Liquid-crystalline main-chain polymers with a poly(*p*-phenylene terephthalate) backbone: 6. Dielectric relaxations in the polyester with dodecyloxy side chains

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Dielectric measurements on three dodecyloxy-substituted poly(*p*-phenylene terephthalate)s are presented and compared with dynamic mechanical measurements reported earlier. The results are interpreted on the basis of a molecular laminate model for the structural arrangement, i.e. main-chain layers separated by partially ordered side chains. Most of the observed relaxations are assumed to originate from side-chain motions. The low-temperature γ relaxation around -160°C is ascribed to local motions of the CH_2 units in the side chains. The β relaxation around -35°C involves a cooperative motion of the amorphous parts of the side chains, while the β^* relaxation just above room temperature is supposed to occur mainly in the crystalline parts of the side chains. Although some main-chain motions may already be involved in the relaxations at lower temperatures, they fully account for the α relaxation observed around 120°C.

(Keywords: aromatic polyester; molecular motion; dielectric relaxation)

INTRODUCTION

In previous papers of this series, the synthesis[1], phase behaviour[1,2], fibre spinning[3] and dynamic mechanical[4,5] (tensile) behaviour of several substituted poly(*p*-phenylene terephthalate)s (PPT) with the structures shown in *Scheme 1* were investigated.

As discussed earlier[1–5], such rigid-rod polymers with flexible side chains were first synthesized by Ballauff[6], and major contributions to their physical characterization have been made by him[6–12] and others[13–20].

Most of our work was focused on PTA12HQ, which shows three different solid-state structures, characterized by the side-chain packing: the highly crystalline modification B, the less crystalline modification A and the largely amorphous phase L_f (for details, see ref. 2 and references therein). In the preceding paper[5], the dynamic mechanical measurements on this polymer were interpreted with the objective of getting a better understanding of the influence of structure and temperature on the mechanical properties. Four different relaxations could be distinguished, which were referred to as the γ, β, β^* and α relaxations.

It is the objective of this paper to use dielectric measurements to elucidate further the molecular mechanisms responsible for these relaxations in PTA12HQ. This technique is useful to show whether polar groups are involved in the relaxations and covers a wider frequency range compared to the dynamic mechanical measurements. Measurements on other polymers with dodecyloxy side chains (PTAHQ12 and PTA12HQ12) will be included in this study, since this will allow more substantiated conclusions with regard to the molecular origin of the relaxations. The crystalline packing of these related polymers shows most resemblance with the B modification of PTA12HQ[3,13]. Details on the phase behaviour[1] of both systems and the dynamic mechanical characterization of PTA12HQ12[5] were reported before.

An overview of the literature concerning molecular motions in unsubstituted PPT, in PPT with alkoxy side chains and in comb-like polymers (rigid as well as flexible backbones) with aliphatic side chains is given in the following.

*Poly(*p*-phenylene terephthalate)*

To our knowledge, only one publication (by Frosnini *et al.*[21]) dealing with molecular motions in this polymer exists. It concerns dynamic mechanical and broad-line n.m.r. measurements. A relaxation with an activation energy of about 55 kJ mol^{-1}, denoted β, was found around 0°C (10^4 Hz). It was suggested that this relaxation involves a local motion of the carbonyl group. Following Blundell *et al.*[22], who interpreted relaxations in aromatic copolyesters, two mechanisms may account for this relaxation. Both involve motions about the phenyl–oxygen bonds. The first mechanism is a motion of the hydroquinone phenyl ring; the second is a motion of the complete terephthalate unit (including the two COO groups). As the β relaxation is also found to be rather strong by dielectric measurements[23], the second possibility seems most likely.

Another relaxation in PPT was found around 200°C and was referred to as the β^* relaxation[21]. Its molecular origin was not discussed further. The glass transition of PPT was reported[21] to be located at 267°C.

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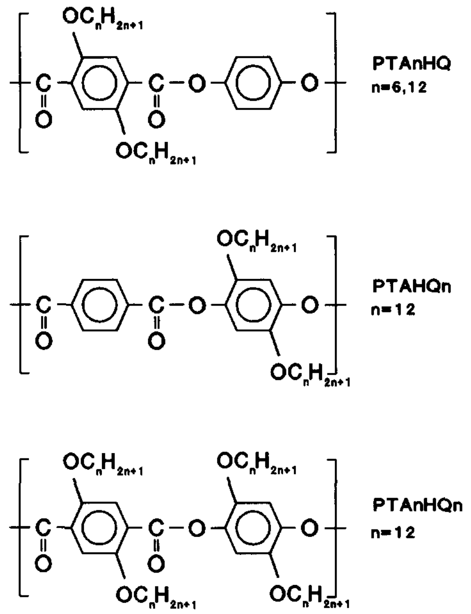

Scheme 1

Poly(p-*phenylene-2,5-di-n-alkoxyterephthalate*)*s*

For PTA*n*HQ the influence of the side-chain length on the dynamic mechanical properties (10 rad s^{-1}) was described by Schrauwen *et al.*[15]. For PTA6HQ, PTA12HQ and PTA16HQ they found a relaxation around −150°C, which they named γ_2. Based on the fact that this motion was not observed by ^{2}H n.m.r. measurements, but was detectable in dielectric spectra, they ascribed this relaxation to some vibrational motion of the carbonyl groups. A second relaxation (denoted γ_1), which shifted to higher temperatures when the side-chain length was increased from $n=6$ to 16, was found between −100°C and 0°C. Based on solid-state n.m.r. this relaxation was ascribed to motions of the ends of the side chains. The third relaxation they found was located around 50°C for PTA6HQ and was denoted β. For this relaxation in PTA6HQ the mobility of the side chains, accompanied by some conformational flips within the main chain (^{13}C n.m.r.), was thought to be responsible. For longer side chains this relaxation splits into two relaxations (denoted β and β'). Both were correlated to the onset of motion of the whole side chain (d.s.c. transition). A fourth transition, denoted α, was found above 100°C for all polymers. The peak temperature of this transition decreased with increasing side-chain length and corresponded with a d.s.c. transition, associated with the transformation to the layered mesophase at T_m.

Falk *et al.*[16] investigated the mobility of different parts of the PTA16HQ polymer in modification A with ^{2}H n.m.r. For a polymer deuterated on the unsubstituted hydroquinone ring, it was concluded that the hydroquinone part is immobile below about −30°C. Above this temperature, motions, ascribed to phenyl flips, start and exist at least up to 70°C. Around this temperature isotropic motion becomes detectable, until a fully isotropic motion is observed at about 190°C. For PTA16HQ deuterated in the middle of the flexible side chain, residual motion was observed below −40°C[16]. At temperatures close to the onset of the side-chain melting, kink motions in the side chains were observed. Above T_s(A) only isotropic motions remained. A polymer with shorter side chains, PTA6HQ, was deuterated on the alkoxy-substituted phenyl ring[17]. No motion of this part of the molecule was observed at temperatures up to 125°C. In the layered mesophase rapid molecular movements were observed, while it was thought probable that rapid internal conformational changes (*trans–cis* of the ester bonds) occurred at still higher temperatures in the nematic mesophase.

In order to study the conformation of the side chains of PTA16HQ around the respective side-chain disordering temperatures T_s(A) and T_s(B), Whittaker *et al.*[18] and Baldwin-Frech *et al.*[19] performed ^{13}C n.m.r. measurements. Below T_s it was found that the packing of the carbon atoms in the side chain, situated closest to the backbone, is better defined in modification B, compared to modification A. The methylene carbons in the middle of the side chain remain in highly extended *trans* conformations up to the transition to phase A′ for both modifications. At the side-chain end more *trans* conformations of the methylene carbons are observed for modification B compared to modification A, indicating that in modification B the chain ends are better incorporated in the crystalline structure. Furthermore, it was pointed out that, above T_s, a small fraction of methylene groups remains in all-*trans* sequences up to the transition to the mesophase.

A very recent publication by Clauss *et al.*[20] is concerned with the side-chain mobility, conformation and structural organization of PTA16HQ (and the corresponding polyamide and polyimide) as studied by 2D solid-state n.m.r. spectroscopy at room temperature. For modification B a model is proposed in which the side chains form crystalline domains (including the chain ends) separated by amorphous domains in which a high mobility is detected. In modification A the side chains are thought to be uniformly extended but not very mobile (conformationally highly ordered, but not crystallized).

Related comb-like polymers

Extensive investigations on poly(L-glutamate)s with n-alkyl side chains of various lengths have been performed by several authors[24–29]. Like PTA*n*HQ, these comb-like polymers are capable of forming liquid-crystalline phases, and their solid phases show layered structures of the main chains, separated by the side chains[24]. At low temperatures a γ relaxation ($E_A \approx 42$ kJ mol^{-1}) is observed, which is ascribed to local twist motions of the terminal alkyl groups (longer than the ethyl group) of the side chains. This transition shifts from approximately −160°C for $n=5$ to −120°C for $n=18$ (110 Hz). A β relaxation ($E_A \approx 160$ kJ mol^{-1} (ref. 27)), ascribed to the motion of the entire side chain, is found between −20 and −40°C. For side chains longer than decyl, side-chain crystallization occurs, and this transition shifts to higher temperatures as a function of side-chain length. Between 50 and 150°C an α transition, associated with the onset of motion of the main chain, is found.

Comb-like polymers with flexible backbones have been studied extensively in the past years[30,31]. Examples are poly(n-alkylethylene)s, poly(n-alkyl methacrylate)s and poly(n-alkyl itaconate)s. Such polymers generally show a γ transition between −100 and −160°C ($E_A \approx 25$ kJ mol^{-1}), ascribed to side-chain motions (probably crankshaft) involving C–C–C–C or O–C–C–C units[32,33]. A β relaxation ($E_A \approx 100$–200 kJ mol^{-1}) can be found in a wide temperature region between 50 and −50°C[30,31]. For some polymers this peak merges into the α relaxation. Its molecular interpretation is not clear and can involve main-chain and/or side-chain motions, depending on the molecular structure. For poly(alkyl itaconate)s it has been proposed by Cowie *et al.* that, owing to their two-phase structure, a dual glass transition can occur[33]. While the transition around −70°C is ascribed to a cooperative motion of the side chains, the transition around room temperature is thought to reflect the glass–rubber transition of the main-chain backbone and the cooperative motion of the total molecule.

EXPERIMENTAL

Materials

The polymers used were synthesized as described earlier[1]. PTA12HQ and PTA12HQ12 films with a thickness of about 40 μm were made by casting from a solution in chloroform. Oriented films were obtained by drawing solution-cast films in the layered mesophase[4].

As PTAHQ12 is insoluble in organic solvents suitable for film casting, no films could be made of it.

Macroscopically unoriented samples (referred to as random samples) were made by compressing dried powders to circular plaques of 0.6 mm thickness and 12 mm diameter at about 40°C.

Dielectric measurements

Dielectric measurements were carried out using a measuring cell in which the sample was placed between two parallel, disc-like, electrodes. The temperature of the cell was controlled by a stream of dry nitrogen gas with an accuracy better than 1°C. The computer-controlled experimental set-up is shown schematically in *Figure 1* and comprises a Solartron 1250 frequency response analyser (FRA). For the feedback element Z_{fb}, different sets of capacitors and resistors are installed automatically, depending on the impedance of the filled cell. The impedance of a low-loss dielectric is measured using a capacitor only. The a.c. voltage applied across the cell had an amplitude of 10 V. To allow accurate measurements, the impedance of the filled cell was measured using at least 10 periods of the sinusoidal signal. Electrical contact between the samples and the electrodes was ensured by evaporating an aluminium coating onto the sample surfaces. The experimental set-up allows measurements on materials with a dielectric loss factor tan δ between 10^{-3} and 10^2, and a capacitance of the filled cell between 10 pF and 1 μF.

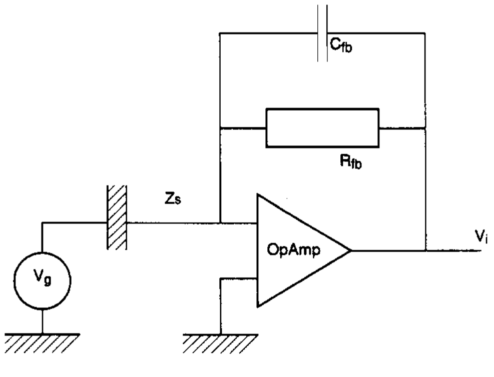

Figure 1 Circuit for measuring the impedance Z_s of a sample. The impedance Z_{fb} of the feedback element of the integrating (high-impedance) operational amplifier contains a variable capacitor C_{fb} in parallel with a variable resistor R_{fb}. Other symbols: V_g, a.c. generator of the FRA; OpAmp, operational amplifier; V_i, input for the correlator of the FRA

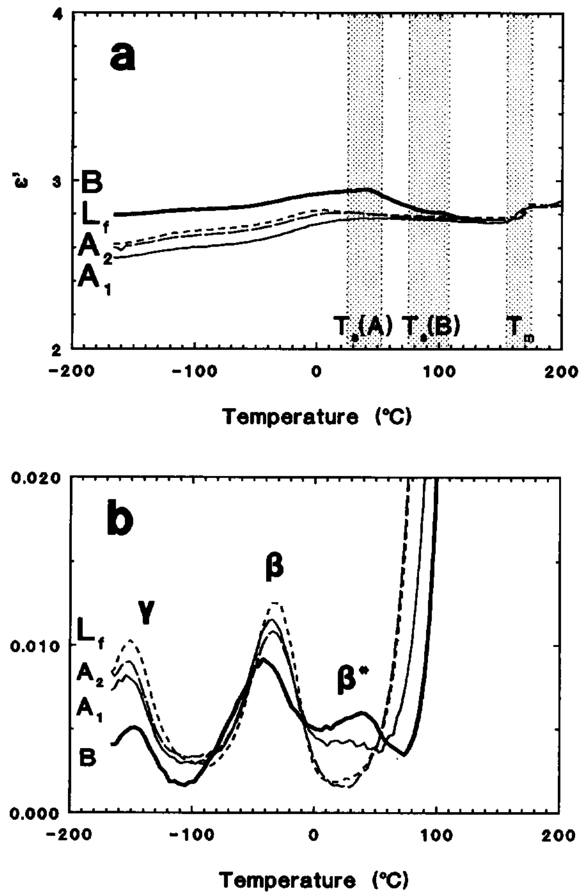

Figure 2 (a) Real part of the relative permittivity ε' at 1000 Hz and (b) dielectric loss ε'' at 10 Hz *versus* temperature of pressed PTA12HQ samples without macroscopic orientation. First, second, third and fourth heating run on modifications B, A (denoted A_1), L_f and A (denoted A_2) respectively. Shaded areas indicate the phase transition regions found by d.s.c.

The experiments to be presented were performed at temperatures between −165 and +250°C. Usually 16 frequencies between 10^{-1} and 10^4 Hz were included, and measurements were performed isothermally every 2.5°C. The effective heating rate was lower than 1°C min^{-1}.

RESULTS

All PTA12HQ and PTA12HQ12 films had the typical sandwich structure, in which the main-chain layers extend parallel to the film surface[4,15]. Results of dielectric measurements on compressed powders (referred to as random samples), as well as results obtained on solution-cast films, are presented.

PTA12HQ: influence of structure and macroscopic orientation

Random samples. Figure 2a shows the temperature dependence of the real part of the relative permittivity ε' of the randomly oriented samples at 1000 Hz. These results were obtained by four successive heating runs (respectively modification B, modification A, phase L_f and modification A, same procedure as outlined in ref. 5). Measurements at other frequencies yielded virtually the same results, although when going to lower frequencies ionic conduction effects become increasingly visible at

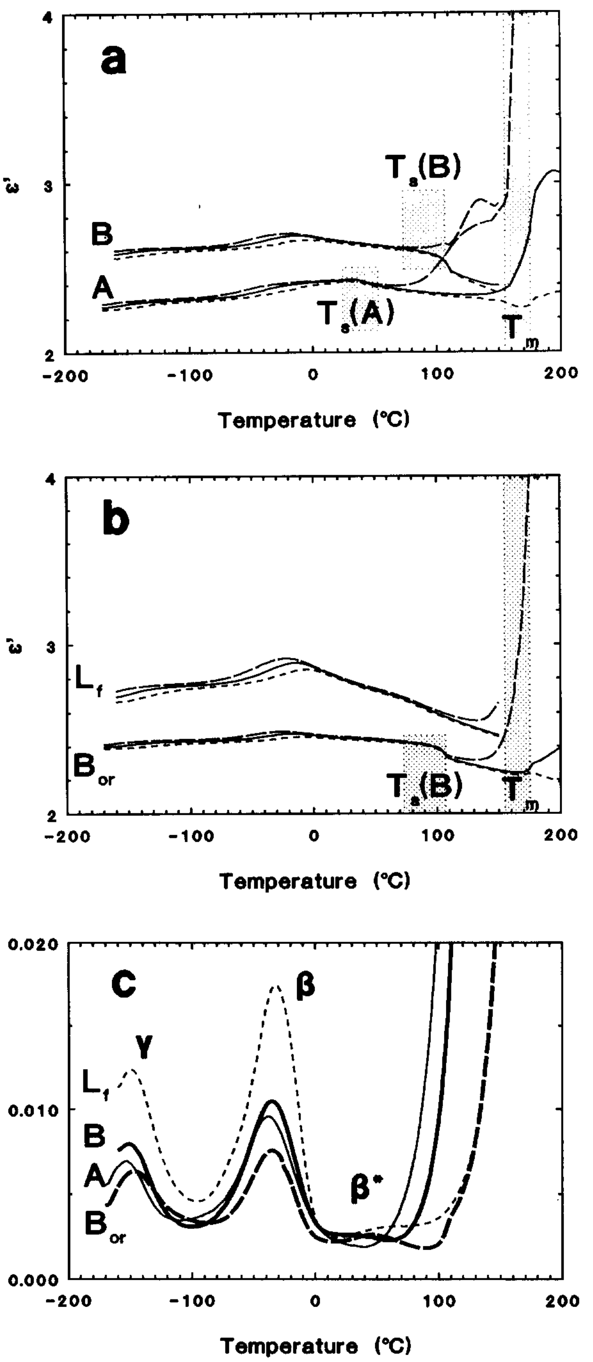

Figure 3 Results of dielectric measurements on films of PTA12HQ. (a), (b) Real part of the relative permittivity ε' at 0.1 (———), 10 (——) and 1000 Hz (------) *versus* temperature for (a) unoriented films and (b) oriented films. (c) Dielectric loss ε'' at 10 Hz *versus* temperature for films of PTA12HQ: unoriented modification B (——); unoriented modification A (——); oriented modification B (———); oriented phase L_f (------). Shaded areas indicate phase transition regions found by d.s.c.

higher temperatures (thus obscuring the transition at T_m, see also *Figures 3a* and *3b*). In *Figure 2b* the dielectric loss curves (ε'' *versus* temperature) are shown at 10 Hz, a frequency in the same range as used for the dynamic mechanical measurements[5]. In these results the effects of ionic conduction are very explicit above 50°C. The apparent activation energies of the γ and β relaxations as derived from Arrhenius plots are collected in *Table 1*. The peak position of the β* relaxation could only be determined for modification B, but no reliable value of the activation energy could be obtained.

From the overall behaviour of the dielectric data, viz. the rather delimited values of ε' and the relatively low intensities of the dielectric relaxations, it can be inferred that polar groups are not directly involved in the observed phenomena. The most notable feature is the very low intensity (B, A_1) or even absence (A_2, L_f) of the β* relaxation. Moreover, in modification B the β* peak temperature coincides with the onset of a notable decrease of ε' with temperature in the region above 40°C. Above T_s(B), where another much smaller decrease is observed in modification B, all phases exhibit the same value of the dielectric constant, in agreement with the phase behaviour (phase A′)[3]. On entering the layered mesophase, a stepwise increase is observed at T_m.

The very low intensity or even absence of the β* relaxation is even more striking in comparison with the results of the dynamic mechanical measurements[5], which revealed the β* relaxation to be very strong. However, also in the dynamic mechanical data there was a pronounced decrease in intensity when going from modifications B and A (first run) to L_f and A (second run). So the influence of structure is well established, but apparently this relaxation does not involve any polar groups. With regard to the γ and β relaxations, it was observed that the intensity of these peaks increases when going from modification B to A to phase L_f, a tendency that was also present in the dynamic mechanical results. The dielectric intensities of the two low-temperature relaxations suggest some indirect involvement of polar groups. Another notable agreement between the dielectric and dynamic mechanical data is the fact that the intensities of the β and the β* relaxations seem to be mutually dependent, e.g. an increase of the intensity of one relaxation is at the expense of the intensity of the other. As will be discussed further on, this may well indicate an involvement of respectively the amorphous and crystalline fractions of the side chains.

Films. The temperature dependences of ε' and ε'' in unoriented and oriented ($\lambda \approx 3$) films of PTA12HQ are shown in *Figure 3*. Compared to the random samples, a notable difference is that the β* relaxation (including its effect on ε') has virtually disappeared for films in modification B. In relation to this, it is observed that the gradual decrease of ε' with temperature now already sets in at the β relaxation and is followed by a large stepwise decrease at T_s(B). The behaviour at T_s(B) may be attributed to the increase of the sample thickness (about 20%) when going from modification B to phase A′ (see ref. 4). A slight decrease of the intensity of the γ and β relaxations is observed upon orienting films in modification B.

Table 1 Activation energies of the γ and β relaxations as derived from dielectric measurements. Except for the case indicated, no orientation dependence was found

Polymer	Activation energy (kJ mol^{-1}) γ relaxation	Activation energy (kJ mol^{-1}) β relaxation
PTA12HQ (B)	29/35^a ± 5	130 ± 30
PTA12HQ (A)	34 ± 5	110 ± 20
PTA12HQ (L_f)	35 ± 5	145 ± 20
PTAHQ12	34 ± 5	90 ± 25
PTA12HQ12	36 ± 10	125 ± 25

[a] Unoriented/oriented film

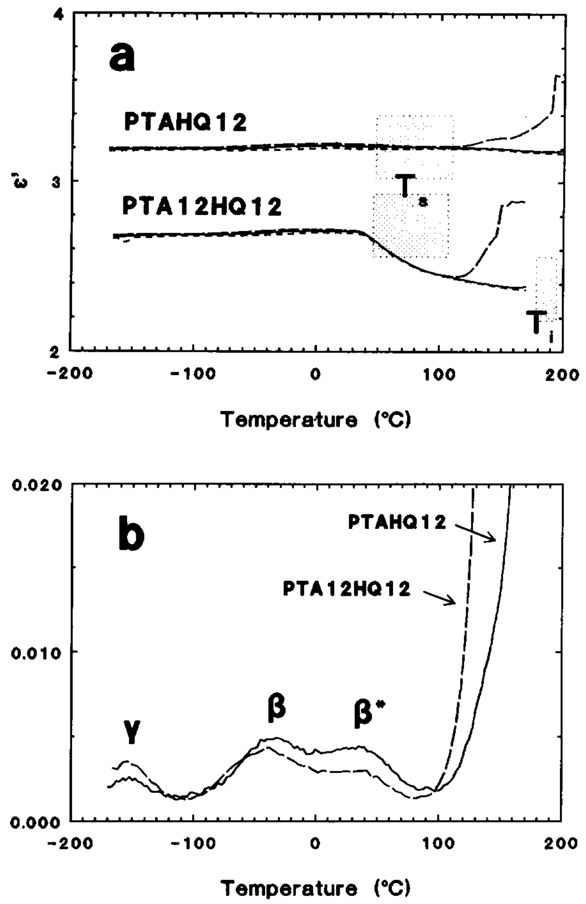

Figure 4 Dielectric measurements on pressed PTA12HQ12 and PTAHQ12 samples without macroscopic orientation: (a) real part of the relative permittivity ε' *versus* temperature at 0.1 (———), 10 (——) and 1000 Hz (– – – – – –); (b) dielectric loss ε'' *versus* temperature at 10 Hz. Shaded areas indicate the phase transition regions as found by d.s.c.

The measurements on modification A show no essential differences compared with the random sample (*Figure 2a*).

For phase L_f the decrease of ε' above the β relaxation becomes very prominent in the (oriented) film. The comparison of the dielectric loss ε'' *versus* temperature curves of the films for the various polymorphs (*Figure 3c*) shows that γ and β relaxations in phase L_f again show the highest intensities, even higher than in the random samples (*Figure 2b*).

PTA12HQ12 and PTAHQ12

Random samples. The values of ε' and ε'' of randomly oriented samples of PTA12HQ12 and PTAHQ12 are shown as a function of temperature in *Figure 4*. As expected, the overall magnitude of the relaxations and the presence of β^* in the dielectric loss curves point to a correspondence with PTA12HQ in the B modification. For PTA12HQ12 the same relaxations were also found with the dynamic mechanical measurements[5]. Only in the case of PTA12HQ12 is the β^* relaxation accompanied by the onset of a strong decrease of ε' with temperature. This decrease was, however, not visible in second heating runs, thereby indicating a relation with thermal history. The relatively low intensities of both the γ and β relaxations, also compared to PTA12HQ, are reflected in the temperature-independent behaviour of ε' over a large temperature range, in PTAHQ12 even up to the melting transition. Once more this corroborates the idea that in the present polymers polar groups do not play a significant role in the relaxation behaviour.

The activation energies of the γ and β relaxations in random samples of PTA12HQ12 and PTAHQ12 are included in *Table 1*.

Films. As PTAHQ12 is insoluble in chloroform, no films could be obtained. For PTA12HQ12 no essential differences with the measurements on random samples were found.

Comparison of the activation energies derived from dynamic mechanical and dielectric measurements

To illustrate how the results of the dynamic and dielectric measurements compare, Arrhenius plots of the data on PTA12HQ are shown in *Figure 5*. A good overall agreement between the two techniques is found (note that

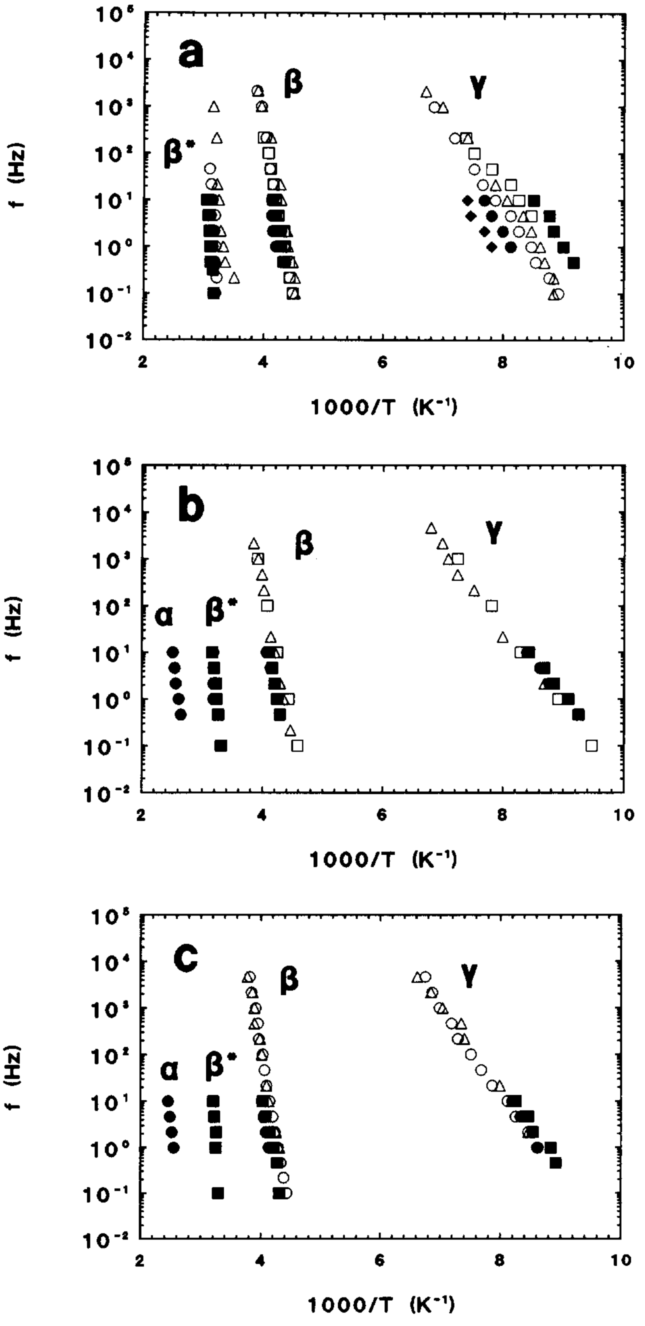

Figure 5 Arrhenius plots of the relaxations in PTA12HQ: (a) modification B, random (Δ), $\lambda=1$ (□), $\lambda\approx3$ (○), $\lambda=5$ (◇); (b) modification A, random (Δ), $\lambda=1$ (□), $\lambda=4.5$ (○); (c) phase L_f, random (Δ), $\lambda=1$ (□), $\lambda=4.5$ (○); open and full symbols refer to dielectric and dynamic mechanical measurements respectively

in the dynamic mechanical data the peak frequencies were taken from the $\tan\delta$ curves and in the dielectric measurements from the ε'' curves). None of the relaxations shows clear evidence for a WLF (Williams–Landel–Ferry) type of behaviour, although the high apparent activation energies of β, β^* and α may be indicative of collective motions. A significant dependence on the orientation was only found for the location of the γ relaxation of modification B of PTA12HQ (*Figure 5a*).

The good agreement regarding the temperature dependence and the activation energies of the relaxations (*Table 1*) in the different structures and polymers investigated makes it very likely that the same molecular mechanisms are involved. This assumption will be used as a starting point in the identification of the molecular origin of the relaxations.

DISCUSSION

For the interpretation of the dynamic mechanical and dielectric results in terms of the molecular identification of the various relaxations, several aspects have to be considered. First of all the observed differences between the B, A and L_f structures of PTA12HQ have to be accounted for. The three structures are distinguished by a decreasing degree of side-chain crystallinity in the given order, with supposedly the less ordered regions (thus most mobile) closest to the backbone[18–20]. It should be kept in mind, however, that the samples may contain small fractions of the other structures; especially the A and L_f structures must be considered as the extremes in a gradual changeover[5]. Furthermore the assignment of the relaxations should be in line with the observed behaviour upon orientation of the dynamic mechanical relaxations. The effect of orientation on the dielectric properties is less accessible since this would require a detailed knowledge of the structure. Therefore the dielectric relaxations will mainly serve to establish the involvement of polar groups. These polar groups are primarily the ester groups in the main chain and the oxygen moieties at the first site of the side chains. In this context it should be noted that a motion of the substituted phenyl ring is strongly hindered by the side chains, while local motions of the unsubstituted rings (phenyl flips) are reported to be frequent[16], but might be difficult to detect with the present techniques.

Finally the interpretation will be compared with the literature, an overview of which was given in the introduction. In the following the relaxations will be discussed separately, starting at the lowest temperatures.

The γ relaxation

In both the dynamic mechanical and the dielectric results the intensity of the γ relaxation in PTA12HQ increases when going from the highly crystalline structure B to the less ordered structures A and L_f. Furthermore, the magnitude of the dielectric relaxation (viz. a low value of ε'' accompanied by a minor increase in ε') indicates a small, probably indirect, involvement of polar groups. These observations lead to the interpretation that the γ relaxation takes part in the aliphatic side chains, more specifically in the less ordered regions. Such regions are located for the greater part close to the main chain and the adjacent polar oxygen moiety. The intensity decrease upon orientation as observed in the dynamic mechanical experiments can be ascribed to the fact that the main chains become more load-bearing. Within this view the observed shift to higher temperatures in better oriented samples of PTA12HQ in modification B (*Figure 5a*) is not completely understood but may be associated with some side-chain rearrangement upon orientation. The experimental value of the activation energy ($\approx 35\,\mathrm{kJ\,mol^{-1}}$) is in accordance with a local relaxation. This is corroborated by the proposal of Heijboer[34] that for a local secondary relaxation the activation energy E_A (in $\mathrm{kJ\,mol^{-1}}$) and the peak temperature T_{max} (at 1 Hz, in K) are related by $E_A = 0.252 T_{max}$. For the present γ relaxation located around −160°C, an activation energy of about $30\,\mathrm{kJ\,mol^{-1}}$ would be calculated in this way, which agrees well with the experimental value of $35\,\mathrm{kJ\,mol^{-1}}$.

For comb-like polymers (see 'Introduction') a similar relaxation in the same temperature region has also been ascribed to local aliphatic side-chain movements, probably of a crankshaft type. Additional evidence for the above assignment can be found in the work on polyethylene by Boyd[35], who proposed that the mechanical γ relaxation (with a calculated activation energy of $35\,\mathrm{kJ\,mol^{-1}}$) is caused by a flip-flop motion (rather than a complete crankshaft motion). On the other hand, Schrauwen *et al.*[15] interpret the γ relaxation in PTA*n*HQ as a vibration of the carbonyl unit. This explanation is, however, thought unlikely, because of the partial double-bond character of the bond between the carbonyl carbon and the alkoxy-substituted phenyl ring. Moreover, the low intensity of the γ relaxation in the dielectric data seems to exclude an involvement of the polar carbonyl unit. In conclusion, it is proposed that the γ relaxation involves a simple type of local molecular motion of the less ordered methylene side-chain units, probably crankshaft or flip-flop.

The β relaxation

Analogous to the γ relaxation, the intensity (both dielectric and dynamic mechanical) of the β relaxation in PTA12HQ is the highest in phase L_f and the lowest in modification B. Also the magnitudes of the two dielectric relaxations are much alike. This leads to the interpretation that the β relaxation also takes place in the less ordered fractions of the side chains. The observed activation energy, however ($100–150\,\mathrm{kJ\,mol^{-1}}$), cannot be ascribed to a local relaxation, but indicates a collective phenomenon. So the β relaxation can be viewed as a 'glass transition' in the side chains. For PTA12HQ films, particularly in modification A and phase L_f, this relaxation marks a major mechanical softening of the polymer[5]. The intensity decrease upon orientation can again for a large part be ascribed to an increased main-chain loading. In films of modification B the β relaxation and corresponding softening even disappear upon orientation, probably as a result of the better crystalline arrangement.

The explanation of the β relaxation in terms of collective motions in the amorphous side-chain regions is in line with reports on comparable comb-like polymers like poly(L-glutamate)s and poly(n-alkyl itaconate)s, which exhibit relaxations in the same temperature region with a similar activation energy (see 'Introduction'). Also the various n.m.r. results on side-chain motions in PTA*n*HQ agree rather well. Schrauwen *et al.*[15] ascribed the occurrence of this relaxation to motions of the ends of the side chains, but this interpretation seems unable to account for all observed effects, especially the strength of the dielectric relaxation. Summarizing, it is proposed that at the β relaxation a cooperative motion of the amorphous part of the side chains occurs.

The β relaxation

For the behaviour of the β^* relaxation around 50°C, two features are the most salient. First, from both the dynamic mechanical and the dielectric measurements, it became evident that there is an inverse correlation between the intensities of the β and β^* relaxations. Secondly, the dielectric loss associated with the relaxation in PTA12HQ is so small that the involvement of a polar group can be ruled out. These two features lead to the obvious interpretation that the β^* relaxation takes place in the crystalline regions of the side chains. This is in accordance with the decreasing intensity (measured by both techniques) going from B to L_f. The low dielectric intensity may be expected in a crystalline packing of aliphatic chains, and moreover these regions are supposed to be somewhat more remote from the backbone. The fact that the β^* relaxation shows up clearly in the dielectric data of PTA12HQ12 and PTAHQ12 as well (although not accompanied by any increase in ε') is in line with the assignment to the highly crystalline regions. Additional support for β^* being associated with the side chains comes from the finding that the linear extrapolations of the Arrhenius plots of the γ, β and β^* relaxations seem to intersect at one point, thus indicating a relation to the same polymeric (sub)system ('compensation rule', see e.g. ref. 36). The proposed mechanism of the β^* relaxation may be similar to that of the α relaxation in polyethylene[30,37,38].

The above interpretation of the β^* relaxation, although very plausible, may not be complete. Some observations do not quite fit into the mechanism presented. First, the activation energy ($E_A \approx 300\,\mathrm{kJ\,mol^{-1}}$, mainly determined from dynamic mechanical results[5]) seems to be too high for a local relaxation (also compared to the α relaxation in polyethylene). Although some experimental uncertainties may be involved[5] in the determination of E_A, its value indicates motions on a larger scale. Secondly, the relaxation is still found to be rather strong in the dynamic mechanical data on the highly amorphous L_f phase (unoriented film). An involvement of main-chain motions mediated by the substituted phenyl ring, although conceivable in this kind of system at the temperatures under consideration (see 'Introduction'), seems unlikely because of the dielectric observations (ε' constant or decreasing in the β^* region). A decoupled local main-chain motion as observed[16] by n.m.r. (phenyl flips) might, however, be related to the observed phenomena. So, as yet, some doubt remains about the given identification of the molecular origin of the β^* relaxation. The interpretation of Schrauwen *et al.*[15], based on a direct relation with the side-chain 'melting' at T_s(A), bears some relation to the present view, but is incomplete. As outlined before[5] the respective side-chain disordering transitions at T_s(A) and T_s(B) (no frequency dependence) can clearly be distinguished from the various relaxations that appear in all structures investigated.

The α relaxation

In the temperature range above 110°C, all structures of PTA12HQ have transferred[2] to phase A′, in which the side chains are disordered. The α relaxation around 120°C is only visible in the dynamic mechanical measurements. Since it is the first relaxation below the melting of the main chains at T_m (around 170°C), it is tempting to explain it as a glass transition of the main chains or the polymer as a whole. The high value of the activation energy is in line with this view. However, the α relaxation is not accompanied by a significant drop in modulus. Moreover, studies on unsubstituted poly(*p*-phenylene terephthalate) show a glass transition around 270°C (see 'introduction'). Consequently the α relaxation might well be related to local main-chain motions only. The interpretation should also be consistent with the molecular identification of the β^* relaxation, so further experimental evidence is needed to reveal the exact nature of the high-temperature relaxations.

CONCLUSIONS

The observed relaxations (dielectric as well as dynamic mechanical) in PTA12HQ were interpreted in terms of a molecular laminate model (main-chain layers separated by the aliphatic side chains). The γ relaxation occurring around -160°C is ascribed to local motions of CH_2 groups in the less ordered or amorphous regions of the side chains. At higher temperatures, around -35°C, the β relaxation shows up, which is associated with a cooperative motion in the amorphous parts of the side chains. The origin of the relaxations above room temperature, β^* and α, is less certain. It is assumed likely that the mechanism underlying the β^* relaxation involves a motion in the crystalline parts of the side chains, but some combined effect, for instance with a local main-chain motion, cannot be ruled out. For the high-temperature α relaxation an interpretation in terms of local main-chain motions is preferred to the identification as an overall glass transition.

The given interpretation of the relaxations encountered in the investigated thermotropic main-chain polyesters with flexible side chains differs in several aspects from other reports. Although the employed experimental techniques determine to some extent the way the relaxations manifest themselves and their interpretation, it is obvious that the molecular dynamics can be very complex in these systems. In order to get a better understanding of the underlying mechanisms, further investigations on systems with alternative groups in the side chains are in progress in our laboratory.

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