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Influence of the Mesophase Structure on the β-Relaxation in Comb-like Polymethacrylates

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ABSTRACT: Broad-band dielectric spectroscopy in the frequency range from 10^{-2} to 10^6 Hz and in a temperature range from 170 to 430 K is employed to study the dependence of the rotation of the mesogenic unit around its long axis (β-relaxation) on the actual liquid crystalline mesophase in comb-like polymethacrylates. As mesogenic units, derivatives of *p*-alkoxyphenyl benzoate are used where different mesophases were achieved by small variation of the mesogenic structure and the spacer length. For all samples, the temperature dependence of the relaxation rate of β-relaxation can be described by an Arrhenius equation whereas both the preexponential factor and the activation energy increase significantly with the order of the mesophase. The width of the dielectric β-peak decreases with increasing order of the liquid crystalline phase. From these experimental results it is concluded that β-relaxation in these polymers is a cooperative relaxation process whereas the cooperativity increases with the order of the mesophase.

Introduction

There is considerable interest in the properties of comb-like polymers, which have calamitic mesogens in the side group, because they can be used as material for optical data storage, holographic applications, and electrooptical devices. For an understanding of the phase behavior of these systems, knowledge about the dynamics is necessary. Dielectric relaxation spectroscopy has been proven very suitable for these investigations.[1−10]

Due to the different possibilities for dipole reorientation in these systems, several dielectric-active relaxation processes can be observed; Zentel et al.[2] have set up an appropriate nomenclature. In order of increasing temperature, the rotational fluctuation of the tail groups and of the spacer groups denotes as γ_1 and γ_2 processes are observed. These processes are followed by a β-relaxation that was assigned to the rotational fluctuation of the mesogenic group around its long axis. This interpretation was further supported by a study on a set of combined main-chain side-group polymers[7] and by a dielectric investigation on comb-like polymethacrylates with laterally substituted mesogens.[11] The relaxation rate of both the γ-relaxations and the β-relaxation shows an Arrhenius-like dependence on temperature. The relaxation rate of the next (with increasing temperature) observed relaxation process, called α-relaxation, shows a curved dependence on $1/T$. Because this temperature dependence agrees well with the glass trnasition temperature T_g at low frequencies, α-relaxation is ascribed to the dynamic glass transition of the system.[2] In polymers having comb-like side groups, an additional process, a so-called δ-relaxation, takes place at higher temperatures than the α-relaxation (or equivalently at lower frequencies). Detailed investigations show that this relaxation process is caused by rotational fluctuations of the dipole component, which is parallel to the mesogenic side group about the local director axis.[3,4,10]

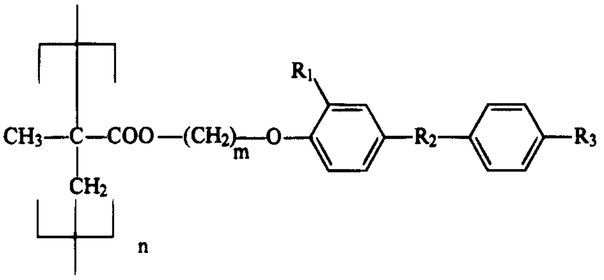

Figure 1. Structure of the repeating unit of the polymers studied.

Much attention was paid to α- and the δ-relaxation. Williams and co-workers investigated the influence of different orientational states on both relaxation processes[8−10] and developed a theoretical approach for the interpretation of δ-relaxation.[9] Much less is known about β-relaxation. This relaxation process might be responsible for the long-term stability of written-in information. In the literature, for the activation energy for this relaxation process a value of approximately 55 kJ/mol was reported that was independent of the spacer length, the tail group of the mesogenic unit, or the chemical structure of the main chain. This seems to indicate that chemical structure plays a minor role for β-relaxation. Recently, Gedde et al.[6] found different values for the activation energy of β-relaxation in a smectic mesophase and in the crystalline state. More recently, our own investigations[11] showed that the activation parameters for this relaxation process are very different for the isotropic state and for a smectic A mesophase. In this contribution we want to focus on the dependence of the β-relaxation on the actual mesophase structure. For that reason, polymethacrylates with comb-like mesogenic side groups with slightly different chemical structure but very different mesophases were investigated by means of dielectric relaxation spectroscopy.

Experimental Section

The chemical structure of the investigated polymethacrylates is given in Figure 1 and Table 1. The mesogenic side groups are derivatives of *p*-alkoxyphenyl benzoate. To achieve

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Table 1. Chemical Structure and Transition Temperatures of the Studied Polymers

code	R_1	R_2	R_3	*m*	T_g (K)	phase sequence^a phase	phase sequence^a temp (K)	ref
P1	OCH_3	CO(O)	OCH_3	6	322	I	322	12
P2	H	CO(O)	OCH_3	4	318	N/I	377	14
P3	H	CO(O)	OCH_3	6	314	S_A/N	345	12
						N/I	383	
P4	H	(O)OC	OCH_3	6	311	S_A/I	370	13
P5	H	(O)OC	OC_4H_9	10	304	S_B/S_A	318	13
						S_A/I	394	

^{a} I, isotropic state; N, nematic mesophase; S, smectic A mesophase; S_B, smectic B mesophase.

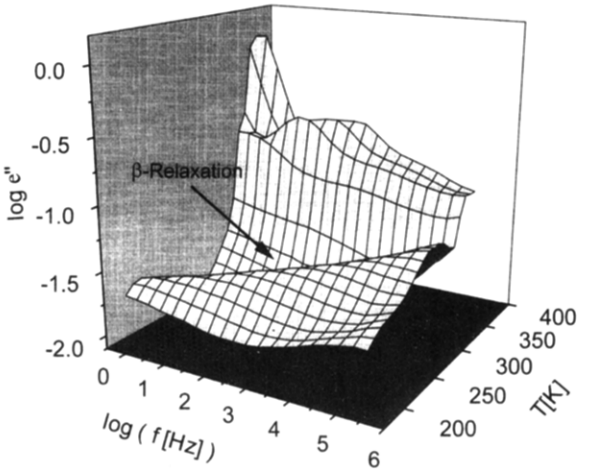

Figure 2. log ϵ'' vs temperature and logarithm of frequency for sample P5.

different mesophases, the number of the methylene spacer groups and the tail group was varied. In one case, the hydrogen in the meta position of the benzoate ring was substituted by a methoxy group. Furthermore, some polymers were studied where the ester group between the aromatic rings were turned. The details of the synthesis and the chemical characterization can be found in the references quoted in Table 1. The thermal behavior was determined by DSC, and the phase characterization was done by X-ray techniques. The low-temperature mesophases that are frozen in at T_g range with increasing order from the disordered isotropic over nematic and smectic A phases to the smectic B state.

For the dielectric measurements, the samples were pressed between two gold-plated stainless steel brass electrodes (diameter 20 mm) at a temperature of 423 K. The spacing of the electrodes of 50 ± 1 μm was maintained by fused silica fibers. The complex dielectric permittivity

$$\epsilon'(f) = \epsilon'(f) - i\epsilon''(f) \qquad (1)$$

(where *f* is the frequency, ϵ' is the real part, ϵ'' is the imaginary part, and $i = -1^{1/2}$) was measured in a frequency range from 10^{-2} to 10^6 Hz by a Schlumberger frequency–response analyzer FRA 1260 interfaced to a buffer amplifier of variable gain[15] (Chelsea Dielectric Interface). The temperature of the sample was varied from 170 to 430 K by a custom-made nitrogen gas jet heating system with a resolution of ±0.02 K. All samples were nominal unaligned.

Results and Discussion

Figure 2 shows the dielectric loss ϵ'' vs temperature and logarithm of frequency for sample P5. According to the classification outlined by Zentel et al.[2], $\gamma_{1,2}$-, β-, α-, and δ-relaxation processes can be detected. In this contribution, we want to concentrate only on the β-relaxation. The other relaxation processes will be discussed in a subsequent paper.

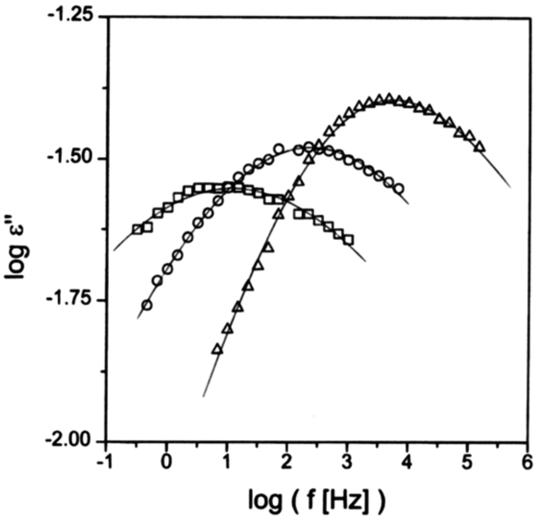

Figure 3. Fit of the HN function to the β-relaxation of sample P5: (□) $T = 192.8$ K, $\beta = 0.236$, $\beta^*\gamma = 0.2$, $\Delta\epsilon = 0.326$, and log $f_o = 0.599$; (○) $T = 207.5$ K, $\beta = 0.268$, $\beta^*\gamma = 0.2$, $\Delta\epsilon = 0.323$, and log $f_o = 2.177$; (△) $T = 227.3$ K, $\beta = 0.357$, $\beta^*\gamma = 0.2$, $\Delta\epsilon = 0.362$, and log $f_o = 2.951$.

To determine the relaxation rate at maximal loss f_p for β-relaxation, the model function of Havriliak and Negami (HN function)[16] is fitted to the isothermal data.[17] The HN function is given by

$$\epsilon'(f) - \epsilon_\infty = \frac{\Delta\epsilon}{(1 + (if/f_o)^\beta)^\gamma} \qquad (2)$$

with the HN parameters $\Delta\epsilon$, intensity; f_o, characteristic frequency, which is nearly equal to the peak frequency f_p; and $\epsilon_\infty = \epsilon'(f)$ for $f \gg f_p$. Here, β and γ denote fractional shape parameters ($0 < \beta, \beta^*\gamma \le 1$). Some examples for the fits of the HN function to the data are given in Figure 3. For sample P1, the β-peak is very broad and weak. In that case, temperature-dependent scans at fixed frequency were constructed from the isothermal measurements. From these plots, the temperature of maximal loss was taken at the selected frequency. For all samples, the temperature dependence of the relaxation rate $f_{p\beta}$ can be described by an Arrhenius equation

$$f_{p\beta} = f_{\beta\infty} \exp\left[-\frac{E_{A\beta}}{kT}\right] \qquad (3)$$

where $f_{\beta\infty}$ is the preexponential factor and $E_{A\beta}$ is the activation energy. The quality of the fits is demonstrated by Figure 4. In Table 2, log $f_{\beta\infty}$ and $E_{A\beta}$ are summarized and compared with the low-temperature mesophase structure which is frozen in at T_g. Several statements can be drawn from this comparison. First, only for the polymer P1 (no mesophases) is the preexponential factor $f_{\beta\infty}$ in the order of magnitude of 10^{13} Hz that is characteristic for truly activated, local motional processes. For all other polymers that show a mesophase sequence, $f_{\beta\infty}$ is significantly higher. Second, the activation parameter seems to be independent of the details of the actual chemical structure. For instance, it does not play a role whether the ester group between the aromatic rings is turned or not (compare the values for P3 and P4). Third, with increasing order of the mesophase, both $f_{\beta\infty}$ and $E_{A\beta}$ increase systematically.

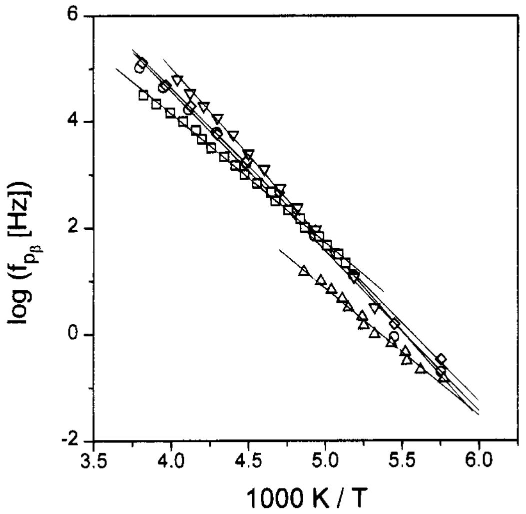

Figure 4. log $f_{p\beta}$ vs 1000/T for the different samples: (△) P1; (□) P2; (○) P3; (◇) P4; (▽) P5. Lines are fits of the Arrhenius equation to the data (see Table 2).

Table 2. Low-Temperature Mesophase and Activation Parameters of the β-Relaxation Frozen in at the Glass Transition Temperature T_g

code	low-temp phase	log($f_{\beta\infty}$) [Hz]	$E_{A\beta}$ (kJ/mol)
P1	isotropic	12.8 ± 0.2	45.7 ± 1.6
P2	nematic	13.8 ± 0.2	46.5 ± 1
P3	smectic A	16.5 ± 0.2	57.5 ± 1.4
P4	smectic A	16.4 ± 0.2	56.4 ± 1
P5	smectic B	18.2 ± 0.2	63.2 ± 1

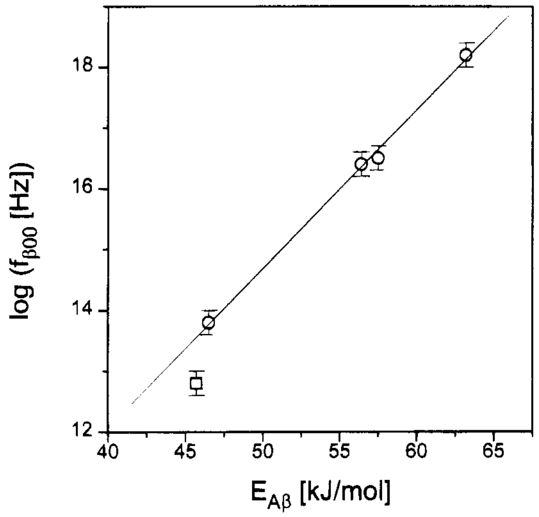

Figure 5. log $f_{\infty\beta}$ vs $E_{A\beta}$ for the different samples: (○) samples P2–P5, showing mesophases; (□) point for the sample P1 (no mesophases). solid line, regression line for the points of the samples P2–P5.

In Figure 5 log $f_{\beta\infty}$ is plotted vs $E_{A\beta}$. For the samples having mesophases, both quantities show a direct correlation. This is an expression of the well-known compensation law.[18,19] At present there is no generally accepted theoretical interpretation of this compensation law, but it seems clear that the physical reason for such a law is directly related to the cooperativity of the underlying processes.[18] This point of view is supported by the fact that the point for sample P1, which shows no mesophases, lies in the frame of the experimental uncertainties below the correlation line. This is expected because in that sample β-relaxation should be noncooperative. So from all observations one has to conclude that the rotation of the mesogenic unit in liquid crystalline side-group polymers is likely not a local motional process. Rather, as the experimental results show, β-relaxation in comb-like liquid crystalline polymers is controlled by both the kind of the mesophase and the local order within a liquid crystalline structure.

Recently, geometric models of isolated side groups were simulated semiempirically in a force field approximation,[12] and the results of these simulations were directly compared to the dielectric experiments.[11] This comparison shows that on the one hand the dielectric relaxation strength seems to be directly related to the extent that a torsional fluctuation of an isolated mesogenic unit around its long axis can take place in principle. On the other hand, the calculated internal activation barriers are much lower than the estimated activation energies. These results fit well in the above developed picture that the actual mesophase structure controls β-relaxation to a great extent.

From a more molecular point of view, in a liquid crystalline material the mesogenic units are incorporated in a mesomorphic environment. A rotational fluctuation of a selected mesogenic unit around its long axis must occur in such a way that the liquid crystalline structure is maintained. Moreover, the quoted model calculations indicated[12] that the rotational fluctuation is likely not a in-line motion. Probably it corresponds to a movement of the mesogenic unit on the surface of a cone. From that considerations it becomes clear that in a well-organized, well-ordered structure such a rotational fluctuation of a mesogenic unit around its long axis is more complicated than in a structure that is not so well organized. In a well-ordered structure, such a process seems to be possible only if mesogenic units move cooperatively together. It is obvious that such a cooperative movement of several mesogenic units should have a higher activation energy than a local one. Because the degree of cooperativity should be dependent on the order of the mesophase, the activation energy should increase with increasing order of the mesophase; exactly what is observed in the dielectric experiments.

Comparison of β-relaxation in the investigated liquid crystalline polymethacrylates with the resolved β-relaxation in poly(n-alkyl methacrylate)s[20] (ester group motion close to the main chain) shows that the β-process in poly(n-alkyl methacrylate)s is much slower than the β-relaxation for the liquid crystalline polymers. This indicates that β-relaxation in poly(n-alkyl methacrylate)s is closely coupled to the main-chain motion. This point of view is supported by a recent NMR study on poly(ethyl methacrylate)[21] and by a dielectric study on several poly(n-alkyl methacrylate)s in a frequency range from 10^{-4} to 10^9 Hz.[22] In liquid crystalline systems, the rotation of the mesogenic unit around its long axis is probably more decoupled from the motion of the polymeric backbone than in conventional poly(n-alkyl methacrylate).

In Figure 6, the dielectric loss in the β-relaxation region reduced to the maximal value of the β-relaxation is plotted vs a reduced temperature scale at a fixed frequency of 1 kHz for the different samples. The width of the β-peak decreases with increasing order of the mesophase. Normally the width of a β-process is attributed to a distribution of relaxation times due to a distribution of molecular environments of the moving unit. Adopting this point of view, the width of a distribution of different environments in a highly ordered mesophase should be much smaller than in a less ordered one. So the analysis of the shape of the β-peak

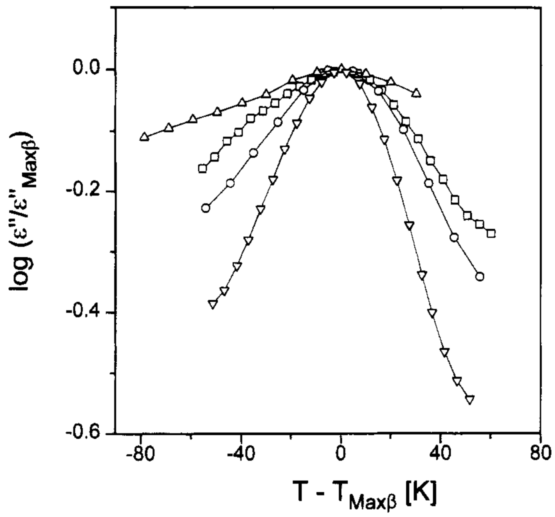

Figure 6. ϵ'' in the β-relaxation region reduced to the maximum value of the β-relaxation at a fixed frequency of 1000 Hz vs temperature minus $T_{\max,\beta}$, whereas $T_{\max,\beta}$ is the temperature at the maximum of the β-peak at 1000 Hz: (△) P1; (□) P2; (○) P3; (▽) P5.

provides additional support that the β-relaxations in liquid crystalline comb-like polymethacrylates is controlled mainly by the actual mesophase.

In conclusion, we have shown by means of dielectric relaxation spectroscopy that the so-called β-relaxation in liquid crystalline comb-like polymers, due to the rotational fluctuation of the mesogenic unit around its long axis, is mainly influenced by the order of the actual mesophase. Both the activation parameter (preexponential factor and activation energy) and the shape of the dielectric β-peak show a significant dependence on the kind and on the order of the mesophase. From the experimental results, we state that β-relaxation is a cooperative process whereas the cooperativity increases with the order of the mesophase.

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