

Liquid-crystalline main-chain polymers with a poly(*p*-phenylene terephthalate) backbone: 5. Dynamic mechanical behaviour of the polyester with dodecyloxy side chains

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Tapes of the thermotropic, comb-like, polymer poly(*p*-phenylene-2,5-didodecyloxyterephthalate) were investigated by dynamic mechanical thermal analysis in tension. This polymer, in which the main chains form layers, exhibits three different low-temperature structures, characterized by the amount of side-chain ordering. The influence of the structure as well as the degree of orientation on the dynamic modulus of films was measured. The results show that the temperature-dependent modulus of oriented films is largely determined by the successive side-chain relaxations and disorderings. The main differences in modulus between the structures arise because of the β relaxation around -35°C ; they level off at higher temperatures on passing the respective side-chain disordering transitions.

(Keywords: aromatic polyester; molecular motion; dynamic mechanical behaviour)

INTRODUCTION

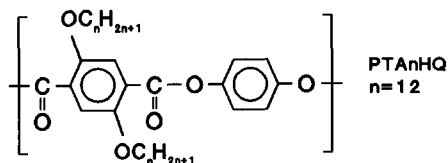
Polymers with backbones built up of rigid aromatic units, connected in a linear way, can be used for the production of high-modulus materials. The possibility of processing from a liquid-crystalline melt has several well known advantages. One of the methods used to obtain melt-processability is the attachment of flexible side chains to the rigid backbone¹. In previous publications by us² and others³, it was shown that, upon attaching dodecyloxy side chains to a poly(*p*-phenylene terephthalate) (PPT) backbone, a thermotropic polymer is obtained. This polymer is designated as PTA12HQ (Scheme 1). The phase behaviour of PTA12HQ is shown schematically in Figure 1. Up to the clearing temperature T_i , the PPT main chains are arranged in layers separated by the interdigitating side chains⁴. Depending on the thermal history, three low-temperature structures can be obtained, characterized by the side-chain arrangement: the highly crystalline modification B, the less crystalline modification A, and the amorphous (quenched) phase L_f . In the A structure the side chains are presumed to form crystalline clusters in between the main-chain layers, whereas in B they are incorporated in the main-chain lattice⁵. As a result, the side-chain disordering temperature $T_s(\text{B})$ is substantially higher than $T_s(\text{A})$. In phase A' the side chains are disordered, but the position of the main chains relative to each other remains strongly correlated. Above the main-chain melting temperature T_m , part of the positional ordering of the main chains is lost and a layered mesophase is formed. X-ray diffraction⁵ at different temperatures showed details about how at

each transition part of the ordering of the side and/or main chains is lost upon heating. These results were found to be in agreement with rheological and mechanical measurements performed earlier^{2,6}. The layered mesophase L_m shows biaxial ordering and behaves like a solid rather than like a liquid.

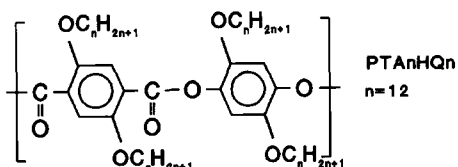
Oriented fibres and films of PTA12HQ could be obtained by drawing in the layered mesophase^{6,7}. In a previous publication⁶, some dynamic mechanical data on oriented films of different draw ratios were presented in order to determine the attainable tensile modulus as a function of temperature. For highly oriented films (draw ratio $\lambda > 4$), it was shown that the experimental moduli of all crystal modifications at low temperatures (-175°C) compare well with the theoretical modulus of 50 GPa, calculated by assuming that the main chains are load-bearing. At room temperature, however, the experimentally obtainable moduli are considerably smaller, especially for modification A and phase L_f (both around 15 GPa compared to 30 GPa for the highly crystalline modification B). The passing of a major relaxation around -35°C is responsible for this behaviour. The dynamic mechanical behaviour of PTA n HQ ($n=6, 12, 16$) was also reported by Schrauwen *et al.*⁸. Since they used very low-molecular-weight polymers and did not specifically study the dependence on crystal structure and draw ratio, a quantitative comparison with their data will not be possible. For the overall behaviour of the dynamic modulus, the influence of side-chain length and the possible interpretation of mechanical relaxations, their results present a good starting point.

In this publication the temperature dependence of the tensile modulus and its relation to the specific structure of PTA12HQ will be addressed in greater detail. The

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Scheme 1



Scheme 2

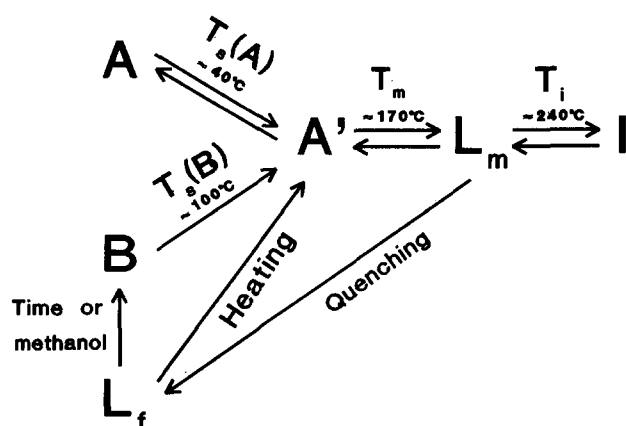


Figure 1 Scheme of the phase behaviour in PTA12HQ fibres⁷. The two room-temperature structures A and B can transfer to the intermediate phase A' at the respective side-chain disordering temperatures $T_s(A)$ and $T_s(B)$. At the main-chain melting temperature T_m , the layered mesophase L_m is formed, and the isotropic melt is reached at the clearing temperature T_i . By quenching from the layered mesophase L_m , the 'frozen-in layered mesophase' L_f is obtained, which slowly transforms to modification B

location, strength and frequency dependence of the relaxations occurring in the various crystal modifications and phases will be reported in order to gain insight into the structure-property relationship of this class of highly anisotropic polymers. As more information can be gained by varying the amount of the substituents, measurements on another polymer, PTA12HQ12, will be included. This polymer (Scheme 2) was characterized in previous publications^{2,7}.

In the accompanying paper⁹, results of a dielectric characterization will be presented. The combined results of dielectric and dynamic mechanical measurements will then be interpreted in order to elucidate further the molecular origin of the relaxations.

EXPERIMENTAL

Materials

The polymers used were synthesized as described earlier². 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 mesophase⁶.

Dynamic mechanical measurements

Dynamic tensile measurements were performed with an apparatus designed at the TNO Plastics and Rubber Research Institute. The temperature of the sample, ranging from -180 to 240°C , is controlled by a stream of heated dry nitrogen gas and is stable within 0.2°C . Measurements of the complex modulus are carried out at fixed temperature intervals and at several frequencies. The effective heating rate was approximately 10°C h^{-1} . The static prestrain amounted to 0.2% and the dynamic strain amplitude was 0.03%. Typical sample dimensions were a length of about 70 mm, a width of 10 mm and a thickness of 40 μm . Whenever possible, the measurements of PTA12HQ in the different phases were performed on the same sample, by a procedure used earlier⁶. In a typical experiment a sample was subjected to the following cycle:

run 1 (on modification B):

B \rightarrow A' (max. 140°C) \rightarrow slow cooling to -175°C

run 2 (on modification A):

A \rightarrow A' \rightarrow L_m \rightarrow quenching to -175°C

run 3 (on phase L_f):

L_f \rightarrow A' (max. 140°C) \rightarrow slow cooling to -175°C

run 4 (on modification A):

A \rightarrow A' \rightarrow L_m

The fourth run was included to test the influence of thermal history on the properties of modification A. It will be referred to when necessary in the description of the results.

RESULTS

Films of PTA12HQ: influence of orientation and crystal form

In Figures 2a to 2f the temperature dependence of the dynamic modulus and the loss tangent of PTA12HQ films in modification B, modification A and phase L_f are shown for different draw ratios λ . The observed frequency dependence is illustrated in Figure 3 (note the logarithmic scale) by plotting the loss data at 1 and 10 Hz for a sample with $\lambda = 3.3$. The regions of the side-chain disordering temperatures $T_s(A)$ and $T_s(B)$, as well as the melting transition to the layered mesophase T_m , as observed by d.s.c. are also indicated in these figures.

The dynamic mechanical data from Figures 2 and 3 display four relaxations that are labelled γ , β , β^* and α , starting from the lowest temperature. We prefer the above labelling (especially γ and β for the two low-temperature relaxations) to the one used by Schrauwen *et al.*⁸, because of its consistency with other comb-like polymers (see the accompanying paper⁹ for a further discussion regarding this point). Whereas these relaxations cause a gradual decrease of the modulus, more pronounced effects are observed on passing the respective side-chain disordering temperatures and the main melting transition, especially at the higher draw ratios. The activation energies associated with the observed relaxations, as derived from Arrhenius plots using the maxima of the $\tan \delta$ curves, are given in Table 1. In general, one can state that the four relaxations are present in all three crystalline modifications B, A and L_f with the same activation energies, suggesting the same underlying mechanisms. No specific dependence of the activation energies with the degree of orientation was observed except for one case: the peak temperature of the γ relaxation in modification B shifts from $\approx -157^\circ\text{C}$ at $\lambda = 1$ to $\approx -147^\circ\text{C}$ at $\lambda = 6$ (data at

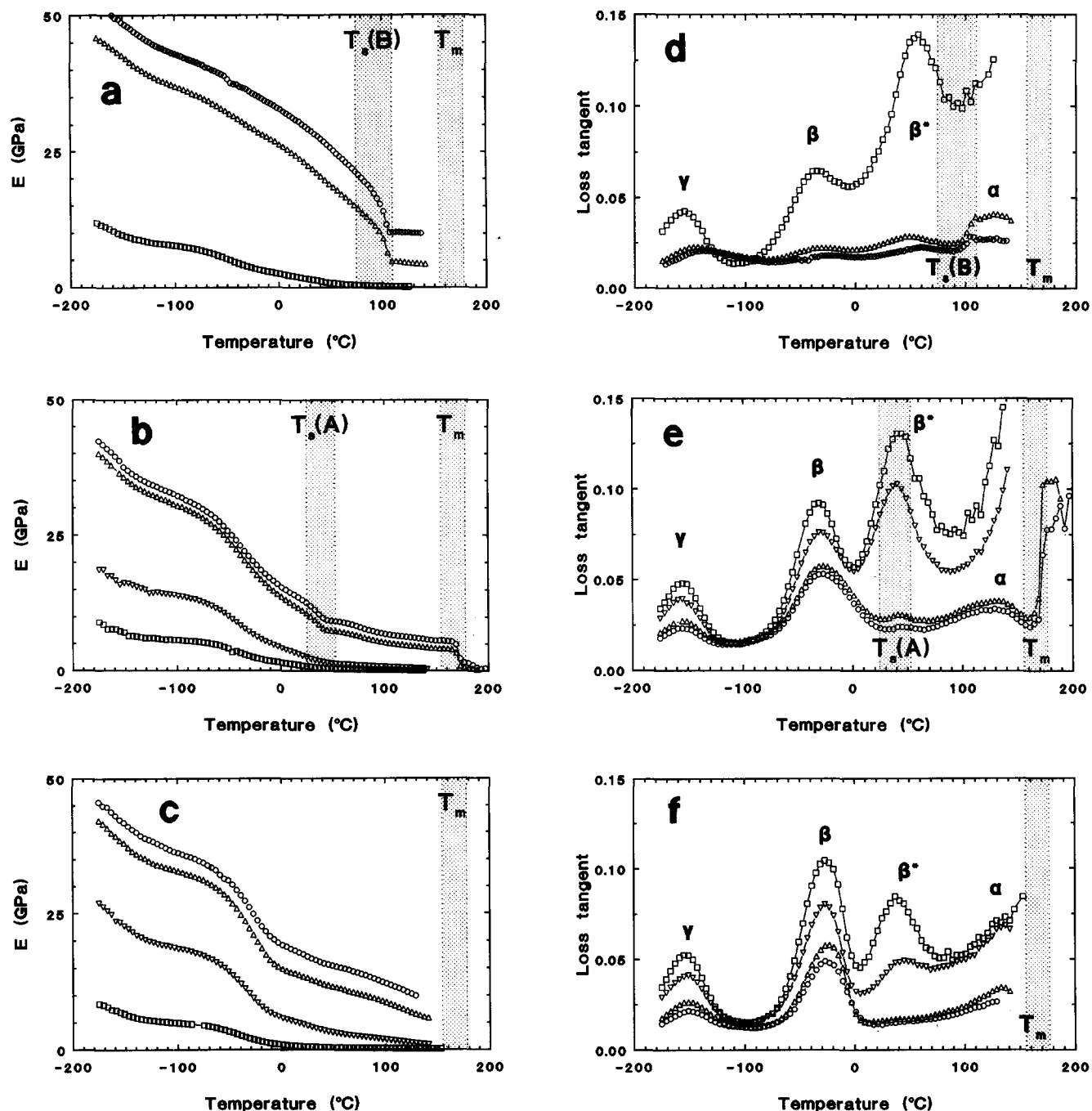


Figure 2 Observed temperature dependence of the dynamic modulus E and the loss tangent at 10 Hz of PTA12HQ films: (a), (d) modification B, $\lambda=1$ (\square), $\lambda=3.3$ (\triangle), $\lambda=6.1$ (\circ); (b), (e) modification A, $\lambda=1$ (\square), $\lambda=1.7$ (∇), $\lambda=3.3$ (\triangle), $\lambda=4.5$ (\circ); (c), (f) phase L_f , $\lambda=1$ (\square), $\lambda=2.2$ (∇), $\lambda=3.3$ (\triangle), $\lambda=5.1$ (\circ). Shaded areas indicate phase transition regions as measured by d.s.c.

1 Hz). The most prominent feature upon orientation is a decrease in intensity of all observed relaxations, as reflected by the loss tangent (note that nevertheless this corresponds to an increase of E''). The extent of the decrease, however, is quite different for the three modifications. As will be outlined further on, this observation mainly accounts for the differences in attainable mechanical properties. The side-chain disordering in modification B is seen as a distinct drop in modulus, whereas in modification A it overlaps with the β^* relaxation but remains visible as an irregularity in the modulus. The melting at T_m is obvious from the results on modification A (Figure 2b). In the following paragraphs we will examine the temperature dependence of the modulus in films of PTA12HQ more closely.

At the lowest temperature investigated (-175°C), the attainable modulus is about 50 GPa for modification B and about 45 GPa for A and L_f . Unoriented films display a modulus around 10 GPa. At still lower temperatures, no significant increase is expected considering the theoretical modulus⁶. The γ relaxation, located at about -160°C , produces similar effects in all three phases. The subsequent β relaxation, located at about -35°C , is much more prominent (higher loss tangent at a comparable degree of orientation) in modification A and phase L_f than in modification B. For highly oriented films in modification B, the β loss peak has nearly vanished and the decrease of the modulus is substantially smaller compared to modification A and phase L_f . As a result the attainable modulus at room temperature in modifi-

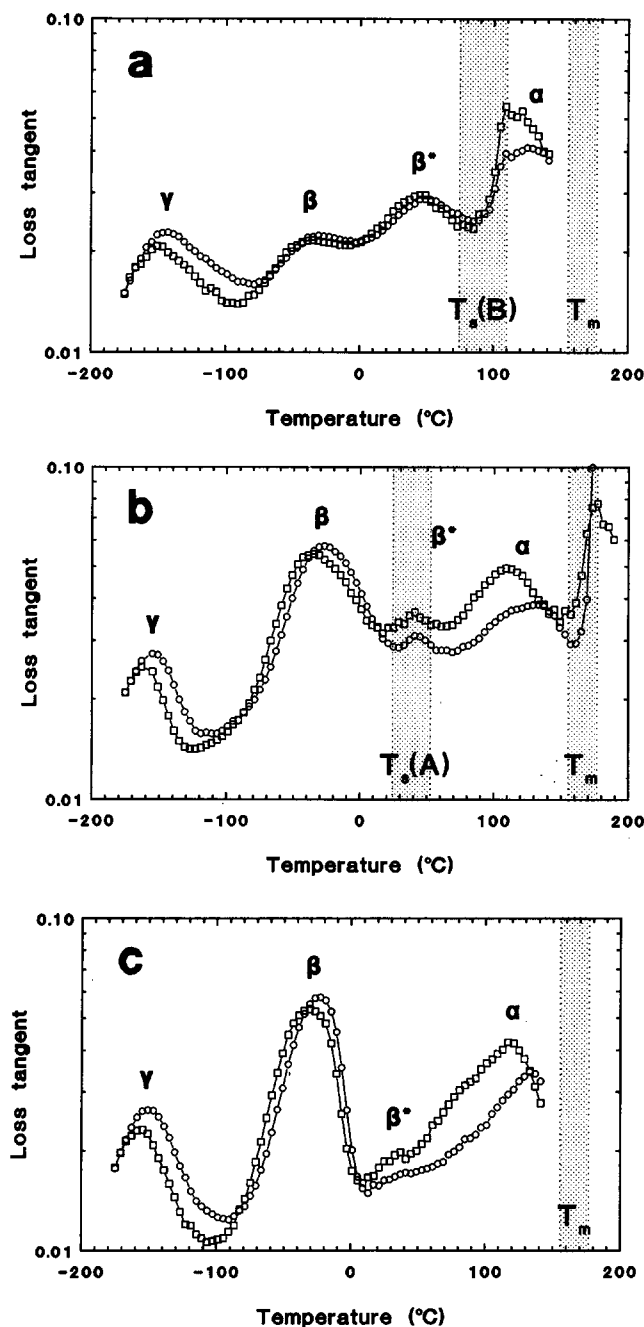


Figure 3 Loss tangent of oriented PTA12HQ films ($\lambda=3.3$) at 1 Hz (\square) and 10 Hz (\circ) in (a) modification B, (b) modification A and (c) phase L_f . Shaded areas indicate phase transition regions as measured by d.s.c.

Table 1 Apparent activation energies for the observed dynamic mechanical relaxations

Polymer	Activation energy, E_A (kJ mol^{-1})			
	γ	β	β^*	α
PTA12HQ (B)	38 ± 10	135 ± 25	360 ± 100	–
PTA12HQ (A)	35 ± 10	150 ± 25	320 ± 100	200 ± 35
PTA12HQ (L_f)	40 ± 10	155 ± 25	280 ± 100	230 ± 40
PTA12HQ12	36 ± 10	125 ± 25	300 ± 100	–

modification B (30 GPa) is about twice as high as in A and L_f . For unoriented films, the situation is even more illustrative: in the order B, A, L_f room-temperature moduli of 2, 1, 0.6 GPa are observed, thereby closely reflecting the intensity increase of the β peak in the same order. Since

the main difference between the three modifications lies in the (crystalline) packing of the side chains, we may anticipate the β relaxation being related to the less-ordered or amorphous fractions of the side chains.

Above room temperature the behaviour of the modulus is governed by the β^* relaxation (around 50°C) in combination with the respective side-chain disorderings. First, it should be noted that the β^* peak displays some peculiarities. For unoriented films, where this relaxation appears very strong in the $\tan \delta$ plots, a shoulder seems to develop in the B modification on the low-temperature side of the loss data at lower frequencies (0.1 Hz). Also in modification A, where the transition at $T_s(A)$ interferes with β^* , some indeterminacy may exist. In particular, it was found that at the highest draw ratios the location of the remaining peak in the β^* region became independent of frequency, thus pointing to a strong relation with $T_s(A)$. Consequently, the determination of the real β^* peak temperature and the activation energy is less reliable in both cases. In phase L_f a 'clean' peak seems to be present, but the intensity is low compared to modifications B and A. A lower intensity was also found when a fourth heating run was performed to measure modification A again. From this we conclude that, without heating to above the main-chain melting temperature T_m , the β^* relaxation in modification A resembles that in modification B, whereas, after having been heated to above T_m , modification A shows more characteristics of phase L_f . Apparently there is a gradual change-over between the A and L_f structures, and the final state is determined by the cooling procedure. Furthermore, it is interesting to note that there is a correlation between the intensities of the β and β^* relaxations: the stronger the β peak the weaker β^* , as can best be seen from the respective data in Figure 3 (all at the same draw ratio). In spite of the observed peculiarities the modulus behaviour in the β^* region is obvious. In highly oriented films the β^* relaxation is weak or even absent and accompanied by a gradual change in modulus only. In the B and A modifications the effect of the side-chain disordering is distinctly more pronounced. Especially, the observed drop in modulus at $T_s(B)$ indicates a rather abrupt loss of correlation between the main-chain layers.

Eventually, around 110°C when the modifications have successively entered the A' phase (see Figure 1), all moduli are at the same level of about 10 GPa. In unoriented films the falling off at $T_s(B)$ and $T_s(A)$ is less pronounced, and a gradual decrease results in a level of 0.1 GPa at 110°C for all cases. The α relaxation has no particular effect on the modulus and seems independent of thermal history, as expected. Finally, on entering the layered mesophase L_m at 170°C, the oriented films lose their stiffness.

Films of PTA12HQ12: doubling the amount of side chains

The temperature dependences of the modulus and loss tangent of unoriented films of PTA12HQ12 are shown in Figures 4a and 4b. For comparison, the data of an unoriented PTA12HQ film in modification B are indicated. The activation energies as derived from the observed frequency dependence are included in Table 1.

For PTA12HQ12, we see that the γ , β and β^* relaxations compare very well with PTA12HQ, with regard to the peak position, the activation energy and the resulting effect on the modulus. Only the intensity of the β^* loss tangent is lower in PTA12HQ12. Moreover,

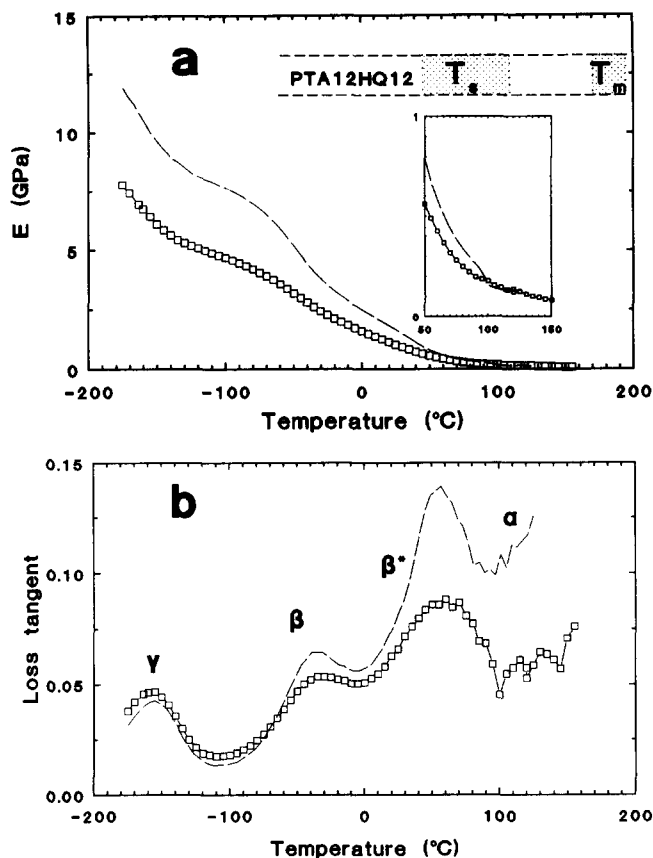


Figure 4 (a) Dynamic modulus E and (b) loss tangent $\tan \delta$ at 10 Hz of unoriented PTA12HQ12 films. For comparison, the data of an unoriented PTA12HQ film in modification B are included as a broken curve. Shaded areas indicate phase transition regions as measured by d.s.c.

the high-temperature side of this relaxation coincides with the side-chain disordering ($T_s \approx 85^\circ\text{C}$). The smaller magnitude of the tensile modulus in PTA12HQ12 can at least partially be ascribed to the lower density of main chains in this system. Above 100°C the moduli of both systems display matching values of the order of 0.1 GPa (insert of *Figure 4a*). This is in agreement with the fact that the mechanical behaviour is now governed by the inter-chain interactions. The loss data in the α region are too inaccurate to allow a detailed comparison. All together the observed temperature dependence in PTA12HQ12 corroborates the behaviour found in PTA12HQ to a large extent.

CONCLUSIONS

In previous research the main-chain liquid-crystalline system PTA12HQ was found to exhibit three low-temperature structures denoted by B, A and L_f , which are characterized by a difference in side-chain packing, viz. from highly crystalline to largely amorphous in the order given. In this investigation, it has been shown that the different side-chain packings can give rise to large

differences in the tensile properties of oriented films, especially in the region around room temperature. The most prominent effects arise because of the β relaxation around -35°C . Since this relaxation is much less pronounced in modification B (maybe even absent at maximum orientation), the room-temperature modulus in this structure turns out to be substantially higher than in A and L_f at the same degree of orientation. From this observation it can be deduced that the β relaxation is associated with the disordered fraction of side chains. Above room temperature, a β^* relaxation appears in all modifications, causing a gradual modulus decrease. In addition, the modifications B and A exhibit side-chain 'melting' with a more distinct drop in modulus. Ultimately, when all structures have entered the A' phase above 110°C , the dynamic moduli reach the same level and after passing the α relaxation the film stiffness is lost at the main-chain melting point around 170°C . Measurements on PTA12HQ12, to study the effect of variation of the amount of side chains, give additional evidence. PTA12HQ12, also with a crystalline side-chain packing and associated melting transition, shows much the same behaviour as modification B of PTA12HQ.

Summarizing, it can be stated that the mechanical behaviour of the described systems can be understood by taking into consideration the structural arrangement: rigid main-chain layers separated by aliphatic side chains. At very low temperatures, the attainable modulus in oriented films is set by the stiffness of the main chains, while the successive disordering processes of the side chains account for most of the observed temperature dependences.

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