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Approximation of the chain modulus of aromatic polyesters and a poly-*para*-phenylene with aliphatic side chains

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A systematic series of well-defined aromatic polyesters and a poly-*para*-phenylene with aliphatic side chains were investigated. Films were mechanically characterized by DMTA. The chain modulus was estimated using an extrapolation method based on the aggregate model. The extrapolated values are comparable with theoretically calculated moduli, but display a fairly large uncertainty. Comparison of the theoretical values with the experimentally attained moduli showed an increasing discrepancy for higher molecular rigidity. The theoretical modulus increases with increasing molecular rigidity, while the experimental moduli (at low temperature and corrected for the cross-sectional area of the side chains) do not exhibit a specific dependence on the molecular rigidity, and range between 140 and 180 GPa. This important effect was ascribed to increasing processing difficulties, which is shown by the maximum draw ratio obtained. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Thermotropic (melt-processable) liquid-crystalline polymers (TLCPs) possess the unique combination of high mechanical properties and thermal resistance, and outstanding processibility into highly oriented structures. These favourable properties are all related to the rigid-rod nature of the polymeric chain; the inherent chain rigidity directly accounts for the achievable mechanical properties and thermal stability, while the processing advantages proceed from the occurrence of a liquid-crystalline melt[1]. The presently available commercial TLCPs are in fact random copolymers based on rigid aromatic units (mostly phenylene or naphthalene) and ester or amide linkages. The melting temperatures of these commercial TLCPs are in the range 250–400°C. The tensile modulus varies from about 10 GPa in injection moulded parts to about 100 GPa in highly oriented fibres, while a tensile strength of about 1 GPa can be reached[1]. Systematic study of the relation between the molecular structure and the resulting mechanical properties of commercial LCPs is hampered by the random nature of the chain. We have chosen to investigate the relation between orientation and mechanical properties of rigid-rod polymers with a well defined structure of the main chain and with flexible side chains for achieving the melt-processability[2]. The chemical structures of the polymers involved in this investigation are depicted in *Scheme 1*. The molecular structure is based on well defined sequences of *p*-phenylene units, either coupled directly or by means of ester groups. Aliphatic side chains of different lengths were included. The rigidity of these chains in solution, as

reflected by the persistence length, was studied by Ballauff and coworkers[3,4] and Petekidis *et al.*[5] Their results indicated an increase in molecular rigidity with a longer sequence of *p*-phenylene units, as expected. In a previous paper[6] we described the structure and orientation development of a number of these polyesters. The determination of the chain modulus or the ultimate modulus of stiff chain polymers has been the subject of many studies. Damman *et al.*[7] measured a low temperature modulus of a PTA12HQ-film very close to the theoretical value obtained by Tashiro and Kobayashi[8], after correcting for the area occupied by the side chains. This meant that they reached a virtually perfect orientation. Furthermore, they showed that solubilizing side chains were not so detrimental for the obtainable modulus as stated by Postema *et al.*[9], who studied a system in which each rigid main chain was completely surrounded by flexible side chains. Apparently, if the main chains remain in sufficient contact with each other as in the layered structure of a PTA12HQ-film, a fairly high modulus can be retained. In this paper the achievable moduli in the systematic range of rigid-rod polyesters are studied and it is attempted to determine the chain moduli by extrapolating the experimental modulus values of highly oriented films at a low temperature to perfect orientation.

EXPERIMENTAL

Materials

The various polyesters and the poly-*para*-phenylene were synthesized according to procedures described by Tiesler *et al.*[3] and Galda[4], respectively. The molecular weights and thermal properties of most of the polyesters can be found in a previous paper[6]. The polyester PES3.5-C6 displayed a

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PTA12HQ

PES1.3/C12

PES1.3/C6

PES3.3/C6

PES3.5/C6
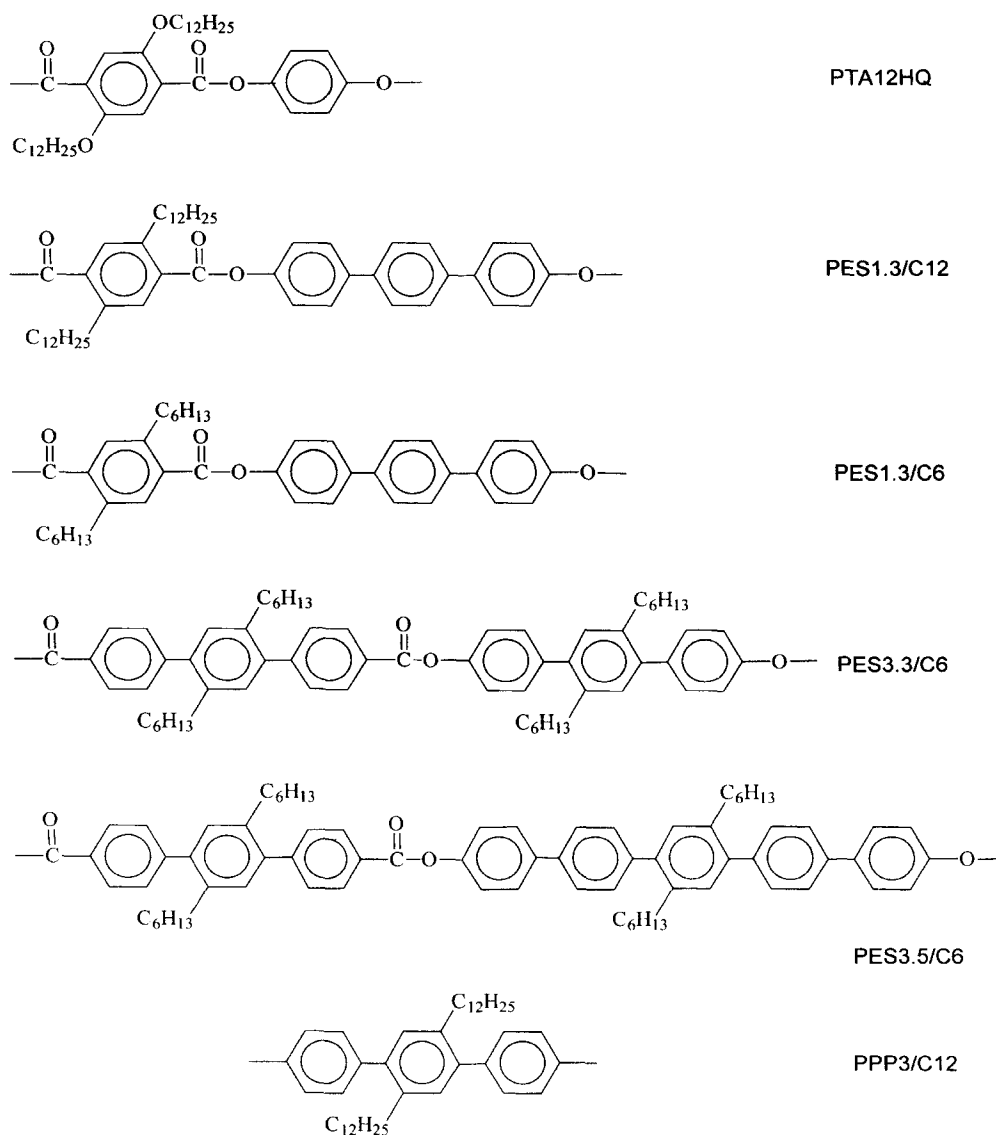
PPP3/C12

Scheme 1

main endothermic transition at 362°C; the intrinsic viscosity could not be determined due to its limited solubility. The poly-*para*-phenylene PPP3-C12 had a main endothermic transition at 144°C, and an intrinsic viscosity of 1.48 dl/g (in chloroform at 25°C).

Film casting and drawing

Films were made by casting from an isotropic solution of 3–6 wt.% polymer in chloroform. Prior to film casting the solution was filtered through a Teflon filter (Millipore, 5 μm pore size) to remove dust particles. Solutions were cast on a glass plate at room temperature with a 1000 μm blade. After evaporation of the solvent, films with a uniform thickness of 30 ± 2 μm were obtained.

Oriented films were obtained by drawing cast films in an oven or on a hot shoe, at 200°C for PES1.3-C12 and PPP3-C12, and at 270°C for PES1.3-C6, PES3.3-C6 and PES3.5-C6. The sample was heated by passing preheated dry nitrogen gas through the oven. The drawing speed was 2 cm/min and the specimen length and width before drawing were 5 cm and 1 cm, respectively. The draw ratio (λ) was determined from the length increase of the film specimen, using ink marks.

Tensile measurements

Tensile measurements on oriented films were performed on a small tensile testing machine designed at TNO. The films were tested at a strain rate of 10%/min. The presented values of tensile strength and elongation at break are an average of at least five measurements.

DMTA

Dynamic mechanical tensile measurements were performed on an apparatus designed at TNO[10]. The polyester films were measured in the temperature range of −175°C to +225°C. The poly-*para*-phenylene film was measured from −175°C to +160°C. Measurements were made at temperature intervals of 4°C and at four frequencies: 1, 2.15, 4.64, and 10 Hz. The static strain was set to 0.2% and the dynamic strain amplitude was 0.03%.

RESULTS AND DISCUSSION

(Dynamic) mechanical measurements

Table 1 summarizes the dynamic tensile modulus, and tensile strength and elongation at break of films, drawn to

Table 1 Dynamic tensile moduli (E) at 10 Hz and 25°C, tensile strength (σ_b) and strain at break (ε_b) of the different polymer films at their maximum draw ratio (λ_{max})

Polymer	λ_{max}	E (GPa)	σ_b (MPa)	ε_b (%)
PTA12HQ (B)[a]	6.1	30.0	158	1.2
PES1.3-C12	4.0	17.8	166	2.0
PES1.3-C6	3	35.5	300	2.8
PES3.3-C6	3.1	31.6	325	2.5
PES3.5-C6	2.8	44.7	300	1.6
PPP3-C12	1.7	3.6	27	2.6

[a] B is one of the three crystal modifications in which PTA12HQ can exist[10]

their maximum draw ratio. The highest room temperature modulus could be achieved for PES3.5-C6, *viz.* 44.7 GPa. A general observation is that the polymers with hexyl side chains display a substantially higher modulus and strength than the polymers with dodecyl side chains. The low values of modulus and strength for PPP3-C12 can be attributed to the relatively low degree of orientation achieved in this polymer, which is related to its low molecular weight compared to the other polymers.

Figure 1 shows the plots of dynamic tensile modulus and loss tangent of both as-cast and drawn films of PES1.3-C12,
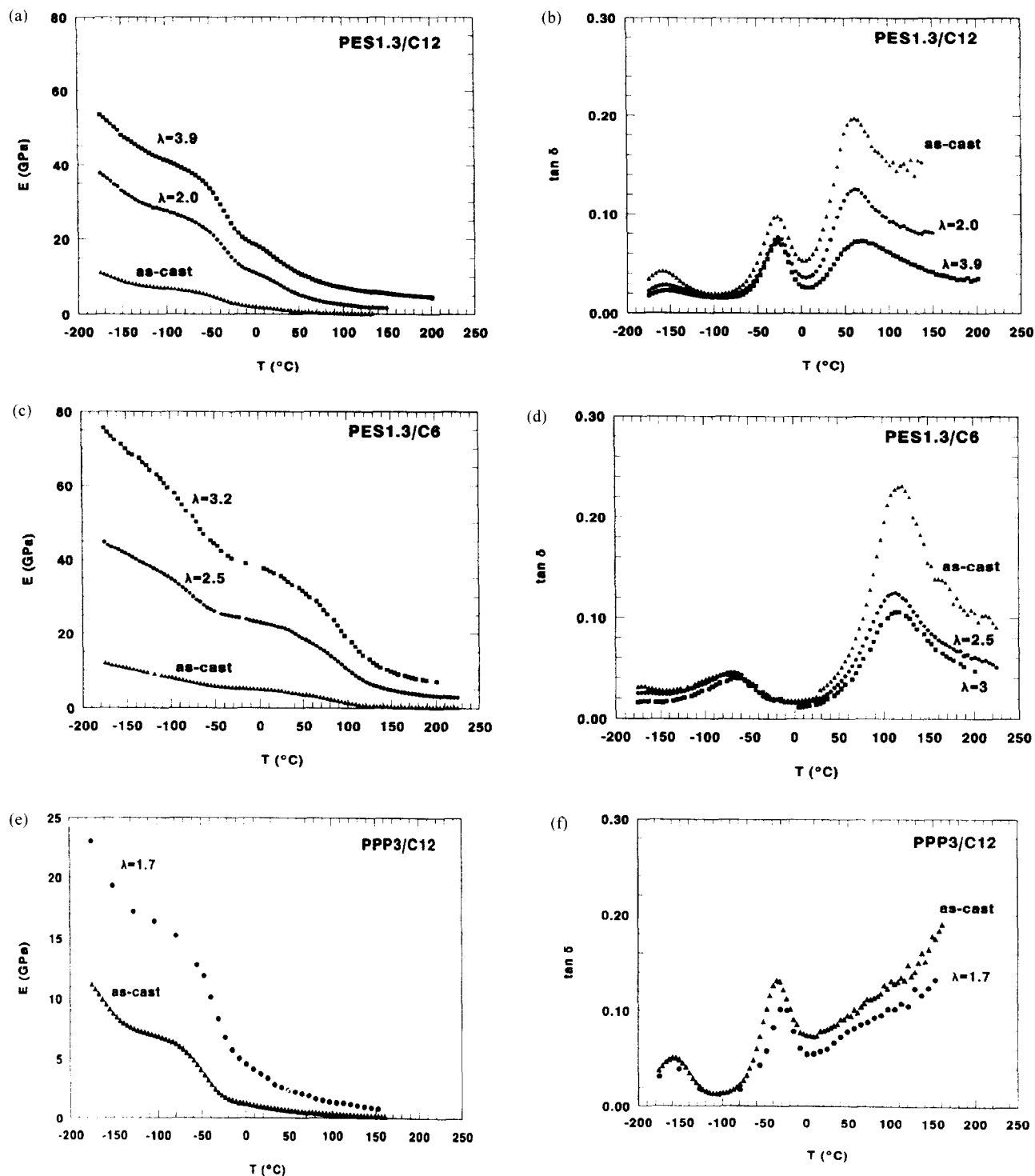

Figure 1 Dynamic tensile modulus (E) and tan δ (at 10 Hz) as a function of temperature and at different draw ratios, indicated in the figures, for PES1.3-C12 (a,b), PES1.3-C6 (c,d), and PPP3-C12 (e,f)

PES1.3-C6 and PPP3-C12, as a function of temperature. The dynamic mechanical properties of PTA12HQ were reported in detail by Damman and coworkers[10,11]. It was shown in an earlier paper that this class of polymers were very efficiently oriented by drawing[6]. This is best reflected by the rigorous increase of all tensile moduli with draw ratio. The modulus decreases with increasing temperature as a consequence of several relaxations. PES1.3-C12 and PPP3-C12 showed two secondary relaxations, at $-150°C$ and $-35°C$, respectively. Frequency dependent measurements showed that these relaxations originate from local motions. The relaxations were located at the same temperatures as the relaxations found in PTA12HQ (denoted as γ and β, respectively), where they were assigned to the onset of mobility of parts of the dodecyloxy side chain[10,11]. It is therefore plausible that the secondary relaxations in PES1.3-C12 and PPP3-C12 are associated with parts of the dodecyl side chains. The extra oxygen atom in the side chains of PTA12HQ does not seem to alter the relaxation temperature, compared to the alkyl side chains. PES1.3-C6 (*Figure 1c,d*) is representative for the polyesters with hexyl side chains; two secondary relaxations are observed, at somewhat lower temperatures ($-170°C$ and $-70°C$) compared to the polyesters with dodecyl side chains. These relaxations are probably associated with (parts of) the hexyl side chains. At higher temperatures, around 60°C for the C12-polyesters and 100°C for the C6-polyesters, a broad relaxation was observed, which was ascribed to collective motions. It could well be associated with the glass transition, although for PTA12HQ it was explained by a combination of local main chain motions and side chain motions[10,11]. Differential Scanning Calorimetry (d.s.c.) measurements could not clarify this matter, since a clear glass transition in these polymers could not be observed by d.s.c. either.

Determination of the chain modulus

In order to estimate the tensile modulus of a perfectly oriented chain (the chain modulus), measurements should take place at high orientations and at a temperature as low as possible. By film drawing, the modulus increases and should reach a plateau value, indicating that a maximum orientation has been reached. Assuming that no major relaxations take place below $-175°C$, the value at this low temperature is comparable with theoretical values. The development of the tensile modulus with draw ratio, at room temperature and at $-175°C$, is shown in *Figure 2* for PES1.3-C12 and PES3.3-C6. The results are representative for all polyesters. As can be seen in this figure, the maximum attainable draw ratio was too low to allow a determination of the plateau value. For PES3.5-C6 and PPP3-C12 the drawing range was even more limited. Only in the case of PTA12HQ was a plateau value reached[7], which means that the chain modulus could be deduced directly from the E versus λ plot at $-175°C$. In this way a value of 50 GPa was found for the chain modulus of PTA12HQ, which agreed surprisingly well with the theoretical value[7]. In an attempt to reach higher draw ratios in the other polyesters as well, PES1.3-C12 was fractionated into a high and a low molecular weight fraction. However, drawing of the high molecular weight fraction did not lead to higher draw ratios, nor to higher mechanical properties.

Since a direct determination of the chain modulus from the plateau value at $-175°C$ turned out to be impossible for most polyesters, an extrapolation method was applied for obtaining an estimate of the chain modulus. This
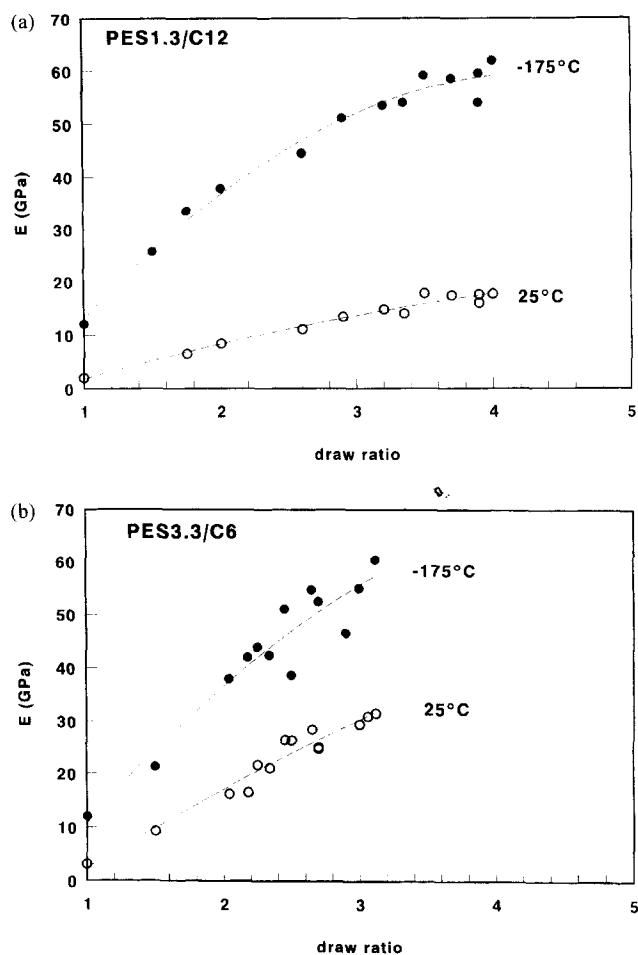

Figure 2 Dynamic tensile modulus E at 10 Hz as a function of draw ratio, at 25°C and $-175°C$: (a) PES1.3-C12, (b) PES3.3-C6. Dashed curves are drawn to guide the eye

extrapolation method must be based on a model that relates the modulus to the degree of orientation. Based on the established applicability in other highly oriented polymers, the interest was focused on the aggregate model, described by Ward and coworkers[12,13]. This model regards the polymer as an aggregate of anisotropic elastic units whose elastic properties are those of the fully oriented polymer. Under certain conditions, which include a highly oriented system, the model provides a simple equation describing the elastic properties:

$$\frac{1}{E} = \frac{1}{E_c} + \frac{1}{G}\langle \sin^2 \theta \rangle \tag{1}$$

with E = experimental tensile modulus; E_c = 'chain modulus', modulus of perfectly oriented sample; G = shear modulus; θ = orientation angle.

Northolt and coworkers[14-16] derived a similar relationship, only differing by a factor two in the term with the shear modulus:

$$\frac{1}{E} = \frac{1}{E_c} + \frac{1}{2G}\langle \sin^2 \theta \rangle \tag{2}$$

The difference with Ward's aggregate model is, according to Northolt[16], a matter of strain definitions. The Northolt relationship successfully described the behaviour of oriented poly-p-phenylene terephthalamide (PPTA) fibres. According to each of the above models, extrapolation of a $1/E$ vs. $\langle \sin^2 \theta \rangle$ plot to $\langle \sin^2 \theta \rangle = 0$ yields the modulus of
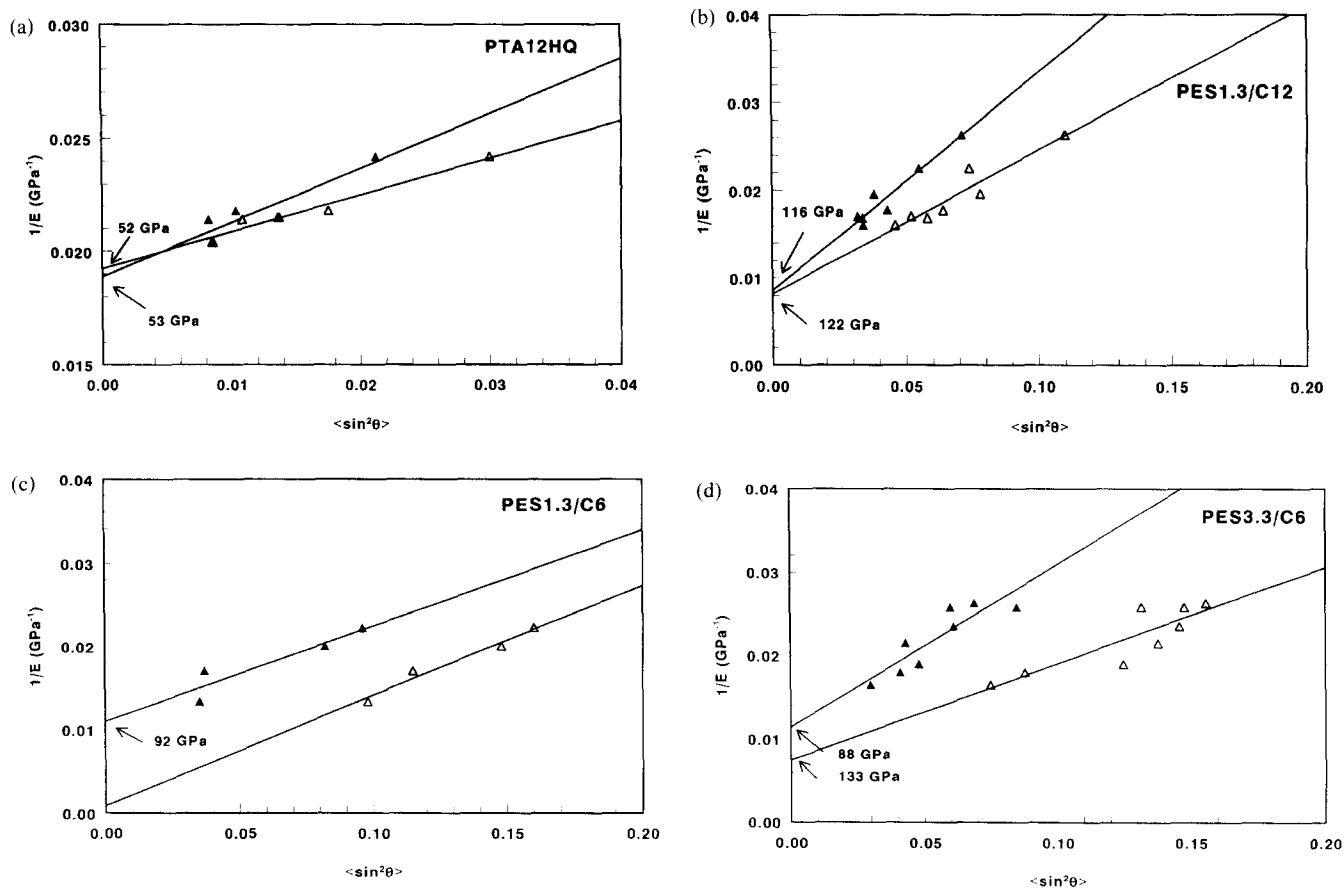
Figure 3 Aggregate model plots for (a) PTA12HQ; (b) PES1.3-C12; (c) PES1.3-C6; and (d) PES3.3-C6. Both orientation values $\langle \sin^2 \theta \rangle_{exp}$ (▲) and $\langle \sin^2 \theta \rangle_{fit}$ (△) are shown; the extrapolated values for E_c are indicated

the perfectly oriented polymer. We have used the modulus values measured at $-175°C$. For the degree of orientation, quantified by $\langle \sin^2 \theta \rangle$, we have used the value derived from WAXD[6] rather than that from Raman or FTi.r.[17]. The behaviour of the modulus of aromatic copolyester fibres[13,18] and aramid fibres[15] was also successfully analyzed on the basis of the orientation derived from WAXD.

Figure 3 shows the results of the extrapolation procedure for the polyesters PTA12HQ, PES1.3-C6, PES1.3-C12, and PES3.3-C6, respectively. The mechanical data for PTA12HQ have been taken from Damman *et al.*[7]. In the cases of PES3.5-C6 and PPP3-C12 insufficient data points were available to apply the model. In the extrapolation figures both the orientation parameters corresponding to $\langle P_2 \rangle_{exp}(= 1 - (3/2)\langle \sin^2 \theta \rangle_{exp})$ and those corresponding to $\langle P_2 \rangle_{fit}$ are included. These are the orientation parameters based on the experimental intensity profile and on the fitted intensity profile of the X-ray reflection, respectively. The difference between $\langle \sin^2 \theta \rangle_{exp}$ and $\langle \sin^2 \theta \rangle_{fit}$ originates from small intensity differences in the tail of both profiles, which, however, have a big influence on the value of $\langle P_2 \rangle$, especially at high orientations. The experimental profile was fitted in the first place to tackle the problem of separating the low intensities at the tail of the intensity profile from the background intensity. Nevertheless, due to remaining uncertainties, both the experimental and fitted profiles were used to calculate $\langle P_2 \rangle$. In our previous paper[6] the determination of the orientation parameters, and the origin of their inaccuracies, are discussed in more detail. From the intercept at $\langle \sin^2 \theta \rangle = 0$, values for the uncorrected chain modulus E_c were derived as indicated in the figures. From the results in *Figure 3* the following observations can

be made:

- for PTA12HQ the extrapolations yield only slightly higher values for E_c than derived before from the plateau value: 52 and 53 GPa, compared to 50 GPa. The standard deviation of the extrapolated value is 9%.
- for PES1.3-C12 both extrapolations result in about the same value for E_c: 116–122 Gpa. The standard deviation is 16%.
- for PES1.3-C6 and PES3.3-C6 the extrapolated values based on $\langle \sin^2 \theta \rangle_{fit}$ and $\langle \sin^2 \theta \rangle_{exp}$ differ considerably, thereby indicating the inaccuracy. The extrapolation based on $\langle \sin^2 \theta \rangle_{fit}$ leads to an unrealistic, high modulus for PES1.3-C6; therefore the values based on $\langle \sin^2 \theta \rangle_{fit}$ may be considered the least reliable. The standard deviation of the extrapolated values based on $\langle \sin^2 \theta \rangle_{exp}$ is 20% for both PES1.3-C6 and PES3.3-C6.

The experimental error in the data points largely stems from the determination of $\langle \sin^2 \theta \rangle$. Furthermore, the accuracy of the extrapolation is also determined by the number of data points and the achieved degree of orientation. To conclude ,we can say that, although the applicability of the aggregate model has been established, the extrapolated values for the chain modulus suffer from large inaccuracies. Only in the case that near perfect orientation can be achieved (PTA12HQ), an accurate value of E_c can be derived.

Comparison of the extrapolated chain modulus with the theoretically calculated modulus

Tashiro and Kobayashi[8] recently described a method to calculate the modulus along the chain direction of aromatic

Table 2 The extrapolated value for the chain modulus (E_c), the ratio of cross-sectional areas with and without side chains (A_c/A_{mc}), the main-chain modulus (E_{mc}, converted from E_c), and the theoretically calculated modulus

	E_c	A_c/A_{mc}	E_{mc}	E (theory)
PTA12HQ	53	3.52	187	180
PES1.3-C12	116	2.72	315	200
PES1.3-C6	92	1.96	180	200
PES3.3-C6	88	2.28	201	220
PES3.5-C6	—	—	—	233
PPP3-C12	—	5.24	—	450

All moduli in GPa

Figure 4 Comparison of the experimentally achieved moduli and theoretical moduli of the investigated polyesters and poly-*para*-phenylene, and the reported values for PPTA

polyester chains (without side chains). In order to compare our extrapolated values with the theoretically calculated moduli, our values have to be corrected for the cross-sectional area occupied by the side chains; in this way the 'main-chain modulus', E_{mc}, is obtained. The cross-sectional area A_c of a chain (including side chains) can be calculated, using the length L and molecular weight M_u of the repeating unit, the experimental density ρ of the polymer, and the Avogadro number N_a, according to[19]:
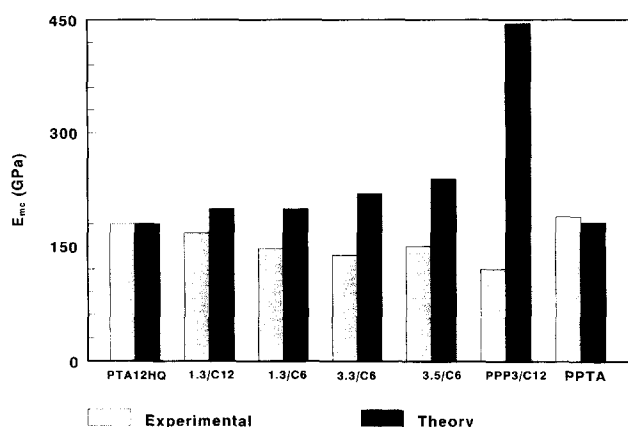
$$A_c = \frac{M_u}{N_a \rho L} \quad (3)$$

L is obtained from the strongest meridional reflection, and the densities of highly oriented tapes were used[6]. For the cross-sectional areas of all the polyester main chains in our series, A_{mc}, we took the value reported in literature[8] for several aromatic polyester chains: 21 Å^2. For the PPP main chain, 14.5 Å^2 was calculated. The chain modulus can now be converted to the main-chain modulus by:

$$E_{mc} = E_c A_c / A_{mc} \quad (4)$$

In this equation, it is assumed that the contribution of the side chains to the modulus is negligible, which is a fair assumption for highly oriented tapes. In *Table 2* the values for E_c (based on $\langle \sin^2 \theta \rangle_{exp}$ results from *Figure 3*), the ratio of cross-sectional areas, and E_{mc}, are summarized, together with values of the theoretical moduli calculated according to the method of Tashiro and Kobayashi[8]. The calculation method for this particular series of polyesters is described in Appendix A. Three out of four of the extrapolated values are within 10% of the theoretical modulus. In the order given in *Table 2* the main-chain modulus is expected to increase, as can be inferred from the theoretical moduli. This tendency, however, is not reflected by the extrapolated data, probably mainly because of the inaccuracy of the extrapolation.

Comparison of the experimentally attained modulus with the theoretically calculated modulus

The chain modulus would be better accessible if processing allowed to achieve higher degrees of orientation. Unfortunately, the processing is getting more difficult with increasing molecular stiffness. This is shown by the rather low maximum draw ratios obtained. The drawability determines to a large extent the attainable level of orientation and stiffness, rather than intrinsic molecular properties. An illustrative way of presenting this is to make a comparison between the maximum experimentally attained modulus and the theoretical value. *Figure 4* shows a bar diagram in which the maximum experimental moduli at $-175°C$, again corrected for the cross-section of the side chains, are compared with the theoretical moduli. The values for the commercial PPTA fibre have been included[8,20,21]. The experimental value of 190 GPa for PPTA at $-175°C$ was derived from the room temperature value of Allen and Roche[20], adapted according to the DMTA results of Northolt and Sikkema[21]. The theoretical value for the PPTA chain calculated by Tashiro and Kobayashi is 182 GPa, while Northolt obtained 240 GPa for PPTA by extrapolation. For PPP3-C12, the big difference between the very high theoretical modulus (due to the significantly smaller cross-sectional area compared to the polyesters) and the fairly low experimental modulus is mainly caused by the low molecular weight, already mentioned. The diagram further shows that a theoretically stiffer main-chain does not result in a proportionally higher experimental modulus. On the contrary, the experimentally attainable modulus appears to be adversely influenced by the chain rigidity. This effect may be influenced by factors like the crystallinity and the morphology of the side chains, but the main cause is most probably the increasing processing difficulties. With the exception of PTA12HQ, the side chain density is presumably too small to bring about an optimum processibility. The somewhat higher modulus obtained in PES1.3-C12 with respect to PES1.3-C6 underlines this view. An optimum role of side chains was apparently present in PTA12HQ. This conclusion does however not imply that raising the side chain density (by substitution on more phenyl rings or by longer side chains) will consistently result in higher attainable degrees of orientation and corresponding main-chain moduli, since the orientation process may also be adversely influenced by too high densities of side chains (e.g. possible loss of liquid-crystalline behaviour).

CONCLUSIONS

A series of rigid-rod polyesters and a poly-*para*-phenylene with alkyl side chains were characterized with respect to the mechanical properties as a function of temperature and draw ratio. All polymers exhibited an extremely efficient orientability, but the plateau value could not be reached. It was attempted to determine the moduli of perfectly oriented structures by an extrapolation method based on the aggregate model. The values obtained from extrapolation showed a relatively large standard deviation that can mainly be ascribed to inaccuracies in the determination of the orientation parameter.

While the extrapolated values compare to the theoretical moduli, lying in the range of 180–230 GPa, the

experimentally attained moduli (also corrected for the cross-sectional area of side chains) of the polyesters varied between 140 and 180 GPa. More specifically, the experimentally attained modulus displays a larger deviation from the theoretical value with increasing molecular rigidity, due to increasing processing difficulties. The possibility for optimization of the processability and orientability, by modification of the side chain density of the investigated polymers with a main chain rigidity above that of PTA12HQ, remains to be investigated.

ACKNOWLEDGEMENTS

APPENDIX A: CALCULATION OF THE THEORETICAL MODULUS ACCORDING TO THE METHOD OF TASHIRO AND KOBAYASHI

Tashiro and Kobayashi[8] presented a relatively simple method to calculate the modulus along the chain direction of an aromatic polyester chain, with an increasing sequence of phenylene rings between the ester linkages. *Figure 5* shows the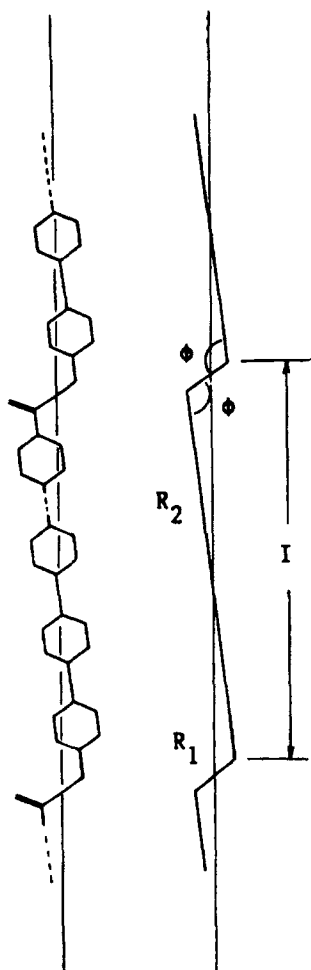 structural model. The bond length of the ester bond is R_1, the series of n phenylene rings is represented by a bond with length R_2, and the bond angle is ϕ. The corresponding force constants for bond elongation and angle opening are K_1, K_2, and H, respectively. With S representing the cross-sectional area and I the repeating distance (fibre period), equation (A1) is obtained:

$$\frac{1}{E_c} = \frac{S}{I^3}\left[\frac{(R_1 - R_2 \cos \phi)^2}{K_1} + \frac{(R_2 - R_1 \cos \phi)^2}{K_2}\right.$$

$$\left. + \frac{(R_1 R_2 \sin \phi)^2}{2H}\right] \tag{A1}$$

where

$$I = (R_1^2 + R_2^2 - 2R_1 R_2 \cos \phi)^{1/2}$$

The parameter values[8] are summarized below:

$R_1 = 1.37$ Å;
$R_2 = 4.14*n$ Å;
$\phi = 114.6°$, the average of: $110.9°$ for C–(CO)–O;$118.3°$ for (CO)–O–C;
$K_1 = 6.0$ mdyn Å^{-1};
$K_2 = 1.55/n$ mdyn Å^{-1};
$H = 0.8$ mdyn Å^{-1} rad^{-1};
$S = 21$ Å^2 (14.5 Å^2 for PPP).

With these data, the theoretical moduli of PESx.y were calculated. It must be remarked that the model structure is built up of a hydroxy-acid type monomer, while our structures are built up of dihydroxy- and diacid monomers. However, since the two angles in the ester linkages are almost equal, we neglected the differences. For the calculations the following n-values have been taken, which resulted in the following theoretical moduli:

PTA12HQ:	$n = 1$	E = 170 GPa
PES1.3:	$n = 2$	E = 200 GPa
PES3.3:	$n = 3$	E = 220 GPa
PES3.5:	$n = 4$	E = 233 GPa
PPP:	$\lim(n \to \infty)$	E = 450 GPa

These theoretical values may be subject to uncertainties in the cross-sectional area S and the chosen n-value. S will decrease slightly with increasing phenylene sequence. However, according to Tashiro and Kobayashi, the cross-sectional areas of the polyesters will not differ much, so 21 Å^2 was taken for all polyesters. Only for PPP, in which bond angles are totally absent, a lower value of S, viz. 14.5 Å^2, was calculated. Using the value of 21 Å^2 would yield a calculated modulus for PPP of 310 GPa. Furthermore, the model does not account for different lengths of R_2 in one chain, therefore $n = 2$ was chosen for PES1.3, and $n = 4$ for PES3.5, which may also introduce an uncertainty.

Figure 5 Structural model for aromatic polyesters, indicating the various parameters for calculating the tensile modulus

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