which has been seen with water.[3,4]

Discussion

It is clear that the lack of dependence of the γ-relaxation of PTFE on the presence of absorbed chemicals does not represent a general pattern. The behavior of isooctane in LDPE is similar to that of perfluorocarbons, Freons, carbon tetrachloride, or chloroform in PTFE. In all of these cases, the weight gain at saturation is about 8% or less. Toluene and *n*-hexane interact more favorably with LDPE and are absorbed more strongly. These compounds reduce the strength of the γ-relaxation even at low concentrations. Actually, the incremental effect of toluene is smaller above 8–10%. Unlike water or methanol in nylon, they are not antiplasticizers. Clearly, the local mode relaxation in polymers of ethylene is not entirely intramolecular. It does depend on the composition of the environment of the polymethylene sequences in the amorphous phase.

In nylon, the γ-relaxation can be suppressed by compounds such as acetic acid which are not antiplasticizers and presumably do not have the same ability as water to form bridges between amide groups. While this relaxation seems to be similar to the γ-relaxation in polyethylene and is thought to reflect local motions in polymethylene sequences, its dielectric activity suggests some involvement of the polar amide groups. This is supported by the fact that it has been observed in nylon 3 and nylon 4 which contain sequences of only two and three methylenes, respectively.[7] A weight gain of 27.4% acetic acid corresponds to about one molecule of acetic acid per amide group in the amorphous regions, assuming about 50% crystallinity. If the acid molecules are bonded firmly to the amide groups at low temperatures, they may well inhibit local chain motions.

It is interesting to find that toluene lowers the temperature of the β-relaxation in LDPE and EPDM in the same way. In EPDM, the β-relaxation clearly has the properties of the glass transition.[8] This is reflected in the mechanical properties and in the increments in the heat capacity and the coefficient of thermal expansion. The present data add weight to the view that the β-relaxation is the glass transition in polyethylene.[9] Support is also found in the blends of LDPE and EPDM.[6] Increasing crystallinity broadens the β-relaxation and shifts it to higher temperatures. The data in Figure 5 indicate that this effect is largely overcome by the sorption of toluene.

Attention is also directed to the recent studies of Popli and co-workers,[10] who concluded that the β-relaxation in polyethylene is associated with chain units in the interfacial regions between crystalline and amorphous domains.

This work combined with the earlier study on PTFE[1] shows that there can be considerable variation in the effect of absorbed chemicals on the local mode relaxations in polymers. In several cases, the strength of the relaxation is reduced, indicating that the corresponding molecular motion is at least partially inhibited. This may reflect any of several kinds of interactions between the small molecules and the polymer. It is generally found that the glass transition or a similar relaxation attributed to the motion of longer chain segments in the amorphous regions is shifted to lower temperatures, frequently by a large amount.

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Dielectric Relaxation of Liquid Crystalline Polyacrylates and Polymethacrylates

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ABSTRACT: A series of liquid crystalline polyacrylates and polymethacrylates was studied by frequency- and temperature-dependent dielectric measurements. Depending on the molecular structure, between two and five different relaxation processes were observed. Three of them are active below the glass transition. They can be attributed to reorientations of dipoles located at the center of the mesogenic group (β-relaxation), at the ends of the spacer group (γ_1-relaxation), and at the end group (γ_2-relaxation). At the glass transition the centers of gravity of the mesogenic groups and the polymer main chain become mobile. Dipole reorientations associated with this motion contribute to the dielectric relaxation (α-relaxation). At higher temperatures the reorientation of the long axis of the mesogenic groups can be observed (δ-relaxation). For the polyacrylates it passes continuously through all phases; in the case of the polymethacrylates it sets in together with a phase transition.

Introduction

Polymeric liquid crystals are complex systems,[1-3] which combine the properties of polymers with those of liquid crystals.[4] For an understanding of the thermal behavior of these systems investigations on the molecular dynamics are necessary.[5-10] Dielectric relaxation measurements are a suitable method for these investigations.[11] The various dipole moments in the molecule act as probes for motions in all its parts. Measurements can be performed over a large frequency and temperature range. This is important because different relaxation processes may become active. One can expect the occurrence of relaxations of local

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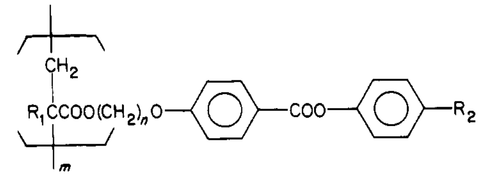
Table I
Phase Behavior of Polymers 1-8 with General Structure



sample no.	R_1	n	R_2	phase transitions[a]/°C
1	H	2	OCH_3	g 62 n 116 i
2	H	6	OCH_3	g 35 S_A 97 n 123 i
3	H	2	CN	g 75 n 110 i
4	H	6	CN	g 33 n 133 i
5	CH_3	2	OCH_3	g 97 n 120 i
6	CH_3	6	OCH_3	g 47 n/s 74 n 111 i
7	CH_3	2	$O(CH_2)_3CH_3$	(g 137)S_A 163 i
8	CH_3	6	$O(CH_2)_3CH_3$	g 39 S_A 109 n 114 i

[a] g: glassy liquid crystal; S_A: smectic A; n: nematic; i: isotropic; n/s: supercooled nematic phase with differing amount of crystalline or smectic phase.

character and also complex relaxation processes such as the dynamic glass process[11] and reorientational jumps of the long axes of the mesogenic groups.[12]

First dielectric relaxation measurements on liquid crystalline polymers were published quite recently.[10] They were performed for one acrylic and one methacrylic polymer and limited to a small temperature region above the glass transition temperature. For both polymers one strong relaxation process was observed, which was attributed to a reorientation of the long axes of the mesogenic group.

In the following we describe the results of dielectric relaxation measurements on a series of eight different liquid crystalline polymers in the temperature range from −150 to +150 °C and in a frequency range from 10^2 to 10^7 Hz. Two of the polymers were also studied by ESR and ^2H NMR experiments reported elsewhere.[6,13]

Experimental Section

The capacitor used for the measurements consisted of two gold-covered plates. A Teflon ring was fixed to the lower plate to prevent an outflow of the sample above the glass transition temperature. The Teflon ring also acted as a distance holder for the capacitor plates (0.5-mm distance). During the measurements the capacitor was placed in a metal vessel which could be cooled or heated. Samples were prepared from the melt directly on the lower capacitor plate.

The measurements were performed with a Schering bridge (10^2–5×10^3 Hz) and a Q-meter (10^4–10^7 Hz). The experimental set-up for the bridge measurements[11] consisted of a generator (Hewlett-Packard, type 203 A), a four-capacitance Schering bridge with "Wagner Hilfszweig" (Tettex AG, type 2801), an electrometer (Keithley, type 604), a selective amplifier (Krohn-Hite, type 3342), and an oscilloscope.

The values obtained by a Q-meter[11,14] (Hewlett-Packard, Model 4342 A) had to be corrected. In the frequency range 10^4–10^6 Hz there is a contribution by the earth capacities leading to an apparent increase of the capacitance. The earth capacities were determined by a comparison with bridge measurements. They turned out to be constant (46.0 ± 0.2 pF, $\tan \delta < 10^{-4}$) and were subtracted. For frequencies higher than 10^6 Hz additional corrections are necessary, which were performed as proposed by Scott et al.[14]

Results

A series of polyacrylates[3] (molecular weights between 18 000 and 43 000) and polymethacrylates[3,15,16] (molecular weights above 100 000) was used for this investigation. The phase behavior of the different polymers is specified in Table I. Phase transition temperatures were determined by differential scanning calorimetry. The type of mesophase was derived from the textures observed in the optical microscope and from the X-ray patterns.[17]

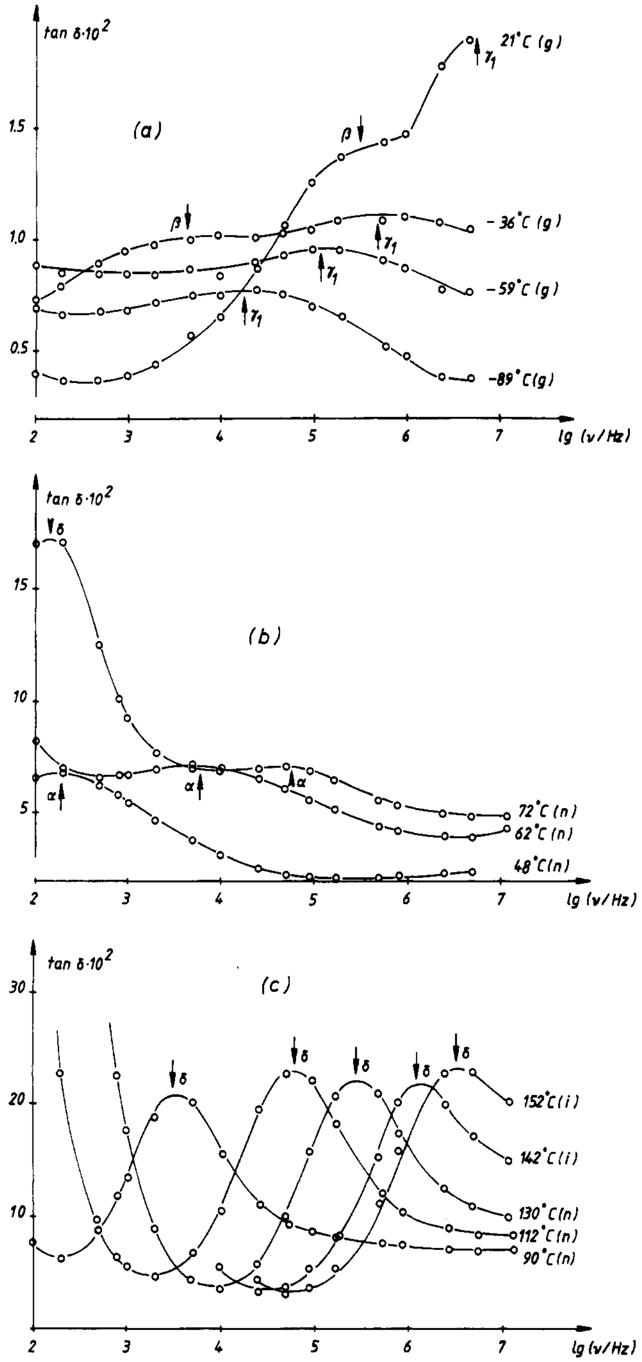


Figure 1. Frequency dependence of dielectric loss tangent measured at different temperatures for sample 4 (spacer length $n = 6$; end group: CN): (a) temperature range of β- and γ_1-relaxation (b) temperature range of α-relaxation, (c) temperature range of δ-relaxation.

For these polymers several local relaxations were found below the glass transition temperature T_g depending on the side-group structure. The relaxation processes observed above T_g depend upon the structure of the polymer main chain.

Liquid Crystalline Polyacrylates. Typical results for the group of polyacrylates 1–4 are shown in Figures 1 and 2 (polymer 4) and 3 (polymer 1). The plots give the frequency dependence of the loss tangent at different temperatures. For polymer 1 one symmetrical relaxation process is observed below the glass transition temperature

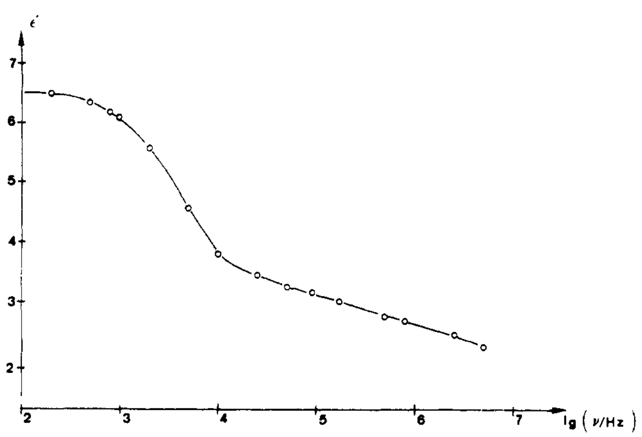


Figure 2. Real part of dielectric constant $\epsilon'(\nu)$ measured at 90 °C for sample 4, showing the δ-relaxation.

(see Figure 3a), which will be called β-relaxation in the following. For polymer 4 in the same temperature range a broad structured relaxation is found (see Figure 1a). It can be separated into one component corresponding to the β-relaxation of polymer 1 and a second relaxation process at higher frequencies, which will be called the γ_1-process.

Both polymers show two relaxation processes above the static glass transition temperature (see Figures 1b,c and 3b,c). The relaxation process at lower temperatures (Figures 1b and 3b) becomes observable approximately 10 °C above T_g at the lowest frequencies and is of similar intensity for all polymers. We shall call it α-relaxation. The relaxation process at higher temperatures (see Figures 1c and 3c) has a very high intensity for polymers with strong dipole moments parallel to the long axes of the mesogenic groups (polymers 3 and 4). For polymers with a weak dipole moment parallel to the long axis of the mesogenic group (polymers 1 and 2) this relaxation process is weak too. It will be called δ-relaxation and is active in the isotropic, nematic, and smectic phases (for polymer 2) and only little affected by the phase transitions. For the samples 1, 2, and 4 the α- and δ-relaxation show up separately. For polymer 3, which has a high T_g value, they show a strong overlap.

Liquid Crystalline Polymethacrylates. Figures 4 and 5 show results which are typical for the investigated polymethacrylates. The loss tangents given in Figure 4 were measured for sample 8 above T_g. In the temperature region between 50 and 100 °C for α-process shows up (Figure 4a). With the transition from the smectic to the nematic phase at 107 °C the δ-process becomes active (Figure 4b) and is superposed. For polymer 6 both relaxation processes show up separately in the nematic phase. In the isotropic phase they are superposed.

A peculiar behavior was found for sample 7. In contrast to the other samples here no clear glass transition step could be observed in the DSC curve. In the loss tangent curves a relaxation process becomes visible at temperatures above 140 °C (Figure 5c). It sets in continuously and increases in strength with temperature. Its frequency is comparable to that of the δ-process of sample 8. This suggests associating it with the same type of motion.

At low temperatures one observes again the β-process (Figure 5b) and at the lowest temperatures another relaxation process, called γ_2 (Figure 5a). This γ_2-process was always observed for polymers with a n-butoxy end group. In the case of sample 8 it was difficult to separate the β- and γ_1-processes, although it was clear from the overall appearance that both processes were present.

The relaxation frequencies derived for the γ_2-, γ_1-, β-, α-, and δ-processes at temperatures different from the corresponding maxima in Figures 1–5 are collected in the Arrhenius plots shown in Figures 6–8.

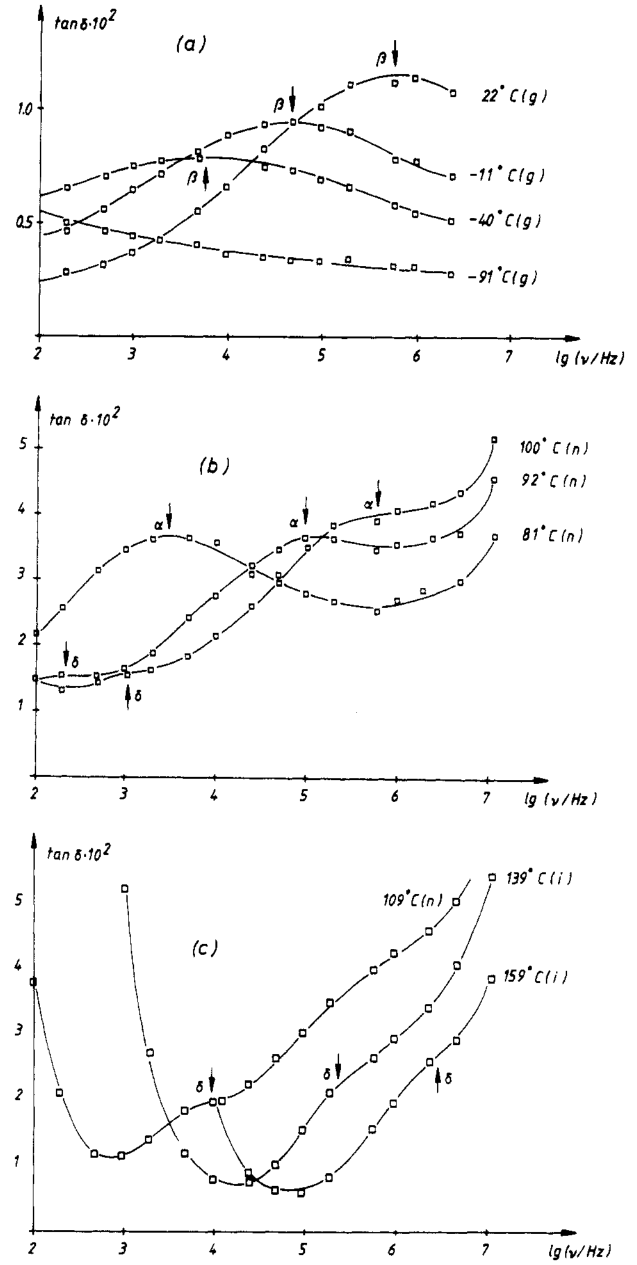


Figure 3. Frequency dependence of dielectric loss tangent measured at different temperatures for sample 1 (spacer length $n = 2$; end group: OCH_3): (a) temperature range of β-relaxation, (b) temperature range of α-relaxation, (c) temperature range of δ-relaxation.

Discussion

The fact that below T_g one to three relaxation processes are found in a systematic dependence on the structure of the side group suggests an assignment to motions localized in the different parts of these groups. The γ_1-relaxation is only observed for long spacer groups and therefore must be assigned to motions within the six methylene groups of the spacer. It becomes dielectrically active because of the coupling to the adjacent dipole moments. The β-relaxation is found for all polymers independent of the chosen spacer and end group. Hence, it reflects a motion of the central phenyl benzoate ester group, which is common for all polymers. The γ_2-relaxation occurs only for polymers with the n-butoxy end group. Consequently, it shows a motion localized in this sequence.

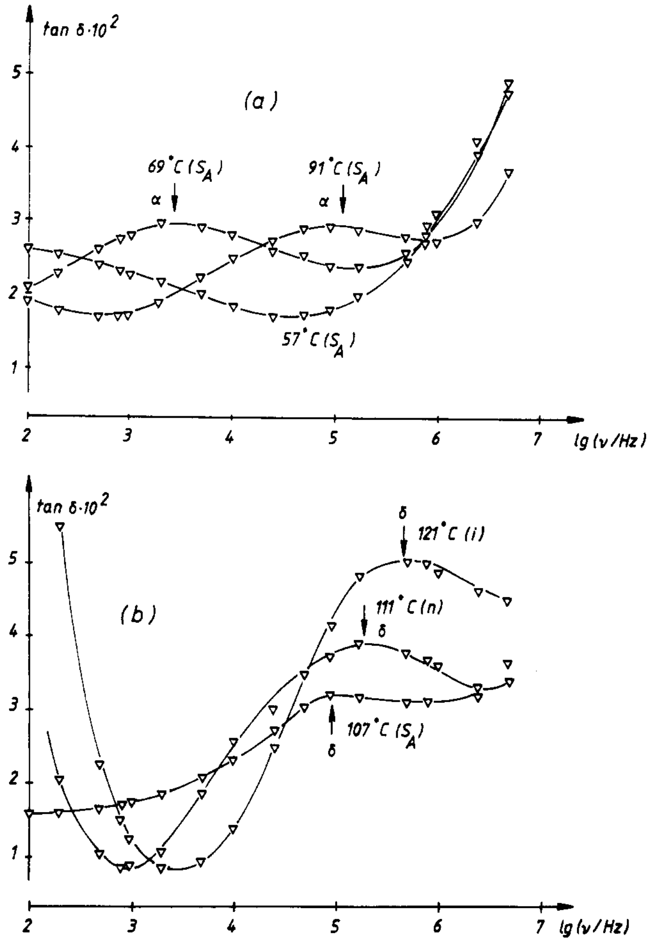


Figure 4. Frequency dependence of dielectric loss tangent measured at different temperatures for sample 8 (spacer length $n = 6$; end group: $O(CH_2)_3CH_3$): (a) temperature range of α-relaxation, (b) temperature range of δ-relaxation.

The straight-line character of the Arrhenius plots in Figure 6 shows that these three low-temperature relaxations are based on activated motions with a temperature dependence of the relaxation frequency

$$\nu \sim \exp(-A/RT)$$

The activation energies can be derived from the slopes of the straight lines. One obtains for the β-process $A = 50 \pm 7$ kJ/mol, for the γ_1-process $A = 35 \pm 10$ kJ/mol, and for the γ_2-process $A = 24 \pm 4$ kJ/mol.

The α-relaxation represents the dynamic glass process. This becomes clear from Figure 8. The Arrhenius plots are curved and directly related in their positions to T_g. The slopes yield the typical high values for the apparent activation energy (150–350 kJ/mol). At the glass transition the polymer main chain and the centers of gravity of the side groups become mobile. It is important to note that the orientation of the mesogenic groups and for smectic phases also the layer structure is preserved. Hence, in liquid crystalline polymers the micro-Brownian motion is restricted compared to normal flexible polymers. The T_g values show that the glass transition is strongly affected by the interaction between the mesogenic groups.[3] They lie intermediate between the T_g values of poly(methyl acrylates) (10 °C) and poly(methyl methacrylates) (105 °C).[22] The α-relaxation can be observed in the dielectric measurement because the main-chain motion causes a reorientation of the adjacent ester dipole.[11] This is indicated schematically in Figure 9.

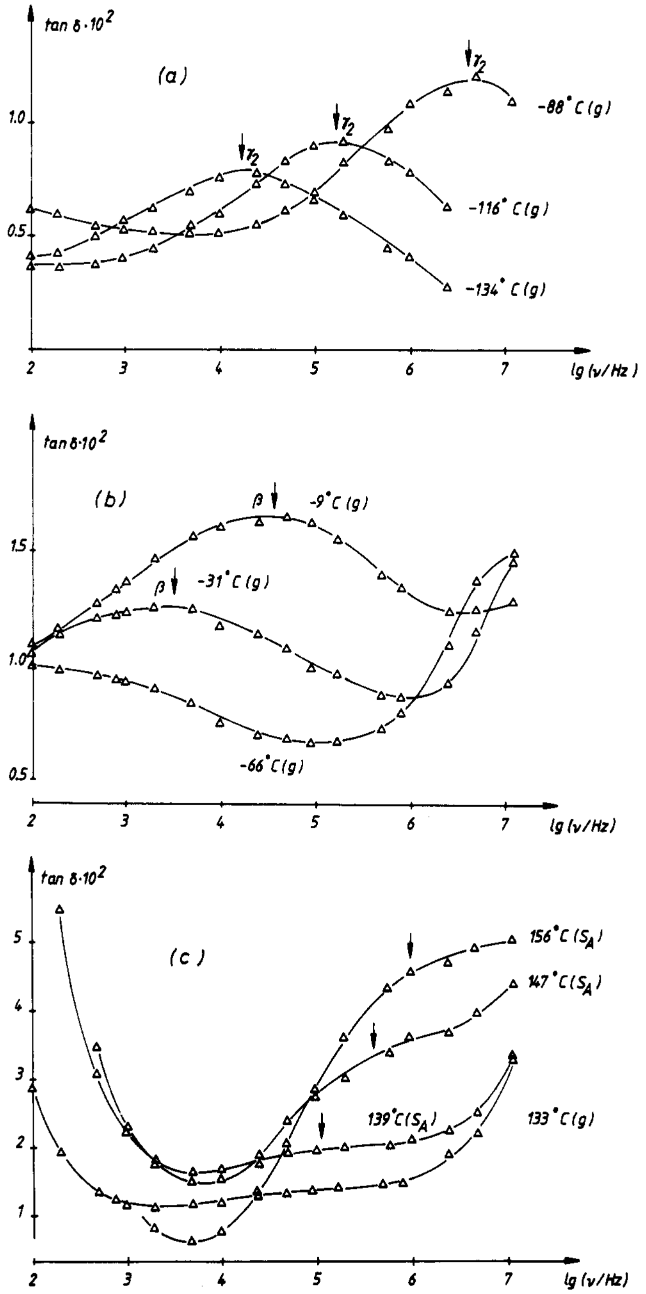


Figure 5. Frequency dependence of dielectric loss tangent measured at different temperatures for sample 7 (spacer length $n = 2$; end group: $O(CH_3)_3CH_3$): (a) temperature range of γ_2-relaxation, (b) temperature range of β-relaxation, (c) temperature range of δ-relaxation.

The different intensities of the δ-relaxation for polymers with different dipole moments parallel to the long axes of the mesogenic groups suggest an assignment of this relaxation to 180° reorientations of the long axes of the mesogenic groups (Figure 9). Such a reorientation is also found for low molecular weight liquid crystals.[4,12] For these compounds the jumps leave the center of mass of a molecule unchanged. For liquid crystalline polymers this is no longer possible. Here the jumps must occur about an axis located at the polymer main chain. Therefore, with every jump also the center of gravity of the side group is shifted. Generally the δ-process can only become active above T_g. Micro-Brownian motion is a necessary prerequisite.

The relation between the α- and δ-relaxation and the state of order of the system is different for the polyacrylates and the polymethacrylates. In case of the polyacrylates the δ-relaxation peak passes continuously without abrupt intensity changes through all mesophases and the isotropic phase. The phase transitions leave the

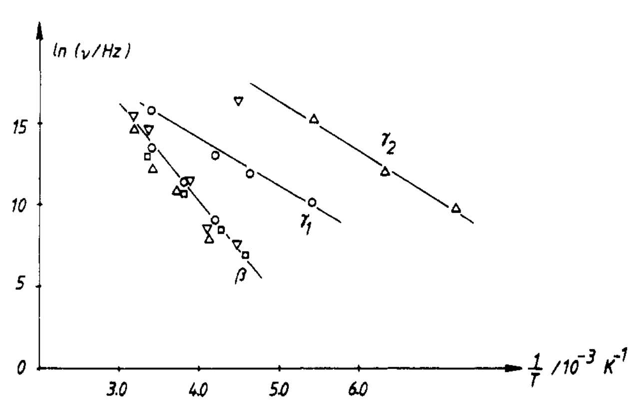


Figure 6. Temperature dependence of relaxation frequencies of the β-, γ_1-, and γ_2-processes (sample 1: □; 4: ○; 7: △; 8: ▽).

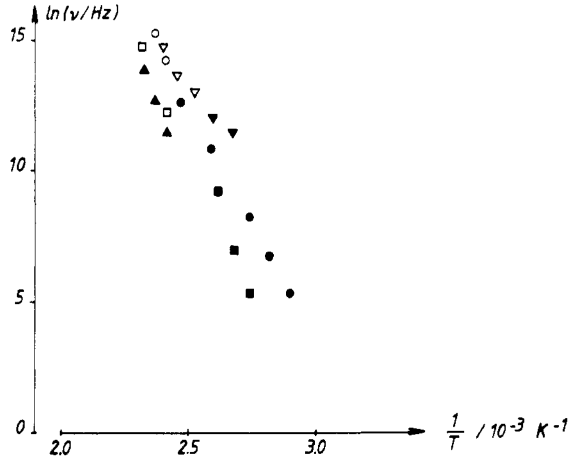


Figure 7. Temperature dependence of the frequency of the δ-relaxation (sample 1: □; 4: ○; 7: △; 8: ▽; filled symbols: nematic or smectic phase; open symbols: isotropic phase).

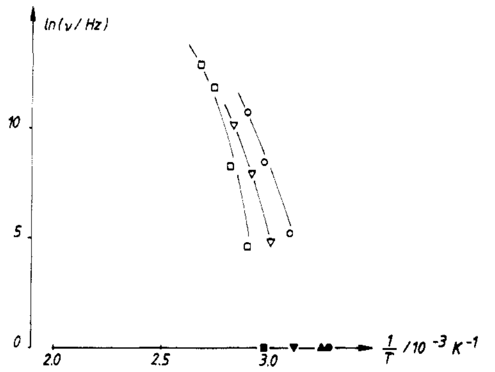


Figure 8. Temperature dependence of α-relaxations observed for samples 1 (□), 4 (○), and 8 (▽). Static glass transition temperatures T_g are indicated on the $1/T$ axis.

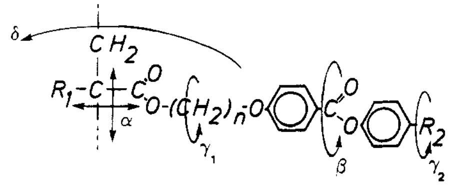


Figure 9. Assignment of observed relaxation processes (α, β, γ_1, γ_2, δ).

state of this motion unchanged. This is in agreement with similar observations on low molecular weight liquid crystals.[12,19,20] The polymethacrylates show a qualtitatively different behavior. For sample 8 the δ-motion is setting in at about 107 °C together with a phase transition. The observation indicates that this phase transition differs in character from the usual smectic–nematic transition and incorporates as an additional factor an abrupt change in the state of motion. The mobility change in the temperature range 140–160 °C showing up in dielectric relaxation spectra of sample 7 can also be considered as indicating a phase transition, which is driven by this chain motion. Hence, the dielectric studies point to a clear difference in the molecular background of the phase behavior for the two investigated groups of liquid crystalline polymers.

In summary, the complex dielectric relaxation spectra observed for a group of liquid crystalline polyacrylates and polymethacrylates can be qualtitatively understood. The five processes found can be assigned to different modes of motion as indicated schematically in Figure 9. The different processes become successively active with increasing temperature. Below T_g, first the γ_2-relaxation of the extended end group becomes mobile, then the γ_1-relaxation of the long spacer group, and finally the β-relaxation of the central phenyl benzoate. The dynamic glass transition is reflected in the α-process. At sufficiently high temperatures 180° reorientational jumps of the long axis of the mesogenic side groups (δ-process) are activated. For the polymethacrylates the activation occurs together with a phase transition and therefore must be considered as one aspect of this transition.

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Nematogenic Polymers Having Rigid Chains. 1. Substituted Poly(*p*-phenylene terephthalates)

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ABSTRACT: We have investigated the effect of Cl, Br, C_6H_5, and C_6H_{13} substituents upon the transition temperatures of poly(*p*-phenylene terephthalate). The substituted polyesters are thermotropic nematogens. A single substituent lowers the crystal–nematic transition temperature, t_{KN}, from 600 °C to the range 290–405 °C, while substitution on both rings reduces t_{KN} to 205–235 °C. The polyester bearing a phenyl substituent on each ring is an amorphous glass. Disubstituted polymers crystallize more slowly and require annealing to exhibit a crystalline X-ray pattern. Substitution also reduces the degree of crystallinity, although most substituted polymers show Bragg spacings of 12 Å or greater, indicating regularity along the chain direction. The nematic–isotropic transition temperature, t_{NI}, is also lowered by substitution. A recent treatment which considers the temperature dependence of the unperturbed dimensions leads to the conclusion that all polymers which can be represented by the Kuhn chain model are in corresponding states at t_{NI}. This implies that a substituent which lowers t_{KN} also reduces the chain extension of the polymer.

Introduction

The possibility that thermotropic nematogens might be spun from the melt to obtain fiber properties similar to those of Kevlar at lower cost created special interest in this class of polymer. Segmented polyesters incorporating both a rigid and a flexible segment in the repeating unit have been extensively investigated in many laboratories. They have transition temperatures in a convenient range for experimental study and provide examples of nematic/cholesteric and several polymorphic smectic mesophases. However, Acierno et al.[1] found that fibers spun from the nematic phases of several of these polymers had poor mechanical properties. These authors offered as possible explanations the lower order parameter of semiflexible polymers, their shorter relaxation times (leading to loss of orientation past the spinneret, but prior to crystallization), and the relatively imperfect crystal structure which appears to be characteristic of this type of polymer.

One evident difference between these semiflexible polymers and poly(*p*-phenyleneterephthalamide) is the much higher chain extension of the latter. Arpin and Strazielle[2] reported a persistence length of 150–200 Å for that polymer, and about 500 Å for the related poly(*p*-benzamide). These values are much larger than the persistence lengths characteristic of typical nonmesogenic textile fibers, and they also exceed those of some other lyotropic polymers. Poly(*p*-phenylene terephthalate) and poly(*p*-hydroxybenzoic acid) are the analogues of poly(*p*-phenyleneterephthalamide) and poly(*p*-benzamide). According to the calculations of Erman, Flory, and Hummel,[3] these polyesters should have even larger persistence lengths than the corresponding polyamides, 784 and 740 Å, respectively.

High melting temperatures are expected[4] for rigid-chain nematogenic polymers due to the relatively small entropy change at the crystal–nematic transition. Frosini and co-workers[5] reported a melting temperature of 470 °C for poly(*p*-phenyleneterephthalamide). However, these workers did not indicate the DSC heating rate used in their studies. More recently Jackson,[6] using a fast heating rate of 80 °C/min, reported a melting temperature of 600 °C for this polymer, and 610 °C for poly(*p*-hydroxybenzoic acid). The latter values are probably the correct ones, and the lower melting temperature obtained by Frosini et al.[4] is most likely due to their use of a slower heating rate which led to thermal decomposition. Economy and co-workers[7] found that poly(*p*-hydroxybenzoic acid) could be compression molded at 440 °C and 4000 psi due to a crystal–crystal transition which occurs in the temperature range 325–360 °C. However, it is clear that the melting temperatures of these rigid-chain polyesters must be substantially reduced to permit fiber spinning.

There are several known ways to reduce the crystal melting temperature of a rigid-chain polymer, some of which are presumed to leave the chain highly extended. One involves the positional isomerism of a substituent on the aromatic ring. An early patent by Goodman, McIntyre, and Aldred[8] disclosed *p*-phenylene terephthalate polyesters bearing a methyl, methoxy, or halogen substiutent on one or both aromatic rings of the repeating unit. These polymers were reported to have melting temperatures in excess of 350 °C, which is still too high for melt spinning. One might have expected these polymers to be amorphous due to random variation along the chain of the position of the substituent; however, their X-ray patterns showed a number of sharp rings. Substituents having additional degrees of rotational or conformational freedom should provide larger reductions in the melting temperature,[4] as illustrated by the terephthalate polyesters involving phenylhydroquinone disclosed by Payet,[9] and those with hydroquinone and phenylterephthalic acid claimed by Harris.[10] Example IC of the latter patent gives melting temperatures of 335 and 300 °C for these two polymers.

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