

In the recent years a strong development of experimental techniques took place. Now measurements in a frequency range from 10^{-4} Hz to

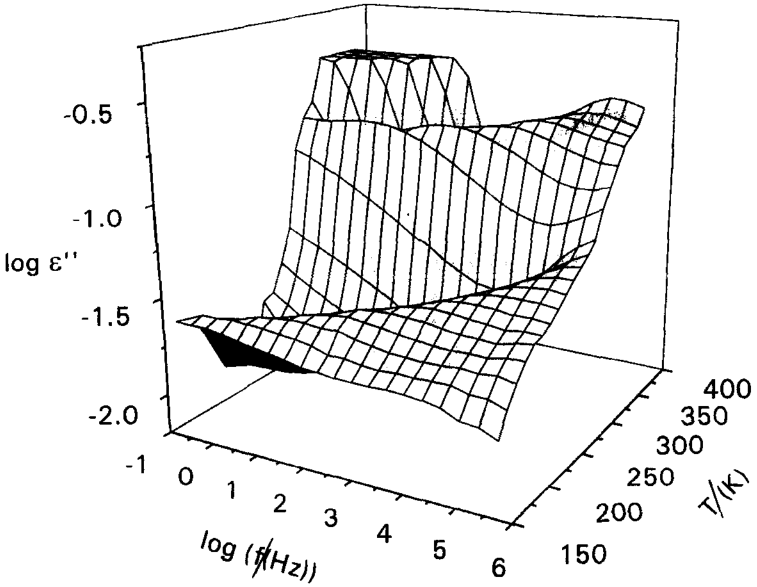

FIGURE 3 Log ε'' *vs.* temperature and logarithm of frequency for a liquid crystalline side chain polymer (sample P4, Tab. I, after [72]).

approximately 10^{10} Hz can be carried out more or less routinely [36]. For a recent review about the experimental techniques see for instance [37]. Clearly, such a broad range cannot be covered with a single apparatus and so a combination of different equipments is used where several methods are available for each frequency band (see Fig. 2 for an example). Mostly, the dielectric response is measured in parallel plate geometry in the so-called lumped-circuit technique. Experiments working with sinusoidal alternating fields are called measurements in the frequency domain. Alternatively the experiments can also be carried out in the so called time domain where a steplike change of $\vec{E}$ is applied. In that case the dielectric behavior is discussed in terms of the time dependent dielectric function $\varepsilon(t)$ which is direct proportional to the dipole correlation function. Therefore the relation between frequency and time domain is given by Eq. (2) and at low frequencies (10^{-5} Hz... 10^{1} Hz) that technique is convenient and saves time in

TABLE I Chemical structure, transition temperatures and activation parameters of the β-relaxation of the studied polymers: I, N, S_x means the isotropic, the nematic and the smectic state (X = A, B, C). The low temperature phase frozen at the glass transition temperature is indicated in bold

	R_1	R_2	R_3	R_4	m	T_g [K]			$log(f_{\beta\infty}[Hz])$	$E_{A\beta}[kJ/mol]$
P1	OCH_3	CO·O	OCH_3	CH_3	6	322	I		12.8 ± 0.2	45.7 ± 1.6
P2	H	CO·O	OCH_3	CH_3	4	318	N/I	377 K	13.8 ± 0.2	46.5 ± 1
P3	H	CO·O	OCH_3	H	2	343	N/I	343 K	14.8 ± 0.2	53.3 ± 1
P4	H	CO·O	OCH_3	CH_3	6	314	S_A/N N/I	345 K 383 K	16.5 ± 0.2	57.5 ± 1.4
P5	H	O·OC	OCH_3	CH_3	6	311	S_A/I	370 K	16.4 ± 0.2	56.4 ± 1
P6	H	CO·O	OC_4H_9	CH_3	6	315	S_A/N N/I	380 K 384 K	17.1 ± 0.2	61.0 ± 1
P7	H	CO·O	OCH_3	H	6	297	S_A/N N/I	367 K 394 K	17.5 ± 0.2	62.8 ± 3.2
P8	H	O·OC	OC_4H_9	CH_3	10	304	$S_{\mathbf{B}}/S_A$ S_A/I	318 K 394 K	18.2 ± 0.2	63.2 ± 2.1
P9	H	O·OC	OC_6H_{13}	CH_3	6	295	$S_{\mathbf{B}}/S_C$ S_C/S_A S_A/I	349 K 358 K 401 K	18.5 ± 0.7	64.9 ± 3.2
P10	H	O·OC	OC_6H_{13}	CH_3	10	296	$S_{\mathbf{B}}/S_C$ S_C/S_A S_A/I	320 K 330 K 399 K	19.4 ± 0.5	68.9 ± 2.1
P11	Br	CO·O	OCH_3	CH_3	6	323	I		------------	------------
P12	H	CO·O	OCH_3	CH_3	8	----	S_A/N N/I	283 K 390 K	------------	------------
P13	H	CO·O	OCH_3	CH_3	10	289	S_A/I	395 K	16.5 ± 0.2	55.3 ± 2.1
P14	H	CO·O	OCH_3	CH_3	2	343	N/I	390 K	------------	------------

comparison to measurements in the frequency domain. Practically the polarization or depolarization current is measured as a function of time. Different time domain spectrometers have been presented in the literature [38–41].

Measurements in the frequency range from 10^{-1} Hz to 10^6 Hz are most easily to perform and several automatic impedance analyzers are commercially available. Furthermore, in recent years equipments based on frequency response analyzer [42, 43] which is in principle a lock-in technique become more and more popular. Also fully digital lock-in setups have been described in the literature [44].

In the frequency range from 10^6 Hz to 10^9 Hz the dielectric properties can be measured by coaxial reflectometer [43] and time domain reflection methods [45]. At higher frequencies cavity resonators and waveguides must be used [46].

2.3. Evaluation of Dielectric Measurements

In general the dielectric relaxation spectra of liquid crystalline polymers are very complex and show various relaxation modes (see Fig. 3 and Section 3.1). Moreover the different processes are very often closely spaced in frequency domain and so the corresponding relaxation peaks in ε'' overlap strongly. In many cases the peaks are also very broad in a plot *versus* frequency. To extract information from such a spectra it has to be resolved in its various components. This is necessary to discuss the behavior of a process in dependence on temperature, chemical structure and mesophase sequence.

In the most cases the dielectric data were analyzed by fitting model functions to the dielectric data. There are several function[4] like the Cole–Cole – Cole-Davidson- and the Fuoss-Kirkwood-function in the frequency domain that are able to describe broad symmetric and/or asymmetric loss peaks. The most general one is the model function of Havriliak and Negami (HN-function) [47, 48] which reads.

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{\left(1 + (i\omega\tau_{\mathrm{HN}})^{\beta_{\mathrm{HN}}}\right)^{\gamma_{\mathrm{HN}}}}. \tag{5}$$

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[4] For references see [27].

τ_{HN} is a time connected with the peak frequency f_p [49]. β_{HN} and γ_{HN} are shape parameters with $0 < \beta_{\mathrm{HN}}; \beta_{\mathrm{HN}}\gamma_{\mathrm{HN}} \leq 1$[5] due to the symmetric and asymmetric broadening of the loss peak. It has been shown that they are related – with respect to τ_{HN}^{-1} – to the limiting low and high frequency slopes of log ε'' *versus* log ω [50]. A general method to apply formula (5) to dielectric data which have been measured in both frequency and time domain has been presented in [31], Figure 4 presents an example how nicely this method works also in the case of liquid crystalline polymers.

As pointed out in some cases the relaxation peaks overlap very strongly. So Eq. (5) cannot be fitted to the data without restrictions which are in the most cases not well found or justified theoretically. If that happens it can be useful to apply another method which goes back

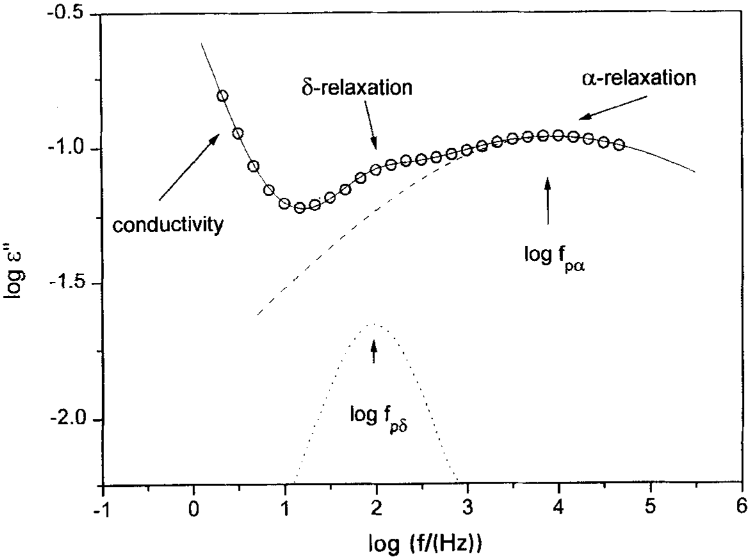

FIGURE 4 Decomposition of a measured ε'' *vs.* frequency curve in its various components (sample P4, Tab. I at 349.7 K). The solid line is the whole fitting function as a sum of two HN-functions. For details see [72]. The molecular assignment of the relaxation processes is discussed in Section 3.1.

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[5] The HN-function is equivalent for $\beta_{\mathrm{HN}} = \gamma_{\mathrm{HN}} = 1$ to the Debye-function, for $\gamma_{\mathrm{HN}} = 1$ to the Cole–Cole-function and for $\beta_{\mathrm{HN}} = 1$ to the Cole–Davidson-function. So the HN-function can be regarded as combination of both the Cole–Cole- and the Cole–Davidson-function.

to van Turnhout [51, 52]. This method is based on taking the derivative of ε' with respect to $\log f$ *i.e.*, $\Delta = \partial\varepsilon'/\partial\log f$. For Debye-like relaxation processes it could be shown that

$$\Delta = \frac{\partial\varepsilon'}{\partial\log f} \sim -\varepsilon''^2 \tag{6}$$

holds. Several conclusions can be drawn from relationship (6): (i) A relaxation peak in ε'' gives a minimum in Δ. (ii) The minimum should be narrower than the peak in ε'' because of the square in (6). So very broad dielectric loss peaks which are typical for crystalline and liquid crystalline materials becomes narrower in such a representation which allows to identify the position of maximum loss also for badly resolved loss peaks. (iii) Conductivity contributions according to $\varepsilon'' \sim 1/f$ do not play any role because for such a dependence the real part ε' is independent of frequency. Therefore electrode polarization and Maxwell–Wagner effects can be analyzed in more detail. The power of this method is demonstrated in Figure 5 which displays both the dielectric loss ε'' and the derivative Δ according to (6) for an liquid crystalline azobenzene containing liquid crystal. In ε'' the processes are

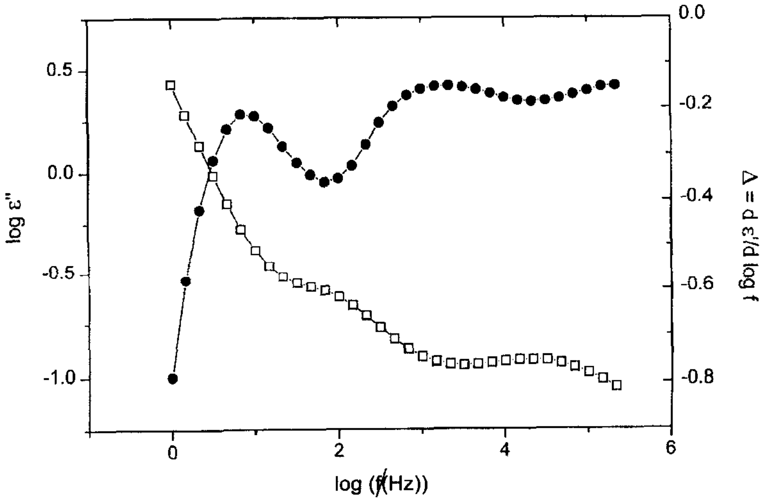

FIGURE 5 Dielectric loss ε'' (□) and $\Delta = d\varepsilon'/\log f$ (●) *vs.* logarithm of frequency for polymer A5 (see Tab. II) at $T = 373.8\,\text{K}$. Lines are guides for the eyes.

badly resolved whereas the Δ-representation shows two processes and the frequency of maximal loss can be estimated with high accuracy.

3. SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

3.1. Nomenclature of Relaxation Processes in Unaligned SCPLC

Zentel and coworker [53] developed a nomenclature for dielectric active relaxation processes which can take place in side chain liquid crystal polymers in their unoriented state. The basic structure of such comblike polymers which can form liquid crystalline mesophase is displayed in Figure 1. The mesogenic moiety is located in the side chain which is coupled *via* flexible spacer groups (in the most cases methylene groups) to a more or less flexible main chain. Clearly the main dipole moment of the system is directed parallel to the mesogenic unit but there are also other components the reorientation of which can be observed by dielectric spectroscopy (see Fig. 2). At very low temperatures rotational fluctuations of the tail or terminal groups of the side chain can be observed. This γ_1 process is followed by a further process[6] called γ_2- or β_1-relaxation. The molecular assignment of it is controversially discussed in literature [20] but it seems quite clear that it is related in some way to molecular motions of the spacer groups. At higher temperatures (or equivalently at lower frequencies) as the γ-processes the β-relaxation[7] becomes active which has been assigned to rotational fluctuations of the mesogenic unit around its long axis [10, 23, 53]. This interpretation is also in accord with NMR-studies [23, 54].

Whereas the temperature dependence of the relaxation rate of these discussed processes is Arrhenius-like, the relaxation rate of the next (with increasing temperature) observed relaxation process, called α-relaxation, shows a curved dependence on $1/T$. Therefore and moreover that this temperature dependence agree well with the glass transition temperature T_g at low frequencies, the α-relaxation is ascribed by the authors of Ref. [53] and others to the dynamic glass transition

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[6] This process is not found in all systems investigated.

[7] Do not match this relaxation process with process called β-relaxation which is characteristic for amorphous polymers and other glass forming systems [52].

of the system which is of course related to the thermal glass transition. It is generally accepted that the thermal glass transition is related to the micro-Brownian segmental motion [55] which should be mainly connected in liquid crystalline polymers with reorientations of the polymer backbone and spacer groups. In contradiction to that interpretation of the α-process Williams and coworker [56] assigned that process to reorientations of the dipole moment vector which is transverse to the mesogenic unit. A more detailed discussion of their model is presented in Section 3.2.

The micro-Brownian segmental motion which becomes active above T_g enables another relaxation process – called δ-relaxation – which is characteristic for liquid crystalline polymers and takes places at lower frequencies than the dynamic glass transition. Detailed investigations show that this relaxation process is caused by rotational fluctuations of the dipole component, which is in parallel to mesogenic side group, about its short axis. Although, the exact molecular motional mechanism is not known up to now. Probably it is rather a complicated multistep process than simple 180° flip – flop jumps of the mesogenic unit between liquid crystalline structures. On the basis of this concept it could be also understood that the δ-peak is rather small and corresponds nearly to a Debye-function, because if the motional mechanism is a multistep process a motional averaging can take place [57].

In Figure 6 the temperature dependence of the relaxation rates of the β-, of the α- and of the δ-process is plotted *versus* inverse temperature for sample P13 (see Tab. I). This figure shows that the temperature dependence of β-relaxation is Arrhenius-like whereas the both others have a very complicated one. In general the temperature dependence of the relaxation rate of the α- and of the β-process can not be described by the famous Vogel/Fulcher/Tammann-equation [58]. A more detailed analysis of the dependence of the β-, α-, δ-relaxation processes on chain and mesophase structure will be given in Section 3.3 for a set of liquid crystalline polyacrylates and polymethacrylates.

3.2. Dielectric Behavior of Aligned SCPLCs – Theoretical Predictions and Experimental Results

For all potential applications of SCPLCs which have been discussed in the literature, for instance as active compounds for optical

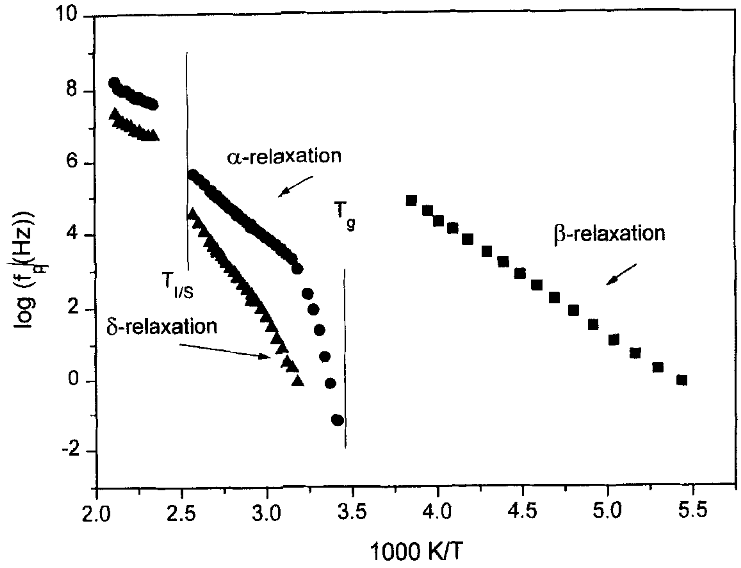

FIGURE 6 Temperature dependence of the relaxation rates of the different processes *vs.* 1000/T for the sample P13 (see Tab. I) ■ β-relaxation, ● α-relaxation, ▲ δ-relaxation.

information storage, optical elements such as Fresnel zone plates or non-linear optical applications, the material has to be aligned. The theory of the dielectric behavior of aligned side chain liquid crystal polymers is based on Maier-Saupe treatment [59] and the Nordio-Rigatti-Segre-theory [60] of dielectric relaxation of nematic low molecular mass liquid crystals. It was developed for uniaxial liquid crystalline phases mainly by Attard and Williams [19, 61 – 64] and has been discussed extensively by Moscicki [20]. For that reason only the main topics should be addressed here.

Starting point is the consideration that each mesogenic unit has two components of its molecular dipole vector longitudinal and transverse to its long axis. Further, one has to bear in mind that dielectric relaxation spectroscopy proofs dipole fluctuations which are in parallel to the outer electric field vector. The orientation of simple liquid crystalline phases like pneumatics can be described by the noematic director [65] which is related to the macroscopic director order parameter S_D:

$$S_D = \langle 3\cos\theta_{n,E} - 1\rangle/2 \qquad (7)$$

where $\theta_{n,E}$ is the angel between the director axis and the direction of the outer measuring field.

Therefore the tensor of the complex dielectric function ε^* must have two main components $\varepsilon^*_{\|}$ and $\varepsilon^*_{\perp}$ (different from zero) which are parallel and perpendicular to the noematic director. Consequently, from a microscopic point of view the dielectric behavior is described (see Eqs. (2) and (3)) by correlation functions of the polarization fluctuations parallel and perpendicular to the noematic director. These can be expressed by four different molecular relaxation modes given by correlation functions of the longitudinal and transverse component of the molecular dipole vector projected parallel and perpendicular to the noematic director. The motional orientation process is described by small step rotational diffusion model. In that semi-macroscopic treatment [62, 63] the measured dielectric behavior comprise different weighted sums of the four underlying relaxation modes depending on macroscopic orientation according to

$$\varepsilon^* = \frac{(1+2S_D)\varepsilon_{\|}}{3} + \frac{2(1-S_D)\varepsilon_{\perp}}{3}. \tag{8}$$

S_D is equal to zero for unaligned materials. It attains a value of 1 for fully parallel and −0.5 for perpendicularly aligned samples. Moreover it follows that the frequency of maximal loss can be shifted by alignment processes. So with regard to an unaligned sample the loss peak is shifted.

As in the case of MLCs [20] a good qualitative agreement was found between the theoretical predictions and the experimental results (see for instance [63, 64]) also for polymeric liquid crystals. But however, when the temperature range of liquid crystalline phases is broad enough, the temperature dependence of the relaxation rate of the low frequency process assigned to dipole fluctuations which are parallel to the director[8] shows a strong curvature in a plot $\log f_{p\|}$ *versus* $1/T$ [66][9] which is analog to the molecular dynamics of glass-forming systems and cannot be explained by a rotational diffusion theory. An appropriate model was developed in [68] which leads to a Vogel/Fulcher/Tammann

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[8] For unaligned material this process is called δ-process (see Section 3.1).

[9] For MCLs that was pointed out by Zeller [67] for the first time.

type of equation [58] depending also on the order parameter S_D. This equation was tested for a set of low molecular mass liquid crystals [69]. But unfortunately, no extensive tests for polymeric systems are known. Furthermore a strong correlation between the temperature dependence of the rates of that relaxation process and that of the α-relaxation (see for instance [14, 16, 23]) has been observed. This will be discussed for a set of liquid crystalline polymethacrylates in Section 3.3 in more detail.

SCPLC can be aligned by the application of an electrical field. The dielectric anisotropy $\Delta\varepsilon_{\text{anis}} = \varepsilon_{\parallel} - \varepsilon_{\perp}$ is mainly determined by the dipolar properties of the mesogenic group. Also the polymer backbone[10] can contribute to $\Delta\varepsilon_{\text{anis}}$ if a chain ordering takes place rather than the mostly unpolar spacer groups. In a simplified version of the Maier-Saupe-theory [70] $\Delta\varepsilon_{\text{anis}}$ by

$$\Delta\varepsilon_{\text{anis}} = \frac{\mu^2}{2k_B T}(1 - 3\cos\Theta_{\mu,D})S_D \tag{9}$$

where $\Theta_{\mu,D}$ is the angle between the dipole moment μ and the director. $\Delta\varepsilon_{\text{anis}}$ can be positive or negative depending on $\Theta_{\mu,D}$.

As a first consequence from this fact follows that the measuring field strength should be low as possible to avoid possible changes of the structure by it.

In principle SCPLC can be aligned by the application of a static electric field above but near the clearing temperature T_c. After a certain time (for polymers several hours) the material should be slowly cooled down through the phase transition. But however, at temperatures above T_g and even more above T_c the molecular mobility is rather high. This means charge transport takes place through the sample which causes an electrohydrodynamical disturbance of the orientation. So in the most cases an AC voltage should be used to align the sample, because the degree of orientation depends on the square of the applied field strength. Moreover it was shown theoretically and experimentally that the kind (homeotropic or planar) of an AC-electric field induced alignment depends on the selected frequency of the applied AC-field. A material with a positive dielectric anisotropy ($\Delta\varepsilon_{\text{anis}} > 0$) will be aligned homeotropic at low frequencies and planar at high

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[10] In general the contribution of the main chain can be assumed as isotropic.

frequencies [62–64]. The kind of the electrically induced alignment changes at a certain critical frequency f_c which is very similar to the isosbestic point well known in UV/VIS-spectroscopy. It can be estimated from a diagram where ε' of a homeotropic, of a planar and of an unaligned sample is plotted *versus* frequency. At f_c all three ε' traces cross. It should be noted that of course f_c depends on temperature. A much deeper discussion of that issue can be found [64] and in the contribution of Gedde in this volume [71].

3.3. Correlation of Relaxational and Structural Properties for Polyacrylates and Polymethacrylates

In the next section relationships between structural and dielectric properties will be discussed for a set of liquid crystalline polyacrylates and polymethacrylates. The discussion is based mainly on own experimental results [72–75, 52]. All samples have been measured in the nominal unaligned state and so for the molecular assignment of the different relaxation processes the scheme developed by Zentel [53] is used.

The chemical structure of the investigated polyacrylates and polymethacrylates is given in Figure 7 and Tables I and II. The mesogenic side groups are derivatives of (*p*-alkoxy-phenyl)-benzoate and of the photochromic azobenzene. To achieve different mesophases the number of the methylene spacer groups, the structure of the mesogenic core and

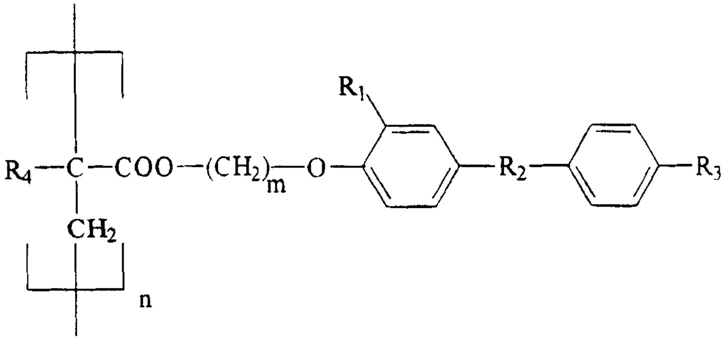

FIGURE 7 Chemical structure of the repeating unit of the polymers studied.

TABLE II Chemical structure, transition temperatures and activation parameters of the β-relaxation of the studied polymers carrying derivatives of azobenzene as mesogenic unit: I, N, S_X means the isotropic, the nematic and the smectic state (X = A, B, C). The low temperature phase frozen at the glass transition temperature is indicated in bold

	R_1	R_2	R_3	R_4	m	T_g $[K]$			$log(f_{\beta\infty}[Hz])$	$E_{A\beta}$ $[kJ/mol]$
A1	H	N = N	OCH_3	CH_3	6	343	S_A/N N/I	365 K 405 K	18.2 ± 0.2	66.8 ± 1
A2	H	N = N	OCF_3	CH_3	2	346	S_A/I	417 K	13.6 ± 0.3	41.6 ± 1.4
A3	H	N = N	OCF_3	CH_3	3	348	S_A/I	395 K	15.7 ± 0.5	51.0 ± 2
A4	H	N = N	OCF_3	CH_3	4	340	S_A/N N/I	369 K 387 K	17.9 ± 0.2	58.9 ± 1
A5	H	N = N	OCF_3	CH_3	5	339	N/S_A S_A/I	395 K 405 K	17.5 ± 0.3	57.9 ± 1
A6	H	N = N	OCF_3	CH_3	6	331	N/S_A S_A/I	363 K 382 K	16.8 ± 0.2	56.0 ± 2

the tail group were varied. Details of the synthesis, the characterization of molecular and mesophase structure can be found in the quoted references.

(a) β-Relaxation

According to [53] the β-relaxation has been assigned to rotational fluctuations of the mesogenic unit around its lengths axis. This interpretation was also supported by own experimental results [72]. It is well known that the temperature dependence of the relaxation rate of the β-relaxation $f_{p\beta}$ can be described by an Arrhenius equation

$$f_{p\beta} = f_{\beta\infty} \exp\left[-\frac{E_{A\beta}}{kT}\right], \tag{10}$$

where $f_{\beta\infty}$ is the preexponential factor and $E_{A\beta}$ is the activation energy. This dependence is also found for the systems given in Tables I and II (see also Fig. 8). In the literature very often a value around 55 kJ/mol is found for $E_{A\beta}$ independent of the spacer length, the tail group of the mesogenic unit or the chemical structure of the main chain. But there are indications that the activation energy of the β-process depends on the actual state of the sample [76].

The study of the materials listed in Tables I and II offer the possibility to look at this problem is a systematic way, because the polymer differ only sightly in their chemical microstructure but have very different mesophases involving molecular orders from the isotropic up to the smectic B state. Figure 8 delivers, that for both systems the temperature dependence of the relaxation rate of the β-relaxation can be described by an Arrhenius law. By fitting of Eq. (10) to the data both the preexponential factor and the activation energy can be estimated. For the systems having phenylbenzoate as mesogenic unit Table I and Figure 9 give that both $\log f_{\beta\infty}$ and $E_{A\beta}$ increase significantly with the order of the mesophase. Details of the chemical structure seem to play a minor role (compare the data for the polymers P4 and P5). Only for the material P1 which has no mesophase $\log f_{\beta\infty}$ is in the order of magnitude which is characteristic for truly activated local motional processes. For all other polymers $\log f_{\beta\infty}$ is significantly higher and cannot be interpreted in physical terms directly. For a liquid crystalline material the mesogenic groups are incorporated in

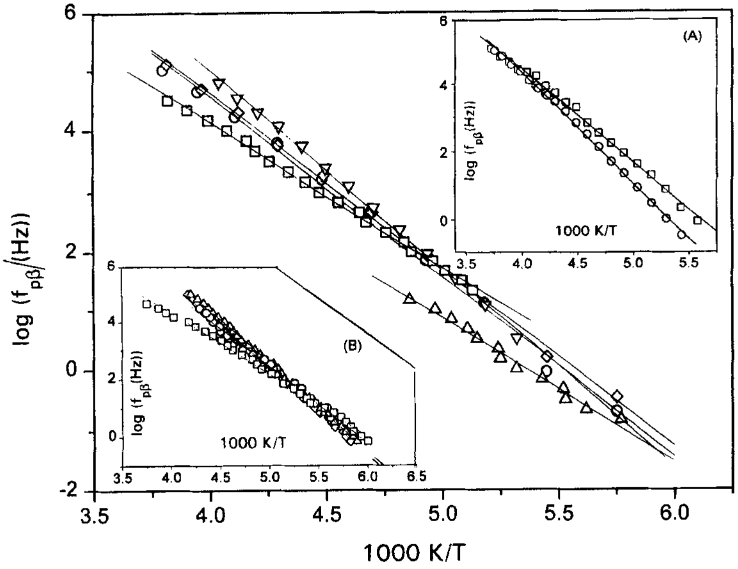

FIGURE 8 $\log f_{p\beta}$ *vs.* 1000/T for the different polymethacrylate samples: △ P1; □ P2; ○ P4; ◇ P5: ▽ P8; inset (A) shows data for the polyacrylates: □ P3; ○ P7; inset (B) shows the data for polymethacrylates having fluorinated azobenzene as mesogenic unit in the side group: □ A2; ○ A3; △ A4; ◇ A5. Lines are fits of the Arrhenius equation to the data (see Tabs. I and II).

mesomorphic environment and a rotational fluctuation of the mesogenic group around its lengths axis can only take place if (i) the liquid crystalline structure is maintained and (ii) the actual mesophasic state has to allow this motional process. This seems to be more complicated for a state with a high liquid crystalline order than for a state with a lower one. As a consequence from this picture arises that the mesogenic units have to fluctuate cooperatively together where the degree of cooperativity depends on the order of the actual state. The high values found for both the preexponential factors and the activation energies can be regarded as an expression for this cooperativity[11]. For more details see [74].

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[11] In a formal way – using the Eyring-equation – the preexponential factor can be splitted up into two contributions: a part which can be regarded as the pefactor for truly activated process and (ii) a second part which corresponds to an activation entropy which increases with the order of the mesophase. Another theoretical treatment of observed result can be found in [77] using a model of cooperative relaxation.

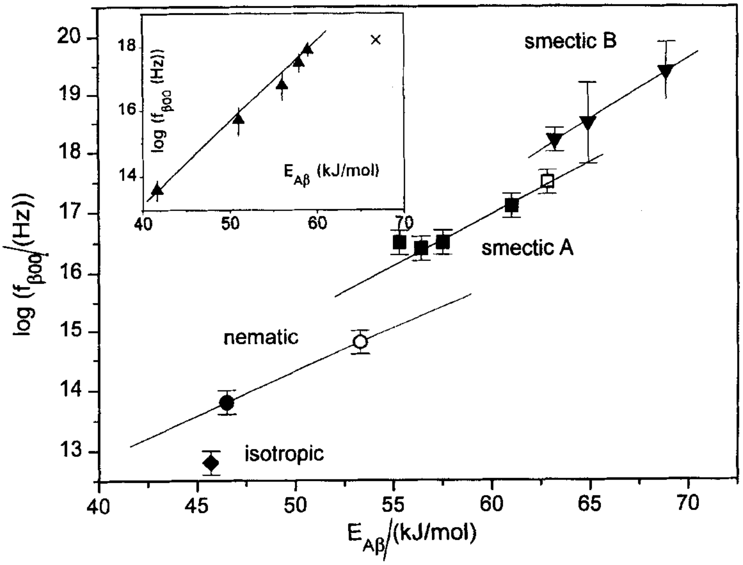

FIGURE 9 log $f_{\beta\infty}$ *vs.* $E_{A\beta}$ for different samples. ◆-isotropic state; ●-nematic state; ■-smectic A state; ▼-smectic B state. Solid symbols represent polymethacrylates whereas open symbols are due to polyacrylates. Lines are linear regressions through the points. The inset shows the data for the polymethacrylates having azobenzene in the side group: × sample A1; ▲ samples A2-A6. In that inset the line is a guide for the eyes.

For the investigated azobenzene containing polymers the behavior of the β-relaxation seems at the first glance more difficult because they have smectic phases and small activation parameters as short spacer lengths (see Tab. I). But although the low temperature phases for the samples A2 and A3 are smectic due to the short spacer lengths the decoupling of the mesogens from the backbone is restricted. This means that the molecular order of that smectic phases is rather low compared with the smectic phases formed by polymers having longer spacers. For that reason the relative low values for the activation parameters can be understood using the concept discussed above. With increasing spacer lengths the decoupling of the mesogenic unit from the main chain is enhanced and the mesogenic moieties in the mesophases are better organized. Consequently the activation parameters for the β-relaxation increase too. For a deeper discussion see [52].

If the discussed model is true, a direct correlation should exist between a structural parameter and a relaxational parameter. For that reason from X-ray measurements the mean lateral distance of mesogens *d* is extracted using the Bragg-equation and plotted *versus* $\log f_{\beta\infty}$ in Figure 10. Although the data show a certain scatter a direct correlation seems to exist between *d* and $\log f_{\beta\infty}$ for all investigated polymethacrylates independent of the type of the mesogenic unit. This nice correlation supports the discussed model that the β-relaxation is rather determined by actual state of the polymeric liquid crystal than by chemical microstructure of the mesogenic unit.

The higher chain flexibility of the polyacrylates compared to the polymethacrylates leads to slightly better ordered mesophases with somewhat lower lateral mesogenic distances for that class of materials. Although the data set for the polyacrylates is limited Figure 10 seems to indicate that the slope of the lateral mesogenic distance *versus* $\log f_{\beta\infty}$ is the same for both classes of main chains. Of course additional investigations are necessary which have to include more polyacrylate samples and also other types of main chains like for instance

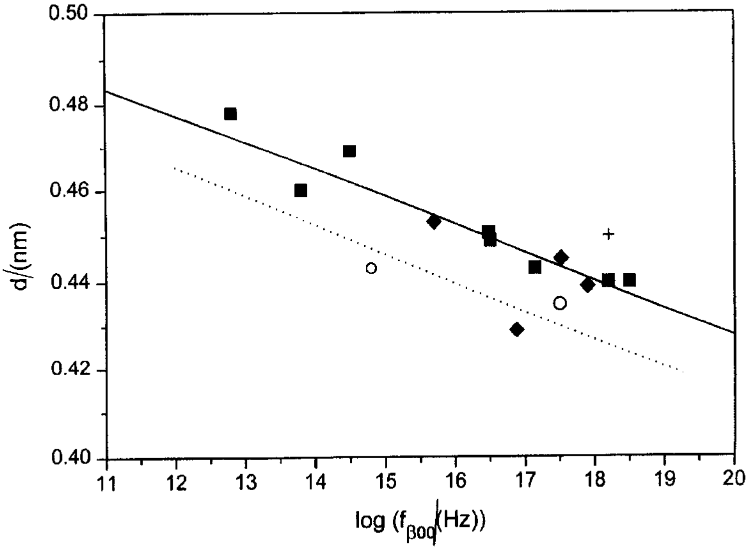

FIGURE 10 Lateral mesogenic distance *d* vs. $\log f_{\beta\infty}$: ■-polymethacrylates with phenylbenzoate in the side group, ◆-polymethacrylates with fluorinated azobenzene in the side group. +polymethacrylate A1. The solid line is a regression through the data points which are due to polymethacrylates. ○-polyacrylates. The dotted line is the parallel shift of the regression line through the data of polyacrylates.

polysiloxanes. Some relevant discussions to this problem can be also found in [78].

(b) α-Relaxation

As is pointed out in Section 3.1 the α-relaxation in side group liquid crystalline polymers is very often related to the dynamic glass transition of the systems [23, 53, 72] which is of course related to the micro-Brownian motion of the chain segments. Own results on SCPLC having phenylbenzoate as mesogenic unit support this model whereas our investigation on polymethacrylates having fluorinated azobenzene as mesogenic moieties gives a different picture. For that reason the discussion concerning the α-relaxation is splitted up in two parts.

Phenylbenzoate Containing Polymers First of all it should be interesting to focus on the question how the onset of liquid crystallinity changes the temperature dependence of the relaxation rare of the α-relaxation in these systems. For that reason in Figure 11 the temperature dependence of the relaxation rate of the α-relaxation $f_{p\alpha}$ for the samples P1 and P11 which have no mesophases is compared to that of the sample P4 which has a smectic low and a nematic high temperature phase. First of all it has to be stated that $\log f_{p\alpha}$ is curved in such an Arrhenius-representation and that it at low temperatures correlates very well to the glass transition temperature estimated from DSC-measurements. This means that the α-process in these systems is at least closely related to the dynamic and thermal glass transition (For the nomenclature see for instance [55]). Secondly, at high temperatures where the sample P4 is in the isotropic state $\log f_{p\alpha}$ for all samples collapses into one curve. Provided that the α-relaxation is due to the dynamic glass transition that means that in the isotropic state all samples have the same dynamic glass transition temperature. With decreasing temperature the temperature dependence of $\log f_{p\alpha}$ for the sample P4 separates from the other ones somewhat below the phase transition temperature from the isotropic to the nematic state. Obviously the change in structure leads to a change in the temperature dependence of $\log f_{p\alpha}$. At the same temperature $\log f_{p\alpha}$ for the liquid crystalline is higher than that for the isotropic materials. And so P4 has also a lower glass

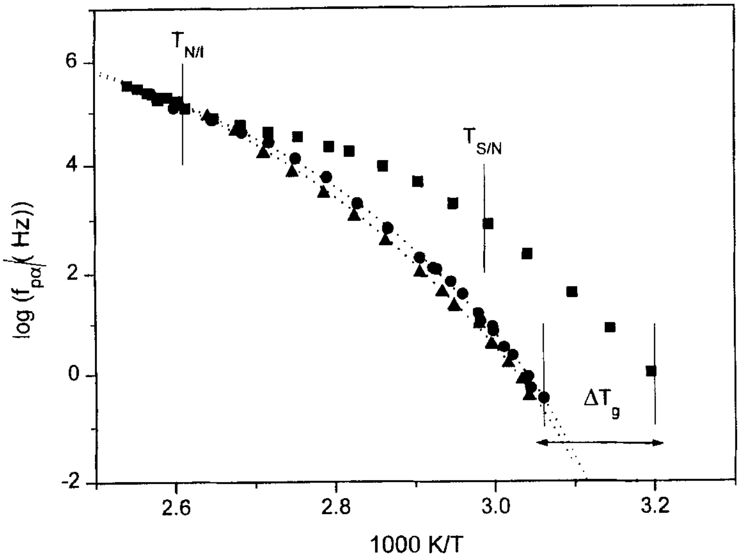

FIGURE 11 Arrhenius plot for the α-relaxation: ■-P4 (liquid crystalline); ●-P1, ▲-P11 (isotropic). The dotted lines are fits of the Vogel/Fulcher/Tammann equation [58] to the data.

transition temperature than the two polymers which have no mesophases.

Because it is known that a structure formation in general leads to an increase of T_g this unusual behavior has to be explained by two competing mechanisms of opposite impact which are in fact structure formation and local demixing[12] [72]. In the isotropic state the mesogenic units are distributed nearly randomly. At the phase transition they are organized in liquid crystalline structures. This process can be regarded as a kind of microphase separation which results in a liquid crystalline structure which is rich in mesogenic units and a remaining microphase rich in backbone segments. Firstly, the glass transition in liquid crystalline polymers has to be assigned to the segmental motion of the polymeric backbones. Secondly, the mesogens are stiff and polar what enhances the glass transition temperature. Taking this two aspects into consideration it follows that the segregation of mesogenic

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[12] The concept of local demixing in PLCs traces back to Lipatov [79].

moieties into liquid crystalline structures decreases the glass transition temperature of the remaining microphase which is rich in backbone segments compared to a corresponding phase which was mixed with mesogenic units.

If that model is true T_g should decrease with increasing spacer lengths because longer spacer enables a better segregation of the mesogenic units into the liquid crystalline structures. For that reason in Figure 12 the temperature dependence of $\log f_{p\alpha}$ is given in dependence on the spacer length. First of all, it has to be stated that again $\log f_{p\alpha}$ at low temperatures compares well to the T_g-values estimated by DSC. Secondly, with increasing spacer length the temperature dependence is spread out to lower temperatures. The same is true for the polyacrylates (see Fig. 13). A more refined discussion can be found in [75].

Azobenzene Containing Polymers Compared to the temperature dependence of $\log f_{p\alpha}$ of the polymethacrylates having phenylbenzoate

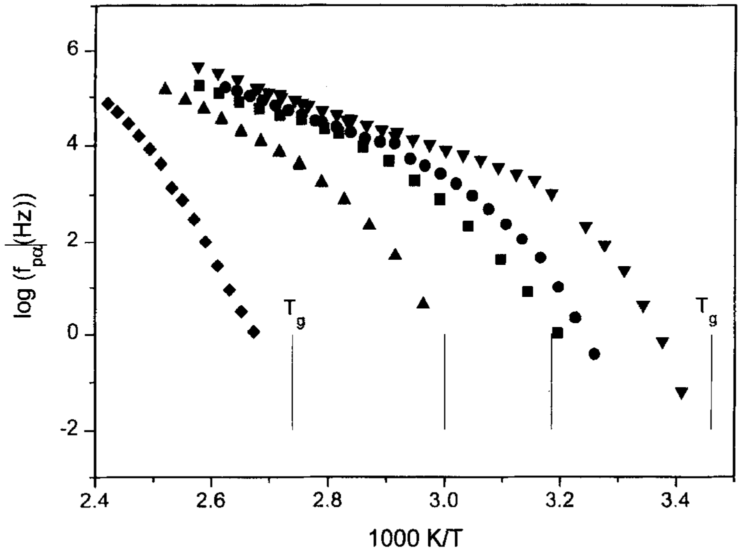

FIGURE 12 Arrhenius plot for the α-relaxation for polymethacrylates. Variation on spacer length: ◆ P14 ($n = 2$); ▲ P2 ($n = 4$); ■ P4 ($n = 6$); ● P12 ($n = 8$); ▼ P13 ($n = 10$). Lines are due to the glass transition temperature estimated by DSC.

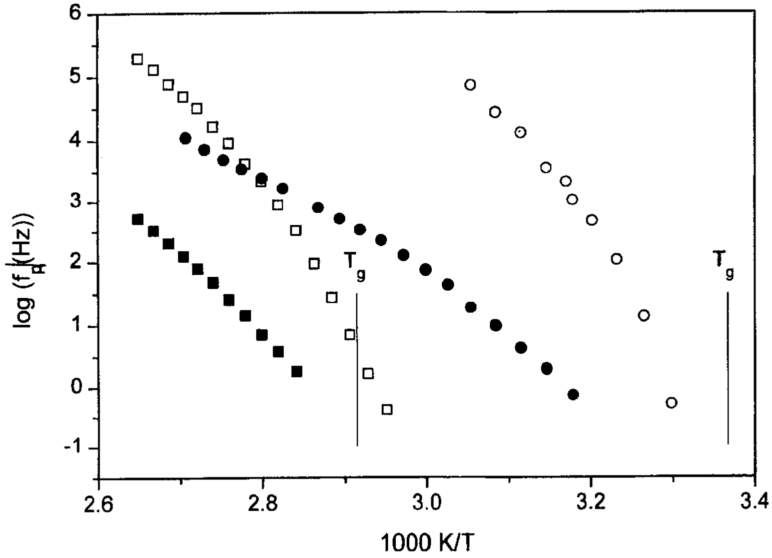

FIGURE 13 Arrhenius plot for the α-(open symbols) and for the δ-relaxation (solid symbols) for the polyacrylates. Variation of spacer length: ■, □-P3 ($n = 2$); ●, ○-P7 ($n = 6$). Lines are due to the glass transition temperature estimated by DSC.

as mesogenic moiety that one for the polymers having fluorinated azobenzene in the side group is quite unusual. As examples for it in Figure 14 $\log f_{p\alpha}$ is plotted *versus* temperature for the samples A4 and A6. Obviously the temperature dependence of the relaxation rate of the α-relaxation has two different regions where the transition between these regions occurs just above the glass transition temperature at a corresponding relaxation rate of around $\log(f_{p,\mathrm{DC}}(\mathrm{Hz})) = 2.5$. That behavior is found for all spacer ($n = 3.6$) and $\log f_{p,\mathrm{DC}}$ seems to be a constant for the discussed system. To analyze the data in a more quantitative manner the Arrhenius equation is fitted to both temperature regions of the α-process in a formal way. The estimated apparent activation energy for both the high and the low temperature regime is listed in the figure captions of Figure 14. It must be stated that the apparent activation energy of the high temperature region is rather high and seems to be characteristic for the dynamic glass transition. Therefore, one can assume that also for these systems the α-relaxation is related to the dynamic glass transition in some way. From the change

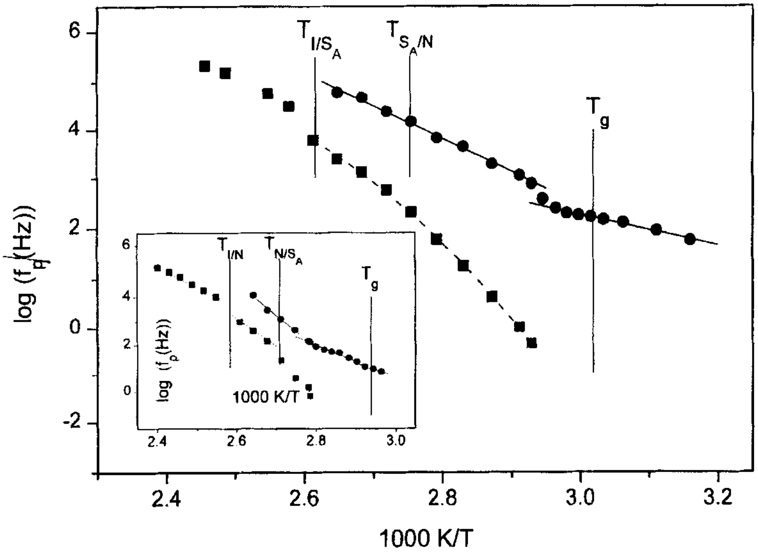

FIGURE 14 Arrhenius plot for the α-relaxation (●) and for the δ-process (■) for polymethacrylates having fluorinated azobenzenes as mesogenic unit in the side group. The main figure gives the data for A6 and the inset displays the values for A4. Solid lines are fits of the Arrhenius equation to the different regions of the α-regions. Estimated activation energies (H means high and L means low temperature process) $n = 4$; $E_{AH} = 253\,\mathrm{kJ/mol}$. $E_{AL} = 136.5\,\mathrm{kJ/mol}$; $n = 6$; $E_{AH} = 131\,\mathrm{kJ/mol}$, $E_{AL} = 57.8\,\mathrm{kJ/mol}$. Dotted lines are guides for the eyes.

in the apparent activation energy one has to conclude that the character of the molecular motion due to the α-relaxation changes. There are at least two speculations for that change in the apparent activation energy. One explanation is that just above T_g an additional phase transition or modification of the liquid crystalline structure takes places which is not visible in the X-ray experiments but changes the molecular mobility of the system. The other explanation starts from confining arguments. It is widely believed that the dynamic glass transition is a cooperative effect where the cooperativity increases with decreasing temperature. It was argued in Section 3.3. (b) that in polymeric liquid crystalline systems the dynamic glass transition is due to microregions which are rich in backbone segments. But the size of these regions is determined also by the liquid crystalline structure. So it might be possible that at some point the degree of the cooperativity of the α-relaxation interferes with the size of the backbone segment rich microphases. But however, additional investigations are required to decide that question.

(c) δ-Relaxation

Figures 13 and 14 present some examples for the temperature dependence of the relaxation rate of the δ-process. It is obvious that $\log f_{p\delta}$ has a curved trace in a plot *versus* inverse temperature. This is found for all investigated samples and means that the temperature dependence of $\log f_{p\delta}$ cannot be described by an activation or at least an apparent activation energy as it is discussed very often in the literature (for an overview see [20]). Moreover at phase transition the temperature dependence of $\log f_{p\delta}$ shows continuous or steplike changes [20].

In the literature it was argued for liquid crystalline polysiloxan [66] that the temperature dependence of $\log f_{p\delta}$ approaches that of $\log f_{p\alpha}$ near T_g. To extend that discussion in Figure 15 the ratio $\log(f_{p\alpha}/f_{p\delta})$ is plotted *versus* temperature for the samples P1, P12 (isotropic) and the sample P4 (liquid crystalline). Such a representation is also justified by

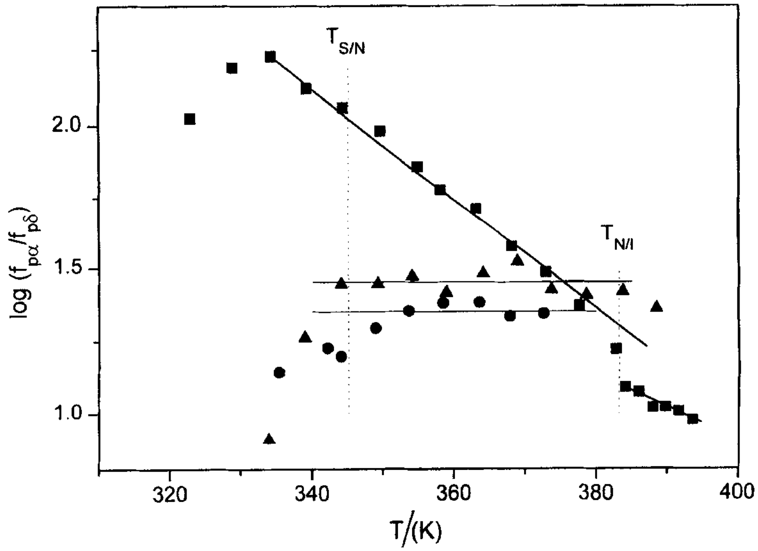

FIGURE 15 $\log(f_{p\alpha}/f_{p\delta})$ *vs.* temperature for the polymers P4 (●), P11 (▲) isotropic and sample P4 (■) liquid crystalline (see [72]). Lines are guides for the eyes.

the following consideration. The δ-relaxation has been assigned to rotational fluctuations of the mesogenic unit around its short axis. Assuming that mechanism, $\log f_{p\delta}$ should be proportional to local friction coefficient which is believed to be proportional to $\log f_{p\alpha}$. As expected for the samples which have no mesophases this ratio is within the framework of the experimental uncertainty constant. Near the thermal glass transition it decreases systematically. This is also found comparing the temperature dependencies of the relaxation rates of the segmental and of the chain dynamics in polymeric melts [80] whereas the molecular reason for it is not clear in the moment.

The liquid crystalline material displays a quite different behavior. In the isotropic state again the discussed ratio is a constant. At the phase transition from the isotropic to a liquid crystalline state it jumps to a higher value and increases further with decreasing temperature. As it found in [66] near T_g $\log(f_{p\alpha}/f_{p\delta})$ decreases and the relaxation processes approach each other.

The increase of $\log(f_{p\alpha}/f_{p\delta})$ with decreasing temperature has been related to the increase of the liquid crystalline order with decreasing temperature by the following consideration. If the δ-relaxation is due to rotational fluctuations of the mesogenic unit around its short axis during such a motional process the mesogenic moiety has to leave a liquid crystalline structure and has to be incorporated into another or back to the same one. Clearly such a process has to be dependent on the molecular order and should be more complicated for highly ordered structure than for a lower ordered one. Furthermore, it could be shown that $\log(f_{p\alpha}/f_{p\delta})$ can be quantitatively linked to a molecular order parameter S_1 [72] by a modified Meier-Saupe theory [81]. For the sample P4 S_1 has been determined and the estimated values agree very well with ones obtained from NMR measurements (see Fig. 16) [72].

Figure 17 compares the discussed ratio $\log(f_{p\alpha}/f_{p\delta})$ for several liquid crystalline polymethacrylates having phenylbenzoates as mesogenic unit but different chemical architecture of the side group like a variation of the spacer length or the tail group. In general a behavior is observed which is quite similar to that of the P4. To compare the different samples the data are plotted in a reduced form *versus* $T-T_g$. A step-like increase of $\log(f_{p\alpha}/f_{p\delta})$ at the transition to the liquid crystalline state and a further increase with decreasing temperature is observed. Clearly the actual behavior depends on the molecular structure which will be discussed in a subsequent paper. Near the thermal glass transition

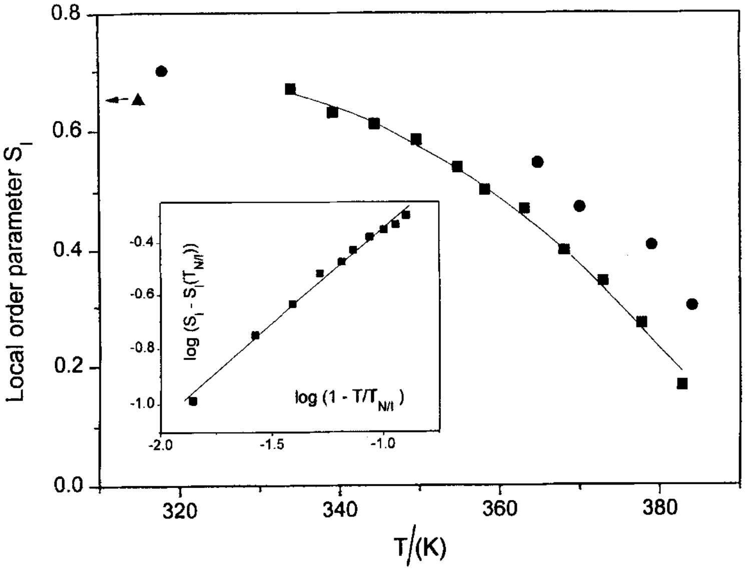

FIGURE 16 Temperature dependence of the local order parameter S_l: ■-estimated from the temperature dependence of the relaxation rates of the α- and the δ-relaxation (see [72]), ●-estimated from NMR measurements [82], ▲-estimated from NMR measurements in the glassy state. The inset shows the power like behavior of S_l near the phase transition.

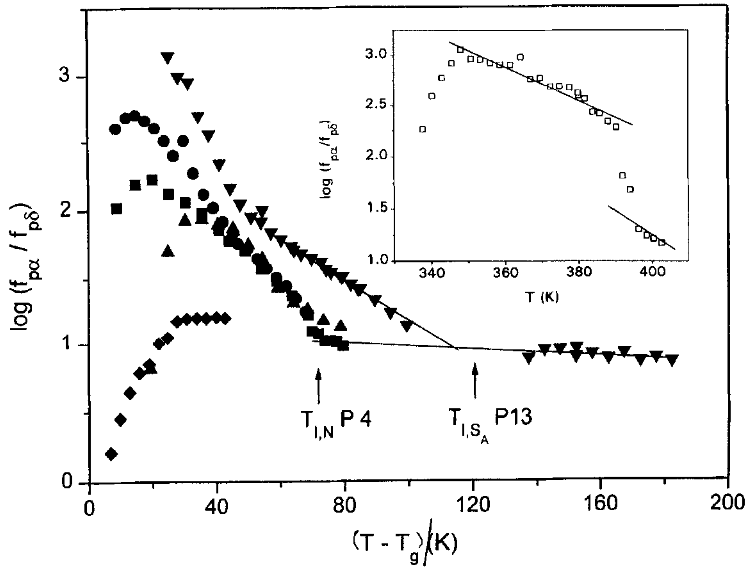

FIGURE 17 log $(f_{p\alpha}/f_{p\delta})$ *versus* $T-T_g$ for different liquid crystalline polymethacrylates: ◆-P14, ▲-P2, ■-P4, ●-P12, ▼-P13. The inset shows data for P8 *versus* temperature. Lines are guides for the eyes.

temperature $\log(f_{p\alpha}/f_{p\delta})$ decreases for all investigated samples. The molecular reason for such a behavior have to be explored.

4. MAIN CHAIN PLCs

Main chain PLCs are widely applied because of their outstanding mechanical properties[13]. So in the most relaxational studies mechanical dynamical spectroscopy is used reflecting the interest in the mechanical properties of this class of material. Systematic studies on the change of molecular dynamics caused by liquid crystallinity are very rare. Moreover nearly all polymers studied were polyesters with the same permanent dipole moment due to the ester carbonyl group. So it seems difficult to draw general conclusions of the dielectric relaxational behavior from that limited set of experimental data and the discussion in the literature is partly controversial. This is also due to the fact that the micromorphology of main chain liquid crystal polymers is quite complicated. So different microdomains which different concentration of the individual constituents exist where the concentration within these microdomains can depend on the thermal history. To illustrate the situation own investigations are presented as an example. For a somewhat extended discussion see for instance [20]. Historically, dielectric investigations on main chain liquid crystal polymers go back to Takase *et al.* [85] and Gedde [6].

Figure 18 shows the dielectric loss of a random copolyester PET/0.6PHB at a fixed frequency *versus* temperature. PET is poly(ethylene terephthalate) and PHB is *p*-hydroxybenzoic acid. In that notation 0.6 is the mole fraction of PHB in the copolymer. It is known that these polymers from liquid crystalline phases for mole fractions of PHB greater than 0.25 [86]. An assignment of the liquid crystalline phases is difficult because of the hierarchical structure of the material. Higher ordered smectic *E* phases are supposed at room temperature some times [87]. As Figure 18 shows the dielectric relaxational behavior of

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[13] Recently it has been also demonstrated that main chain liquid crystalline polymers can be used as active material in light emitting diodes [83] and can also show ferroelectric properties [84].

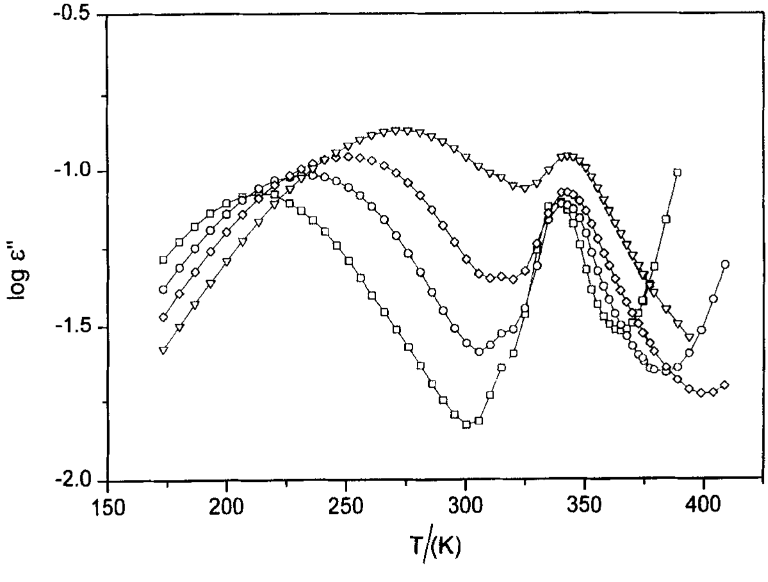

FIGURE 18 log ε'' *vs.* temperature for PET/0.6PHB at different frequencies: □-10 Hz, ○-147 Hz, ◇-10^3 Hz, ▽-10^4 Hz.

such a material is quite complex with two main relaxational regions: the high temperature α-region and the low temperature β-process.

The β-relaxation is quite broad and strong compared to the α-relaxation. This implies that the molecular mechanism for it should involve motions of the polar COO groups rather or in addition to fluctuations of the CH_2 groups proposed by Zachmann [88]. In general it was found that this process shows a close resemblance to the β-relaxation of PET [6, 7] but also units of hydroxybenzoic acid should play a role [7]. The temperature dependence of the relaxation rate of the β-process shows an Arrhenius-like behavior where it was found that the activation parameter depends on thermal treatment of the sample [88].

A closer inspection of the α-transition zone shows that the relaxation is splitted off into two processes (see Fig. 19). At low temperature a relaxation process, called α', with a low intensity can be identified whereas the α-process at higher temperatures is much more pronounced. A similar behavior was found in [6] but with the opposite intensity ratio. The molecular reason of that multiple behavior and the question if both processes are due to molecular movements is discussed controversial in

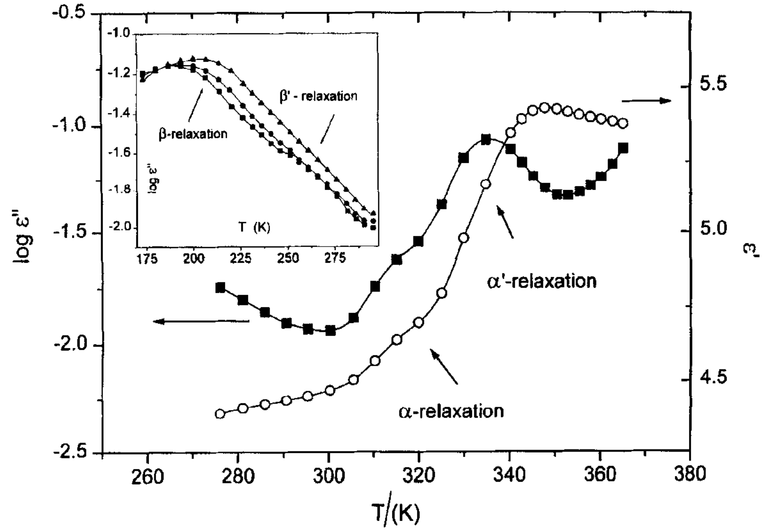

FIGURE 19 log ε'' and ε' *vs.* temperature for PET/0.6PHB in the α-transition region at a frequency of 1 Hz. The inset shows log ε'' *versus* temperature in the β-relaxation region for different frequencies: ■-0.1 Hz, ●-0.215 Hz, ▲-1 Hz.

the literature [6, 7, 89, 91]. One explanation starts from the observation that the micromorphology of PET/xPHB liquid crystals consists in different microdomains. So the two peaks have to be assigned to different PET-rich regions. In [7] it was argued that the α'-peak has to be linked to PET-microdomains which are rich in PHB-segments while the α-peak is due to PET-rich islands. It follows also from such an argumentation that if such a model is true also the β-relaxation should have two contributions. Taking isochronal scans of ε'' *versus* temperature at low frequencies in the β-relaxation region it becomes clear that also the β-process has two peaks (see inset of Fig. 19). That observation supports the picture discussed above although additional investigations are necessary. This requirement is supported by Figure 20 where the dielectric loss for a sample PET/0.5PHB is plotted *versus* temperature [90]. In contrast to Figure 18 both relaxation peaks in the α-zone have comparable intensities. It should be also noted that the sequential distribution of comonomers in the main chain copolyester is not stable at high temperatures (transester reactions). That process and so the thermal history at high temperatures can also influence the dielectric data, particularly the dielectric α-relaxation.

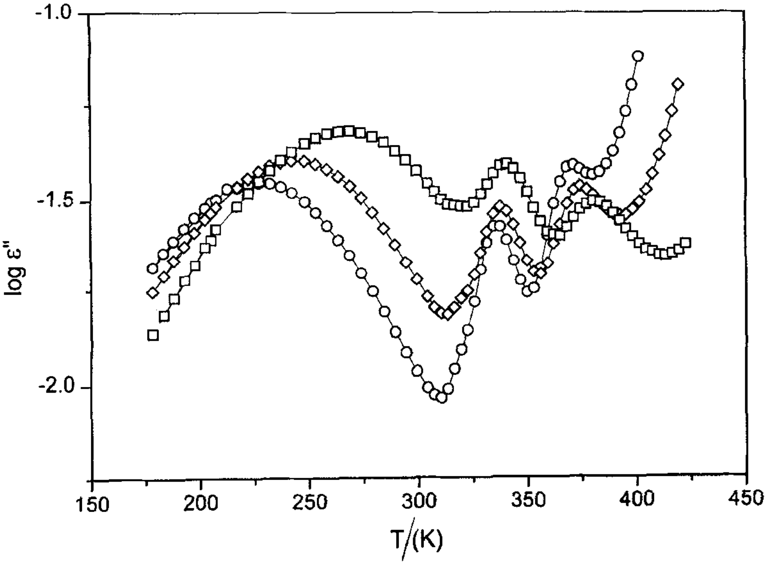

FIGURE 20 log ε'' *vs.* temperature for PET/0.5PHB at different frequencies: ○-147 Hz, ◇-10^3 Hz, □-10^4 Hz [90].

The most striking fact in the behaviour of PET/xPHB liquid crystal is that the glass transition temperature decreases on increasing PHB units and that the value is below the T_g of pure amorphous PET. This observation is also confirmed by dielectric investigations. Our explanation of this unusual behavior (unusual because the introduction of stiff chain units should increase T_g) starts from consideration that the stiff PHB-units can prevent the system from the densest packing otherwise possible in the system. This means that copolymerization introduces an additional amount of free volume which causes plasticizition of the system and lowers the glass transition. So the value of the glass transition temperature can be understood as the result of the competition of increasing chain stiffness and introduction of additional free volume both due to copolymerization.

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