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Liquid crystalline main chain polymers with a poly(*p*-phenylene terephthalate) backbone: 3. Drawing, structure development and ultimate mechanical properties of films of the polyester with dodecyloxy side chains

S. B. Damman* and F. P. M. Mercx

TNO Plastics and Rubber Research Institute, PO Box 6031, 2600 JA Delft, The Netherlands

and P. J. Lemstra

Eindhoven University of Technology, Centre for Polymers and Composites, PO Box 513, 5600 MB Eindhoven, The Netherlands

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Solution-cast films of poly(*p*-phenylene 2,5-didodecyloxyterephthalate) were characterized by X-ray diffraction, differential scanning calorimetry and mechanical measurements. Three different structures, in which the main chains are arranged in layers separated by the interdigitating side chains, could be distinguished. In the as-cast films these layers are parallel to the film surface. Upon drawing, the backbones of the chains orient parallel to the drawing direction, while most of the parallel orientation of the layers with respect to the film surface is maintained. At room temperature the Young's moduli of the less-ordered phases, termed A and L_r, are approximately 15 GPa, which is rather low in comparison with the value of almost 30 GPa found for the third modification, termed B. However, below the β-relaxation at ~ -20°C the moduli of all three phases are of the same order of magnitude. At -175°C they are in line with the theoretically predicted modulus of 50 GPa.

(Keywords: rigid rod polymer; thermotropic; modulus; orientation)

INTRODUCTION

Thermotropic main chain polyesters have been studied extensively in the past and much effort has been devoted towards a better understanding of their physical and mechanical properties in relation to the molecular structure. In our studies, we have focused on poly(*p*-phenylene terephthalate)s with alkoxy substituents on the hydroquinone and/or the terephthalate moiety^{1,2}.

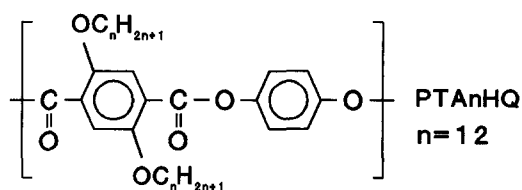
In this paper, some results are presented concerning the polyester with dodecyloxy side chains on the terephthalate moiety, poly(*p*-phenylene 2,5-didodecyloxyterephthalate) (PTA12HQ). The chemical structure is depicted in *Scheme 1*. This polymer has been studied earlier by Ballauff and Schmidt³, Schrauwen *et al.*⁴ and the present authors^{1,2}. It was shown³ that in this polymer layered structures, in which main chain layers are separated by interdigitating side chains, exist up to the transition to the isotropic melt. Based on the work of Ballauff and Schmidt³ and our own measurements we proposed¹ the extended phase behaviour shown in *Figure 1*. Schrauwen *et al.*⁴ showed that the main chain layers extend parallel to the film surface in solution-cast films. They also presented some results of mechanical measurements of oriented PTA12HQ films.

We were able to synthesize PTA12HQ of a higher molecular weight, which enabled us to draw solution-cast films. These films, ranging from isotropic to nearly perfectly oriented structures, could be studied in all the phases shown in *Figure 1*.

The aim of the investigation presented here was to study the mechanical properties of these oriented samples in the light of recent reports in the literature that solubilizing side chains could have a detrimental effect on the experimentally obtainable Young's modulus⁵.

EXPERIMENTAL

Two batches of PTA12HQ were used in this study, a medium-molecular-weight batch (MM) with an inherent viscosity of 2.3 dl g⁻¹ (chloroform, 25°C), and a relatively high-molecular-weight batch (HM) with an inherent viscosity of 3.1 dl g⁻¹. The synthesis of this polymer has been described elsewhere¹.



Scheme 1

* To whom correspondence should be addressed

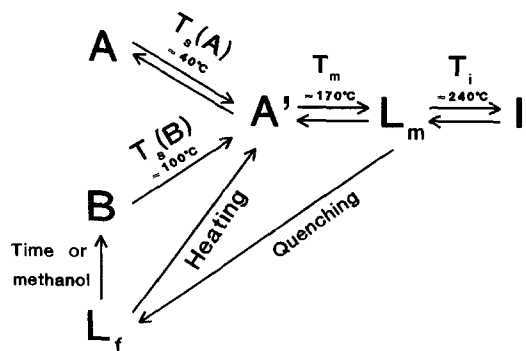


Figure 1 Schematic representation of the phase behaviour in PTA12HQ fibres². The two room temperature structures A and B can transfer to the intermediate phase A' at the side chain disordering temperature T_s . At the main chain melting temperature T_m the layered mesophase L_m is formed and the isotropic melt I is reached at the clearing temperature T_i . By quenching from the layered mesophase the 'frozen-in layered mesophase' L_f is obtained, which slowly transfers to structure B

For film casting a clear and isotropic solution of 6% (w/w) (at higher concentrations gelation occurred) of polymer in chloroform was used. Before film casting this solution had been filtered (at a lower concentration to reduce the viscosity) on a Teflon filter of pore size $0.5 \mu\text{m}$ to remove dust particles.

Differential scanning calorimetry (d.s.c.) thermograms were recorded under nitrogen atmosphere with a DuPont 9900 DSC. A heating rate of $20^\circ\text{C min}^{-1}$ was used.

Oriented films were obtained by drawing the cast films in an oven. The oven and sample were heated by passing preheated dry nitrogen gas through the oven. The drawing speed was 2 or 5 cm min^{-1} and the specimen length and width, before drawing, were 6–7 and 2–4 cm, respectively. The thickness of these films could be measured with an accuracy of $\pm 2 \mu\text{m}$.

Flat-plate X-ray diffractograms were made using Ni-filtered $\text{Cu K}\alpha$ radiation. Orientation was quantified by measuring the half-width at half-height of the equatorial reflections.

Dynamic tensile moduli of the films were measured with a dynamic mechanical analyser, built and designed in these laboratories, which will be described in more detail in a subsequent publication. The static strain was 0.2% and the dynamic strain amplitude 0.03%. Temperature control was within 1°C . The applied heating rate was approximately 10°C h^{-1} .

RESULTS AND DISCUSSION

Preparation and characterization of solution-cast films

Both PTA12HQ polymers, MM and HM, were cast from a chloroform solution at room temperature on a glass plate. After evaporating the solvent, thin films were obtained with a reasonably uniform thickness of approximately $40 \mu\text{m}$.

X-ray diffraction. X-ray diffraction measurements confirmed the existence of layered structures in the cast films. The typical X-ray diffraction patterns, with the primary X-ray beam respectively perpendicular to and parallel with the film surface, are shown in Figure 2a and b. The isotropic diffraction rings shown in Figure 2a and the appearance of the layer distance d on the equator in Figure 2b confirm the model proposed by Schrauwen

*et al.*⁴. In this model, which is shown in Figure 3a, the main chain layers extend uniformly over the whole sample, parallel to the film surface.

For the MM film, a layer distance d of 15.2 \AA typical³ for modification B was found. The HM film showed a layer distance d of 16.7 \AA . This distance was also found

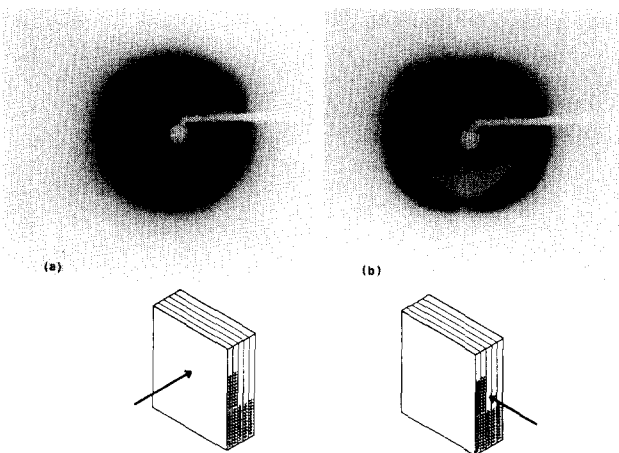


Figure 2 Flat-plate X-ray diffractograms of as-cast PTA12HQ film 1 (MM polymer) with the beam (a) perpendicular to and (b) parallel with the film surface. Sample-to-film distance 6 cm

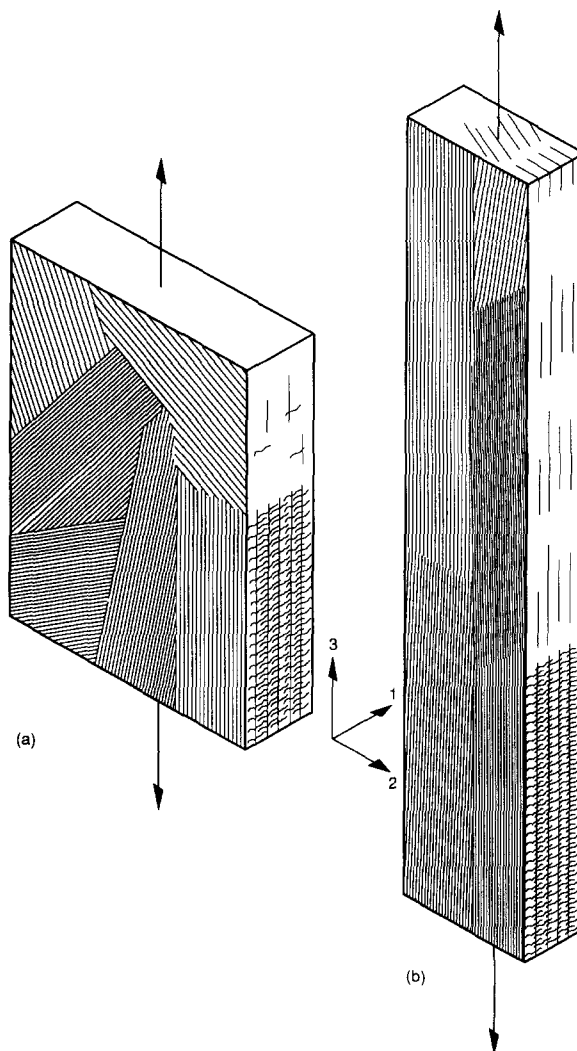


Figure 3 Structure of the solution-cast films as proposed by Schrauwen *et al.*⁴. (a) As-cast film. (b) oriented film. The direction of the X-ray beam is indicated

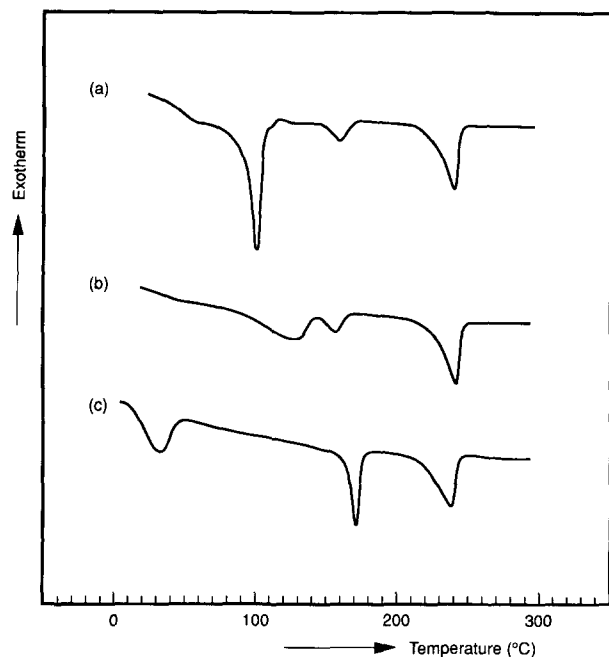


Figure 4 D.s.c. thermograms of PTA12HQ: (a) film 1 (MM polymer); (b) film 2 (HM polymer); (c) second heating run for film 1 (second heating run for film 2 is similar)

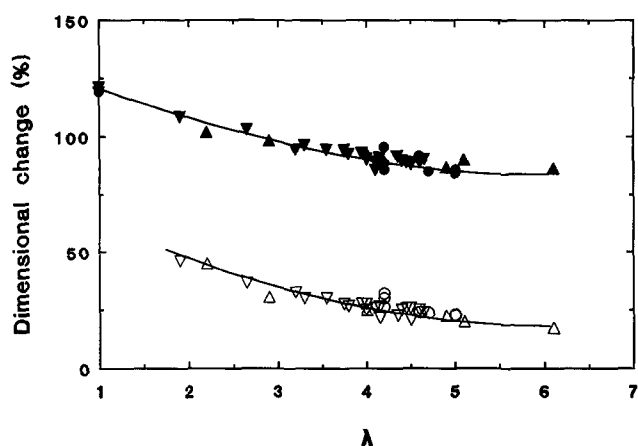


Figure 5 Change in room temperature thickness and width of the PTA12HQ films after drawing at 205°C. (○) Film 1 (MM polymer), 2 cm min⁻¹, (▽) film 2 (HM polymer), 2 cm min⁻¹, (△) film 2, 5 cm min⁻¹. Closed symbols refer to the thickness, open symbols to the width

by Schrauwen *et al.* and was considered to be an insignificant deviation from the modification B layer distance⁴.

D.s.c. Figure 4 shows the thermal behaviour of the as-cast films. Curve a, for the MM polymer, is typical for the thermal behaviour of modification B, which was also observed earlier for powders¹ and fibres². Clearly the HM film (curve b) shows different thermal behaviour. Though we do not know the exact cause of this difference, it is clear that the structure in the HM film cannot be regarded as an insignificant deviation from modification B. For the film-drawing experiments, however, this point is of no importance since the structures in both the MM and the HM films change to modification A after heating to above the main chain melting temperature T_m . As an example of this the second heating run of the MM film

is shown in Figure 4, curve c. Identical thermal behaviour was observed earlier for powders¹ and fibres² in modification A.

Drawing behaviour of PTA12HQ films. The solution-cast films, both MM and HM, could be drawn quite easily above the main chain melting temperature T_m , i.e. in the layered mesophase. The films deform homogeneously upon drawing and no necking is observed whereas the width of the sample decreases almost proportionally to the draw ratio λ (see Figure 5). This observation conforms with aligning of domains, rather than deforming individual chain molecules.

The thickness of the specimen increases upon heating to the drawing temperature before drawing, i.e. $\lambda=1$, and upon deformation only a slight decrease is observed (Figure 5). This observation can be explained in terms of the phase transition from B to 'frozen-in layered mesophase', L_f , via layered mesophase, L_m (Figure 1), which is accompanied by an increase of about 20% in the layer distance d to about 20 Å.

As the thickness of the films does not decrease significantly during drawing (Figure 5) it is inferred that the main chain layers retain most of their parallel ordering with respect to the film surface on drawing (see Figure 3). This was investigated in more detail by X-ray diffraction. In Figure 6 the X-ray diffraction patterns along the three principal directions of a film stretched to $\lambda=2.1$ are shown. The diffractogram with the beam parallel to the drawing direction (Figure 6c) shows that the layer distance d is found on the equator, which is in agreement with main chain layers extending parallel to the film surface (Figure 3). The clearly distinguishable patterns shown in Figure 6a and b also agree with this.

The alignment of the main chains parallel to the drawing direction can be expressed quantitatively by plotting the orientation angle ϕ as a function of the draw ratio λ (Figure 7). The orientation angle ϕ was derived from the half-width at half-maximum intensity of the major equatorial reflections. If the degrees of orientation obtained are compared with the degree of orientation obtained earlier for drawn PTA12HQ fibres ($\phi=6$ at $\lambda=7$, see ref. 2) it can be concluded that drawing of films is more effective. The degree of orientation obtained in the fibres is comparable to that of a film with $\lambda \approx 3$. This can be explained by the starting structures in the unoriented films and fibres, which have a relatively high and low degree of ordering respectively (the as-cast films show in-plane ordering, while the fibre was 'quenched' from the isotropic melt). The lower molecular weight (inherent viscosity 2.3 dl g⁻¹) of PTA12HQ used for fibre spinning also influences the maximum obtainable degree of orientation.

Modulus at different temperatures. The moduli of the films in modifications A and B and phase L_f were measured by dynamic mechanical thermal analysis (tensile). To allow a good comparison between the moduli of these three different structures in the solid state, most mechanical measurements were performed starting with PTA12HQ films in modification B (obtained by recrystallization in methanol as described earlier for fibres²). The other two solid-state structures (with essentially the same degree of orientation) were obtained during the measurement, as will be explained with reference to Figure 8. During measurement, phase

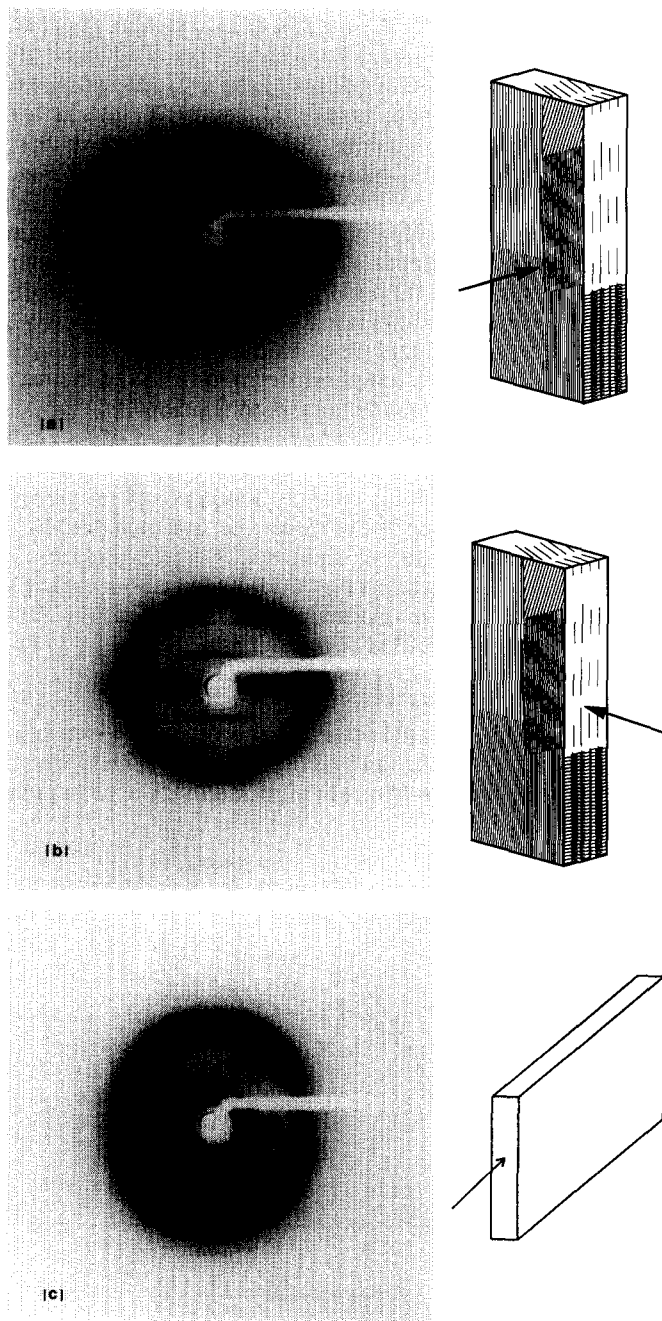


Figure 6 Flat-plate X-ray diffractograms of a PTA12HQ film in the 'frozen-in layered mesophase' L_r ($\lambda=2.1$) with the beam (a) along direction 1; (b) along direction 2; (c) along direction 3. Sample-to-film distance 6 cm

transformations according to the scheme shown in *Figure 1* occur.

In *Figure 8a* (solid curve), the dynamic tensile modulus of a highly oriented PTA12HQ film in modification B is shown as a function of temperature. This measurement was started at -175°C and continued until a temperature of 140°C was reached. At this temperature the structure of the polymer has changed from modification B to structure A' (ref. 2). On cooling a transition from structure A' to modification A occurs and a new measurement was started at -175°C (*Figure 8a*, dashed curve). This measurement is continued until the polymer is in the layered mesophase at about 180°C . By quenching the sample to -175°C phase L_r is obtained². The modulus of this structure can be measured to 140°C (*Figure 8b*, short-dashed curve), where the polymer is

again in structure A'. Subsequent cooling to -175°C yields structure A which is again measured (*Figure 8b*, long-dashed curve). The advantage of this method is that all structures can be characterized in a relatively easy way.

From the loss tangent, also shown in *Figure 8*, it is clear that several relaxations, of which the location and intensity depend on the solid-state structure, exist in PTA12HQ. Most of these relaxations were also found recently by Schrauwen *et al.* in films with a lower degree

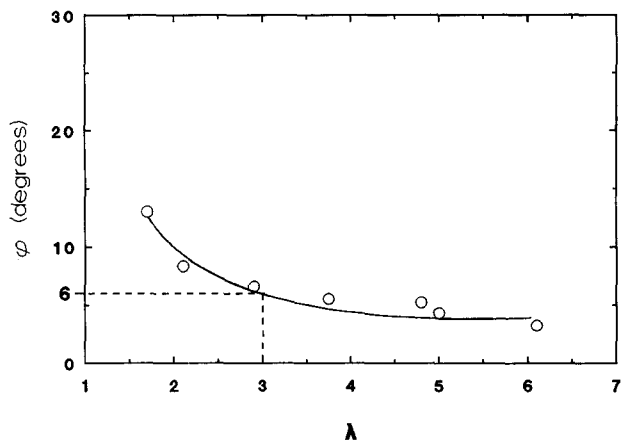


Figure 7 Orientation angle ϕ as a function of the draw ratio λ . An angle ϕ of 6° is indicated to make a comparison with orientation angles obtained for fibres²

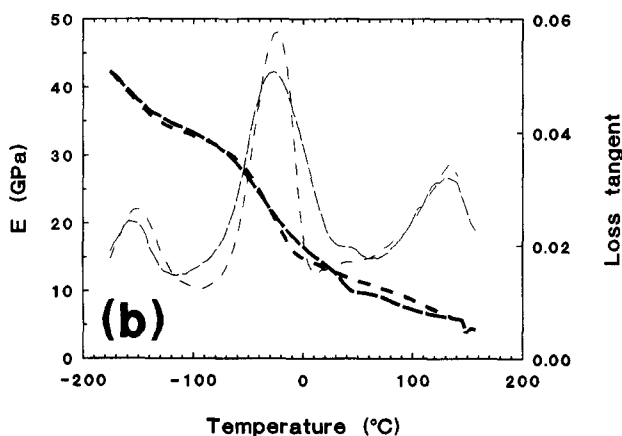
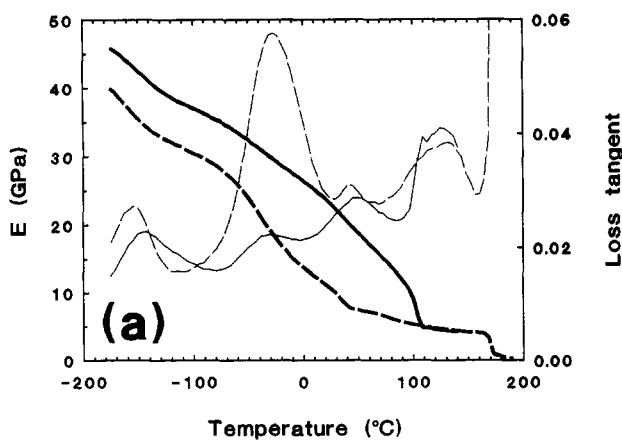


Figure 8 Dynamic tensile modulus and loss tangent at 10 Hz as a function of temperature ($\lambda=3.3$). (a) First and second heating runs (modulus and loss tangent respectively): (—, —) modification B; (---, ---) modification A. (b) Third and fourth heating runs (modulus and loss tangent respectively): (---, ---) phase L_r ; (—, —) modification A

of orientation⁴. In a subsequent paper⁶ the possible molecular origins of these relaxations, denoted as γ , β , β^* and α , will be discussed. As the modulus can drop significantly upon passing such a relaxation, the moduli at -175°C , -95°C and 25°C (temperatures just before or after the major relaxations, see Figure 8) are used to illustrate the mechanical behaviour of PTA12HQ in the remainder of this paper.

As stated above, the main objective of this work is to determine the ultimate mechanical properties that can be achieved in the system under consideration. Therefore in Figure 9 the dependence of the modulus of the three different solid phases, measured at 25°C , has been plotted as a function of the draw ratio. In this figure three regions can be discerned. In region I ($\lambda=1-2$) the modulus is largely determined by intermolecular interactions between the chains and moduli of 1-3 GPa are obtained. Such moduli are comparable to that found for unoriented flexible polymers. In the intermediate region II ($\lambda=2-3$) the rigid main chains become load-bearing and start to influence the modulus. In region III the main chains are aligned to a very high degree and govern the film properties. At an infinite draw ratio, where a perfect orientation is obtained, the modulus will reach its limiting value.

At this point it is very instructive to make a comparison with previous results obtained by this group on fibres² and by Schrauwen⁴ on films of PTA12HQ. As noted earlier (Figure 7), the fibre moduli reported in ref. 2 can be compared with film moduli at $\lambda=3$. This is done in Figure 9, which shows a good agreement between the film and the fibre moduli at a comparable orientation angle ϕ . The value reported by Schrauwen⁴ (≈ 0.8 GPa at $\lambda \approx 3$) cannot be brought into line with our results. Most probably their films could be drawn less effectively because of the lower molecular weight (inherent viscosity $=1.45$ dl g⁻¹) of the polymer they used. This is in agreement with our experiments on PTA12HQ films with an inherent viscosity <2 dl g⁻¹. The lower molecular weight might also lead to more defects and thus a lower modulus.

As was already clear from Figure 8, the modulus increases upon lowering the temperature. Upon passing the relaxation at about -20°C (which is associated with the side chains^{4,6}) the moduli of the two least-ordered

phases, modification A and phase L_f , start to approach the modulus obtained for modification B (Figure 10). Apparently the lower modulus of the less-ordered phases at room temperature is caused by weak interactions between the main chains, obstructing effective force transfer between the main chains. At this point it is not clear whether this poor force transfer takes place within the main chain layers or between two adjacent chains (over the layer distance d) in the planes formed by main and side chains. It can only be concluded that the strong relaxations in modification A and L_f , taking place at $\approx -20^\circ\text{C}$, are largely responsible for the substantial differences in room temperature moduli found between these less-ordered phases and modification B.

At the lowest measurement temperature of -175°C another relaxation has been passed. From Figure 11, in which the modulus at this temperature is plotted as a function of the draw ratio, the limiting moduli at this temperature can be deduced. For modification A and phase L_f the limiting modulus is about 45 GPa. The limiting value estimated for modification B is approximately 50 GPa.

Comparison with the theoretical modulus

The experimentally determined limiting low-temperature values of the moduli of oriented PTA12HQ can be compared with the theoretical modulus of a substituted

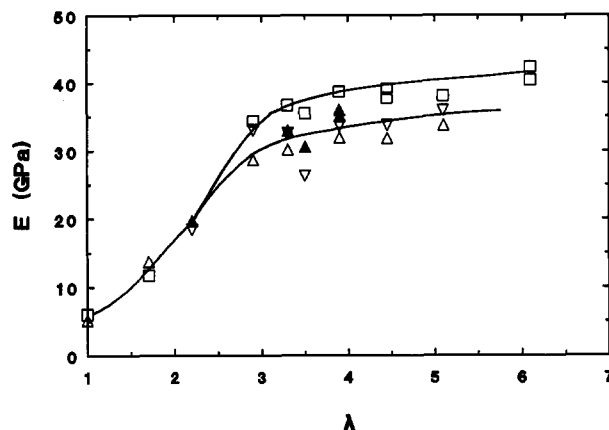


Figure 10 Modulus at 10 Hz and -95°C as a function of the draw ratio λ : (\square) Modification B; (\triangle , \blacktriangle) modification A (\triangle , second and \blacktriangle , fourth heating run); (∇) phase L_f

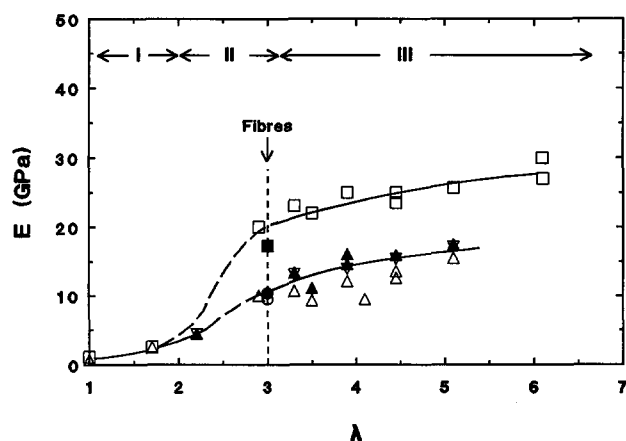


Figure 9 Modulus at 10 Hz and 25°C as a function of the draw ratio λ . (\square) Modification B; (\triangle , \blacktriangle) modification A (\triangle , second and \blacktriangle , fourth heating run); (∇) phase L_f ; (\blacksquare , \bullet , \circ) fibres (\blacksquare , modification B, \bullet , modification A and \circ , phase L_f)

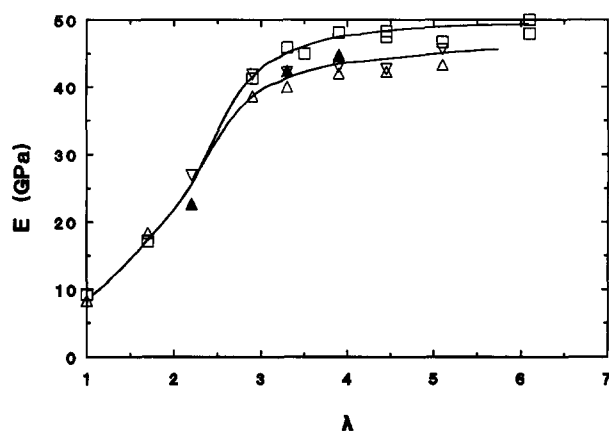


Figure 11 Modulus at 10 Hz and -175°C as a function of the draw ratio λ . (\square) Modification B; (\triangle , \blacktriangle) modification A (\triangle , second and \blacktriangle , fourth heating run); (∇) phase L_f

poly(*p*-phenylene terephthalate) (pPT) main chain. Based on lattice dynamic equations Tashiro and Kobayashi⁷ calculated a theoretical Young's modulus, E_{pPT} , of 178 GPa for non-substituted pPT by using an effective cross-sectional area of the chain A_{pPT} of 21 \AA^2 . From these values the maximum contribution of the PTA12HQ main chains to the fibre modulus, E_{max} , can be calculated by taking the effective cross-sectional area of a PTA12HQ chain, A_{PTA12HQ} , into account according to the following equation:

$$E_{\text{max}} = E_{\text{pPT}} A_{\text{pPT}} / A_{\text{PTA12HQ}}$$

This equation is derived from the Halpin–Tsai equation for multiphase composites by assuming a large aspect ratio of the load-bearing main chains (Voigt average) and by neglecting the contribution from the side-chain matrix (estimated to be in the order of 1–2 GPa⁸).

The effective cross-sectional area of a PTA12HQ main chain can be calculated from the molecular weight of the repeat unit, the experimental density of the fibres and the repeat distance of the main chain, which were reported earlier², and are 77, 76 and 74 \AA^2 for phase L_f , modification A and modification B, respectively. The resulting calculated moduli of the main chain contribution differ only slightly for the three solid phases and are about 50 GPa.

According to Ii *et al.*⁹ the comparison between the measured modulus and the experimental modulus should be made at absolute zero. This value can be estimated from the modulus–temperature curves by extrapolation. As no strong relaxations below -175°C are expected, the zero temperature moduli of the different structures are estimated to be close to (within 10%) the values at -175°C ($\approx 50 \text{ GPa}$, see *Figure 11*). We may therefore conclude that the experimentally determined moduli of PTA12HQ agree well with theoretical values.

CONCLUSIONS

Upon orienting a PTA12HQ film the sheet-like structure of main and side chains, which resembles a sandwich, is largely preserved while the domains are aligned.

The modulus at room temperature depends on the

solid-state structure and is in good agreement with measurements on fibres with a comparable degree of orientation. At low temperatures the moduli of the different solid phases are almost equal. From this it is concluded that the lower values of the room temperature moduli of modification A and L_f are mainly caused by a poor force transfer between the main chains. The relaxation associated with this process is located at approximately -20°C .

A comparison of the experimentally determined moduli extrapolated to absolute zero with the theoretically predicted modulus of 50 GPa shows good agreement (within 10%).

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