Thermotropic polyesters: effect of *m*-phenylene disruptors on chain modulus

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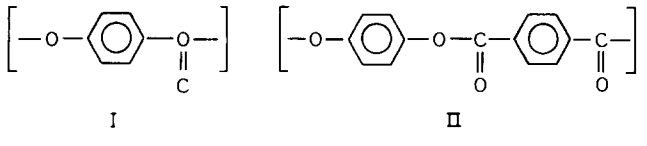
Computer-generated atomic models are employed to evaluate the effect of disruptor units containing an *m*-phenylene ring on the modulus of aromatic polyester chains. The incorporation of isophthaloyl units results in quasiplanar chains which affect the chain modulus in a complex way. At a given concentration of disruptor units the chain modulus is strongly influenced by chain regularity and length. Chains containing *m*-phenylenedioxy and *m*-oxybenzoyl units cannot be represented by quasiplanar models and this implies a stronger detrimental effect of such units on chain modulus. The intuitive notion, employed in the design of thermotropic polymers, that the fewer disruptor units the better, is clearly a misconception.

(Keywords: aromatic polyesters; thermotropic; nematic; liquid crystalline; chain modelling; chain modulus)

INTRODUCTION

Main-chain thermotropic copolyesters are now being exploited as specialty engineering materials with exceptional processing behaviour (low viscosity at relevant shear rates, low mould shrinkage); their properties are also very attractive: high strength and stiffness, outstanding dimensional stability and excellent environmental resistance[1,2]. Since rigid-chain homopolymers, such as poly(*p*-oxybenzoate) (POB; repeating unit I) or poly(*p*-phenylene terephthalate) (PPT; repeating unit II), do not melt without decomposition, various chemical modifications are used to obtain melt-processible nematogenic copolymers[2,3]. We have concentrated on copolyesters containing angular disruptors[4–8]. Whilst this approach yields melt-processible nematogenic materials, it is expected to result in reduced chain stiffness which, together with the chain cross-sectional area, determines the chain modulus. For polymers where chain folding is ruled out, the tensile modulus is determined by the chain modulus together with the intermolecular shear modulus and chain orientation; this follows from application of both the aggregate model[9–11] and from other theoretical concepts[12]. Thus, evaluation of the chain modulus is the first step in formulating the relationship between the structure and mechanical properties of such materials.

This paper is concerned with the effect of a rigid angular disruptor, namely the *m*-phenylene ring, on chain moduli of copolymers. The *m*-phenylene ring can be incorporated into a polyester chain by means of the following units: isophthaloyl (COMCO), *m*-phenylenedioxy (OMO), and *m*-oxybenzoyl (OMCO) (*Table 1*). The isophthaloyl units together with rod-like *p*-oxybenzoyl (OPCO) and *p*-phenylenedioxy (OPO) units are used in poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate)s[4,5,9] (POPI). Poly(*p*-oxybenzoate-*co*-*m*-phenylene terephthalate)[6,13,14] (POMT) chains consist of rod-like *p*-oxybenzoyl (OPCO) and terephthaloyl (COPCO) units, and angular *m*-phenylenedioxy (OMO) units. Thus, in POMTs and POPIs the direction of ester groups linked to the *m*-phenylene ring is reversed. In poly(*p*-oxybenzoate-*co*-*m*-oxybenzoate)s[15], where the sequences of rod-like OPCO units are disrupted by angular *m*-oxybenzoyl (OMCO) units, one of the ester groups is linked to the *m*-phenylene by carbonyl as in POPIs, and the other by an oxygen atom as in POMTs.



I II

The main problem in evaluation of chain moduli of random copolymers is the choice of a suitable model. Whilst it must be realistic, its complexity must not rule out its application. Essentially, we have followed the approach used recently by Ward and co-workers[16] who calculated the moduli of planar copolymer chains containing 2,6-oxynaphthoyl units by means of Treloar's method[17,18]. They also explained why more recent techniques[19–21] cannot be used as yet for random copolymers. Whilst we are aware of the limitations of Treloar's method, its application enabled us to gain an understanding of the effect of *m*-phenylene rings which can be applied to the 'design' of thermotropic copolyesters.

THEORETICAL

Chain modelling

Due to the complications arising from the presence of angular disruptors the modelling was limited to quasiplanar chains, where the ester groups, *m*-phenylene rings and virtual bonds representing *p*-phenylene rings are confined to a plane.

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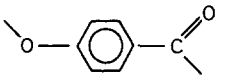
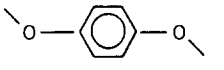
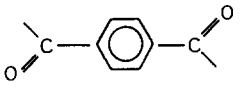
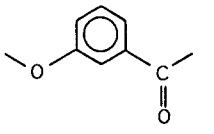
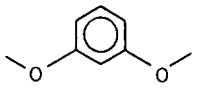
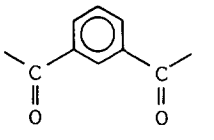
Table 1 Constituent units

Unit	Abbreviation	Structure
p-Oxybenzoyl	OPCO	
p-Phenylenedioxy	OPO	
Terephthaloyl	COPCO	
m-Oxybenzoyl	OMCO	
m-Phenylenedioxy	OMO	
Isophthaloyl	COMCO	

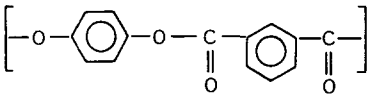
The procedure for generating planar atomic models of POPI chains was described previously[22]. Two types of models were considered, referred to as '*trans*' and '*cis*-based', respectively. Comparison of one-dimensional Fourier transforms calculated for both these models with the observed meridional WAXS traces suggested that the more extended '*trans*' conformations are preferred in reality[22,23]. Quasiplanar chains, resulting from the out-of-plane rotation of *p*-phenylene rings dictated by intramolecular interactions between the carbonyl oxygen atoms of ester groups and hydrogen atoms of aromatic rings[24], gave one-dimensional Fourier transforms which were identical with those obtained for the planar chains[23]. Comparison of the orientation parameters calculated for the rod-like segments constituting the model chains, with those evaluated from the observed azimuthal spread of the equatorial scatter, also ruled out the less extended '*cis*-based' models[23]. Thus, in the case of POPIs, the quasiplanar '*trans*' conformation model chains are considered to be sufficiently realistic. However, it should be noted that, for the evaluation of chain moduli by Treloar's method[18], the planar and quasiplanar models are equivalent since the *p*-phenylene ring is treated effectively as a virtual bond.

Apart from '*trans*' model chains generated for random sequences of the constituent units representing the melt-processible POPIs (50/50, where the molar fractions of the units are [OPCO]=[OPO]=[COMCO]=0.33 (*Figure 1*)), and 67/33, where [OPCO] = 0.50 and [OPO] = [COMCO] = 0.25, we have also constructed '*trans*' models of copolymers with regular sequences of the constituent units (*Table 2*). The appropriate models of the parent homopolymers were also generated. For poly(*p*-oxybenzoate) the '*cis*' conformation has been identified by investigation of its crystal structure[25,26]; indeed, the '*trans*' chains are curved because the outgoing bonds of an ester group are not parallel[22]. However, for direct comparison of the chain modulus of poly(*p*-oxybenzoate) with those of the '*trans*' copolymers we also constructed straightened '*trans*' chains of this homopolymer, using the same values (114.6°) for both C(b)–C(=O)–O and C(=O)–O–C(b) angles. In the case of poly(*p*-phenylene isophthalate) (PPI; repeating unit III) it is appropriate to use the '*trans*' conformation[5] (*Figure 2*). For a direct comparison with this parent homopolymer we used the corresponding rigid-chain polymer, poly(*p*-phenylene terephthalate), where the '*trans*' conformation is realistic[27] (*Figure 2*).

Planar and quasiplanar models of POMT chains, containing OMO disruptor units, can be constructed in the same way. However, from considerations of intramolecular interactions it follows that such models are unrealistic; in this case the required rotations result in non-planar chains[6]. This also applies to polymers containing OMCO units.

Chain cross-sectional area

The chain cross-sectional area Q_C in a crystal is readily obtained from the unit cell dimensions and geometry.



III

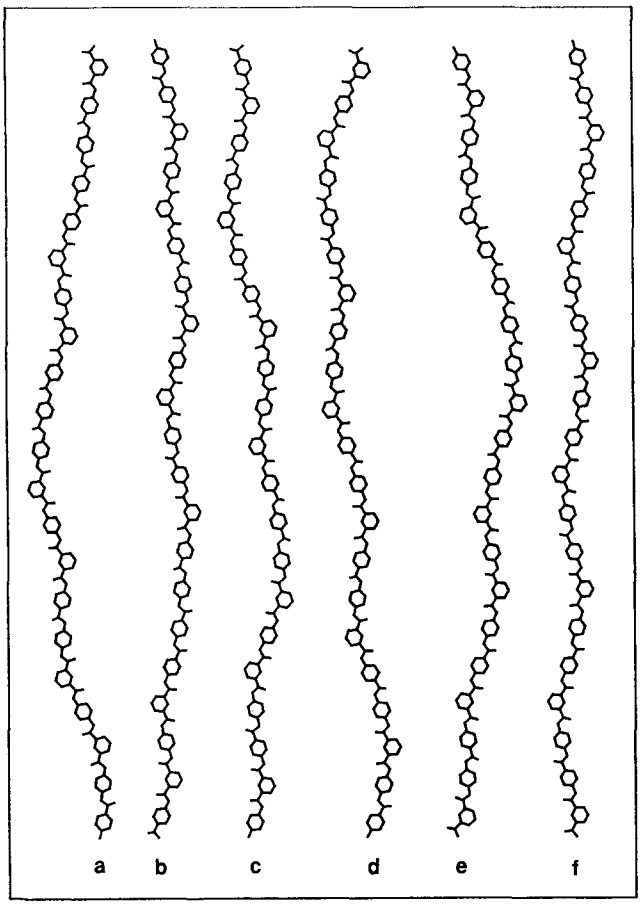


Figure 1 Planar '*trans*' conformation models of POPI (50/50) copolymer chains with 21 units: (a)–(e) random; (f) regular; chain moduli *E* (GPa): (a) 50, (b) 82, (c) 46, (d) 40, (e) 64, (f) 90

Table 2 Properties of regular poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) '*trans*' conformation chains: length of rod-like sequence (L_R); angle between the rod-like sequence and chain axis (ϕ); chain modulus expressed in terms of stress (E_C) and specific stress (S_C)

Composition	[COMCO]	Unit sequence	L_R (nm)	ϕ (deg)	E_C (GPa)	S_C (N tex^{-1})
100/0	0.000	–OPCO–	∞	–	159	106
80/20	0.167	–COMCO–(OPCO)$_2$–OPO–(COPO)$_2$–	3.74	7.65	124	85
75/25	0.200	–COMCO–(OPCO)$_2$–OPO–(COPO)–	3.12	9.87	105	72
67/33	0.250	–COMCO–OPCO–OPO–COPO–	2.50	11.35	114	78
50/50	0.333	–COMCO–OPCO–OPO–	1.87	13.82	90	61
0/100	0.500	–COMCO–OPO–	1.25	15.05	127	85

Table 3 Properties of poly(*p*-oxybenzoate) (POB), poly(*p*-phenylene terephthalate) (PPT), and poly(*p*-phenylene isophthalate) (PPI): chain cross-sectional area obtained from unit cell dimensions (Q_C); chain modulus expressed in terms of stress (E_C) and specific stress (S_C); components of specific chain compliance $(1/S_C)_j$: $j = 1$ – bond stretching, $j = 2$ – benzene rings deformation, $j = 3$ – angle opening

Polymer	POB		PPT	PPI
Conformation	'*cis*'	'*trans*'[a]	'*trans*'	'*trans*'
Q_C (nm^2)	0.214[25]	–	0.210[27]	0.219[5]
E_C (GPa)	108	159	160	127
S_C (N tex^{-1})	72	106	108	85
$(10^3/S_C)_1$ (tex N^{-1})	2.3	2.3	2.3	2.3
$(10^3/S_C)_2$ (tex N^{-1})	3.3	3.2	3.1	2.4
$(10^3/S_C)_3$ (tex N^{-1})	8.3	3.9	3.9	7.0

[a] Straightened chains– see text; chain cross-sectional area as for the '*cis*' conformation

The values for the relevant homopolymers are summarized in *Table 3*. However, it should be noted that even in the case of homopolymers, the differences in crystal perfection and, in particular polymorphism, may result in considerable variation in chain packing density. This has been established by Lieser[25] for poly(*p*-oxybenzoate).

With few exceptions, the density of chain packing in the crystal exceeds that in the less ordered phases. In copolymers, the achievable level of crystallinity is inevitably low and the average chain packing density is therefore lower than in either of the homopolymer crystals. Here, the chain cross-sectional area used for a copolymer is the larger of the two parent homopolymer values, i.e. 0.219 nm^2 for POPIs. However, this is still likely to underestimate the value of Q_C for the copolymers and consequently their moduli will be somewhat overestimated. As shown below, this effect is rather small.

For a fibre consisting of extended chains parallel to the fibre axis, the average chain cross-sectional area Q_C (m^2) is

$$Q_C = 10^{-3} M_L/(N_A \rho L) \quad (1)$$

where M_L (g mol^{-1}) is the molecular weight of the sequence of units of length L (m), N_A (mol^{-1}) is the Avogadro constant, and ρ (kg m^{-3}) is fibre density. Since possible voids and flaws result in a decrease of the measured fibre density, this approach is likely to overestimate the value of Q_C. Using the density of 1400 kg m^{-3} for the POPI (50/50) fibre, we get a value of 0.232 nm^2 as the upper limit of Q_C; this exceeds the value adopted for POPI copolymers by only about 6%. Thus the error in the chain moduli arising from the uncertainty of the chain cross-sectional areas is not expected to be very serious in comparison with those resulting from the approximations used in the calculation of chain deformation.

Chain modulus

According to Treloar's approach[17,18] the total extension of the selected unit sequence is expressed in terms of three separate contributions:

(1) bond stretching (excluding benzene rings);
(2) benzene ring deformation;
(3) valence angle deformation (excluding benzene rings).

The influence of neighbouring chains is disregarded.

The deformation per unit force arising from bond stretching is expressed as

$$(\delta L_1/F) = \sum \frac{\cos^2 \theta_i}{(k_1)_i} \quad (2)$$

where $(k_1)_i$ is the bond stretching force constant of the ith bond (*Table 4*) and θ_i is its inclination to the direction of the applied force F.

The second contribution arises from the deformation of the benzene rings. For the case of symmetric application of forces the contribution from a *p*-phenylene ring is[18]

$$(\delta L_2/F) = \frac{l^2}{4k_\alpha} + \frac{3}{4k_1} \quad (3)$$

and that arising from an *m*-phenylene ring is[28]

$$(\delta L_3/F) = \frac{l^2}{12k_\alpha} + \frac{3}{4k_1} \quad (4)$$

where l is the length of the aromatic carbon–carbon bond and k_α and k_1 are the appropriate angle opening and bond stretching constants, respectively (*Table 4*).

The third contribution arises from the opening of bond angles α_i. The couple operating at each vertex is dependent on its distance d from the line of action of force F; hence

$$\delta\alpha_i = F d_i/(k_\alpha)_i \quad (5)$$

where $(k_\alpha)_i$ is the angle opening constant (*Table 4*). The position of line of action for the applied force is obtained by ascertaining that the net couple is zero for each chain sequence. Initially the line of action was chosen to be the position of the first and the last skeletal oxygen atoms in the chain. Subsequently, an iterative program was developed to find the exact position of the line of action

Table 4 Values of force constants[19]

Bond stretching Bond	k_l (N m^{-1})
O-C(=O)	618
C(=O)-C(b)	450
C(b)-C(b)	643
C(b)-O	509
Angle opening Bonds	$k_\alpha \times 10^{18}$ (N m rad^{-1})
O-C(=O)-C(b)	0.800
C(b)-C(b)-C(=O)	0.934
C(b)-C(b)-C(b)	0.934
C(b)-C(b)-O	0.934
C(b-O-C(=O)	1.300

C(b) denotes aromatic carbon

of the applied force. In this procedure all the couples at each vertex are summed and if necessary the whole chain is moved laterally until the residual couple is reduced to zero. This position is then used to calculate the changes that take place in the inclination of each bond in the chain sequence. Finally the contribution to chain extension due to angle opening is obtained by summation of the individual contributions from each bond, according to the formula

$$(\delta L_3/F) = \sum - l_i \sin \theta_i \, \delta\theta_i \qquad (6)$$

where $\delta\theta_i$ denotes the change in inclination of the ith bond of length l_i to the line of action.

The total deformation $(\Delta L/F)$ for the sequence of units of initial length L is obtained by the summation of all the contributions due to bond stretching, deformation of rings and angle opening. The longitudinal chain modulus is then expressed as

$$E_C = (L/Q_C)(\Delta L/F)^{-1} \qquad (7)$$

Specific modulus

In physics it is customary to express the tensile properties of materials in terms of stress σ (i.e. force F per unit area). However, for applications where high stiffness and strength as well as low mass are desirable (e.g. aerospace), the tensile properties expressed in terms of specific stress $s = \sigma/\rho$ give a more appropriate measure of material performance[29]. It can be shown that the specific stress is also expressed as

$$s = F/C \qquad (8)$$

where C is the linear density defined as mass per unit length. Unlike the cross-sectional area, the linear density is easily measured for fibres of complex cross-sectional shapes[29]. The unit of linear density used in fibre science and technology is tex (1 tex = 1 g km^{-1} = 10^{-6} kg m^{-1}); the accepted unit of specific stress is therefore N tex^{-1}.

In order to evaluate the maximum achievable specific moduli of fibres produced from the materials investigated we expressed the calculated chain moduli in terms of specific stress, i.e.

$$S_C = E_C/\rho \qquad (9)$$

Then, using equations (1) and (7) we get

$$S_C = (\beta L^2 N_A/M_L)(\Delta L/F)^{-1} \qquad (10)$$

where $\beta = 10^3$ and 10^{-3} when S_C is expressed in N m kg^{-1} and N tex^{-1}, respectively. Comparison with equation (7) shows that the chain cross-sectional area Q_C, whose choice for copolymers was rather arbitrary, is replaced by mass per chain length. This quantity, which represents a molecular equivalent of linear density, is easily calculated for the model chains.

For appreciation of the effects of chemical structure it is useful to consider the specific chain compliance expressed in terms of contributions due to bond stretching, benzene ring deformation, and angle opening:

$$(1/S_C) = \sum_{j=1}^{3} (1/S_C)_j \qquad (11)$$

where

$$(1/S_C)_j = (M_L/\beta L^2 N_A)(\delta L_j/F) \qquad (12)$$

RESULTS AND DISCUSSION

Homopolymers

Results obtained for homopolymers are summarized in *Table 3*. The chain modulus of the rod-like homopolymer, poly(*p*-oxybenzoate) (POB), is strongly influenced by the choice of conformation. The value calculated for the realistic '*cis*' conformation, found in POB crystals[25,26] is only about two-thirds of that obtained for the 'straightened *trans*' conformation. The numerical values are in excellent agreement with those obtained by Ward and co-workers[16]. The effect of conformation on the chain modulus has also been noted for the corresponding polyamide, poly(*p*-benzamide)[19]. As the components of the specific chain compliance show, the difference between '*cis*' and '*trans*' POB chains is entirely due to the change in the angle opening contribution.

In contrast with POB, the '*trans*' conformation is favoured in a related rod-like homopolymer, poly(*p*-phenylene terephthalate) (PPT)[27] (*Figure 2a*). Its chain modulus is practically identical with that calculated for '*trans*' POB.

The result obtained for the '*trans*' conformation[5] poly(*p*-phenylene isophthalate) (PPI) (*Figure 2b*) chain shows that replacement of rod-like COPCO units in PPT by angular COMCO units causes an expected decrease of chain modulus; this is again due to changes in angle opening contribution. However, it is surprising that the chain modulus of PPI actually exceeds that of the POB '*cis*' conformation.

Poly(p-oxybenzoate-co-p-phenylene isophthalate)s

The chain moduli calculated for '*trans*' conformations of random copolymers 67/33 ([COMCO] = 0.25) and 50/50 ([COMCO] = 0.33), representing the limits of the nematogenic composition range of practical interest[4,5], showed a considerable scatter due to the effect of unit sequence (*Figures 1* and *3*). In both cases an increase in the number of constituent units, n, results in a decrease of the mean value of the chain modulus (*Figure 3*). The calculations have been limited to $n = 20$ and 21 for [COMCO] = 0.25 and [COMCO] = 0.33, respectively. Whilst this exceeds the values corresponding to correlation lengths estimated from the meridional X-ray diffraction (19 and 16, respectively)[22], the actual chains must be considerably longer. However, it should be appreciated that the use of longer chains resulted in computational

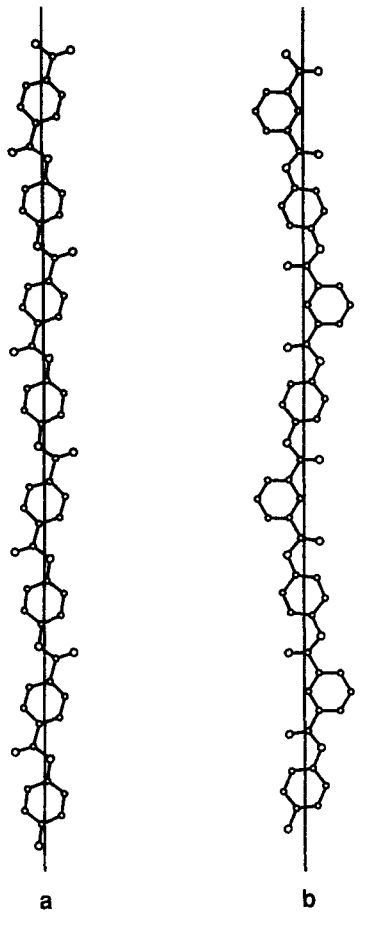


Figure 2 Planar '*trans*' conformation models of (a) poly(*p*-phenylene terephthalate) and (b) poly(*p*-phenylene isophthalate)

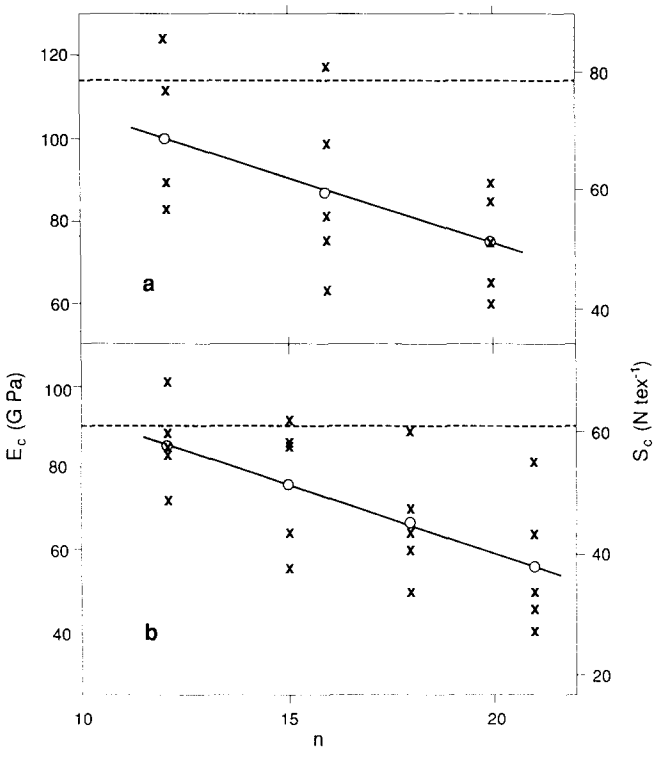


Figure 3 Effect of number of units *n* on chain modulus of POPI random copolymers: (a) 67/33, [COMCO] = 0.25; (b) 50/50, [COMCO] = 0.33. (×) Individual values for different model chains; (○) mean values; dotted lines indicate values for the corresponding regular chains

difficulties. The chain moduli obtained for the corresponding regular copolymers (*Table 2*) represent in effect the upper limits achievable with random copolymers (*Figure 3*).

Figure 4 shows the chain moduli S_C calculated for '*trans*' conformations of regular copolymer chains in comparison with random copolymers and both parent homopolymers. Although the '*trans*' conformation of the rigid homopolymer, POB, is unrealistic, it is an obvious starting point for consideration of the effect of angular COMCO units on the chain moduli of these copolymers. As expected, the moduli of copolymers decrease as the concentration of COMCO increases, but the decrease is not monotonic. The effect of the symmetry of the sequence is clearly noticeable. Furthermore, the moduli of chains with [COMCO] between 0.20 and 0.33 are actually lower than that of PPI where [COMCO] = 0.50; only for [COMCO] as low as 0.167 does the copolymer modulus match that of PPI. It is also worth noting that the modulus obtained for the realistic '*cis*' POB chain is lower than those of regular symmetric chains with [COMCO] = 0.167 and 0.25.

Figure 5 shows that the differences arising from the changes in composition are almost entirely due to the angle-opening contributions. These contributions depend on the distances of the bond apexes from the line of action. A fully extended chain containing angular units can be viewed as a sequence of rod-like segments[23]. The length of the segments, L_R, increases with increasing concentration of angular units whilst the effect of composition on the angle ϕ between the rod-like segments and the chain axis is rather small (*Table 2*). Consequently, as the concentration of angular units decreases, the copolymer chain wanders further away from the line of action and this must result in an increase in the angle opening contributions. Thus, the direct effect of the concentration of angular units and its indirect

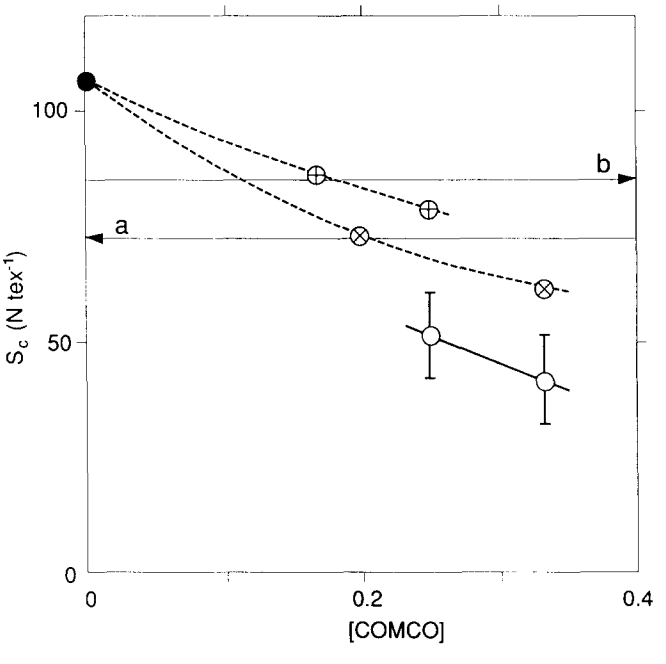


Figure 4 Effect of angular COMCO units on chain modulus S_C: (●), poly(*p*-oxybenzoate) 'straightened *trans*'; (⊕), POPI regular symmetrical '*trans*'; (⊗), POPI regular asymmetrical '*trans*'; (○), POPI random '*trans*'; line a, poly(*p*-oxybenzoate) '*cis*'; line b, poly(*p*-phenylene isophthalate) '*trans*'

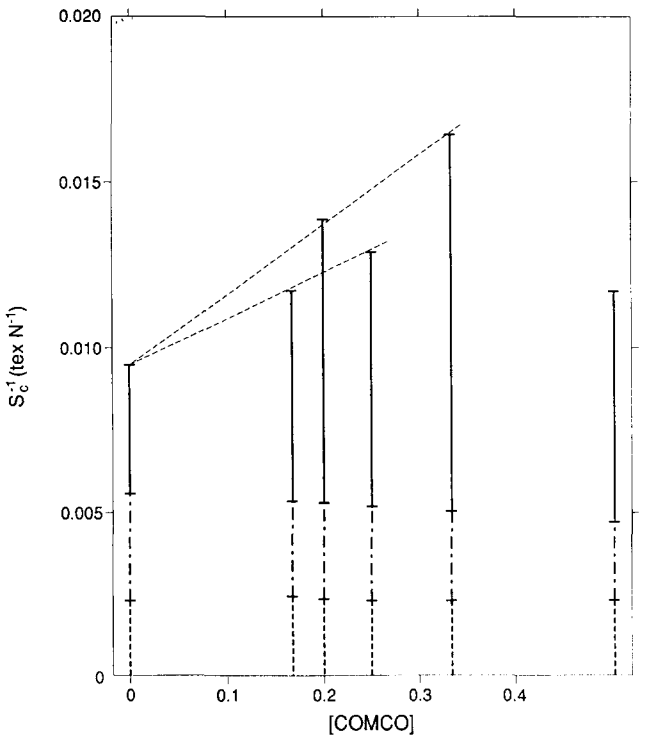


Figure 5 Effect of angular COMCO units on components of specific compliance of regular '*trans*' conformation chains: (---) bond stretching; (-·-·-) benzene rings deformation; (——) angle opening

Table 5 Moduli of 'as-made' poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) (POPI) and poly(*p*-oxybenzoate-*co*-*m*-phenylene terephthalate) (POMT) fibres

Copolymer	POPI		POMT
Disruptor unit	COMCO		OMO
Molar fraction	0.33	0.35	0.25
Modulus (GPa)	30	50	22
Reference	30	30	6

effect, via the chain sinuosity, influence the chain modulus in opposite ways and the overall outcome can only be evaluated by calculation.

In random copolymers the rod-like segments are of unequal lengths. The longer segments, resulting in larger departures from the line of action, have a more pronounced detrimental effect on the chain stiffness. Furthermore, an increase in the chain length results in an increased probability of a larger departure from the line of action. In this way it is possible to gain an understanding of the results obtained for random copolymers (*Figures 3* and *4*).

Results obtained for POPIs show that COMCO disruptor units affect the chain modulus in a complex way. Within the composition range of practical interest ([COMCO] between 0.25 and 0.33) the calculations predicted an increase in chain modulus with decreasing concentration of disruptor units, but they also showed the importance of chain regularity and length.

Experimental data[30] for highly oriented[23] 'as-made' POPI fibres are given in *Table 5*. In agreement with the modelling results, the modulus of the 67/33 fibre ([COMCO] = 0.25) is indeed higher than that of the 50/50 fibre ([COMCO] = 0.33). However, the measured moduli are significantly lower than those calculated for the chains with correlation lengths estimated from the broadening of the meridional X-ray reflections[22]. This discrepancy is due to factors affecting both the calculated and measured moduli. The actual chain lengths which are relevant to the mechanical behaviour certainly exceed the X-ray correlation lengths, which may be limited due to possible deviations from planar chain contour or to the presence of '*cis*' conformation units. Both the increase in chain length and deviations from quasiplanar '*trans*' conformation would result in a decrease of the chain moduli. As far as the measured moduli are concerned, they are adversely affected by imperfect chain alignment along the fibre axis and by defects which were detected in these fibres by SEM.

At this stage it is not possible to predict accurately the absolute values of moduli achievable with different compositions. Nevertheless, the modelling is useful in that it shows that the moduli of copolymers may be lower than those of either of the parent homopolymers. It also highlights the importance of the chain conformation, regularity, symmetry and length.

Copolymers containing m-phenylenedioxy and m-oxybenzoyl disruptor units

As already stated, realistic models of chains containing OMO and OMCO units are non-planar. Since tensile deformation of such chains involves rotation around bonds which cause deviations from planarity, Treloar's method cannot be used for evaluation of chain moduli. It is well established that the crystal moduli of homopolymers with helical conformations are substantially lower than those of similar planar homopolymers[31]. Thus the lack of planarity of chains containing OMO and OMCO units implies that their moduli are expected to be lower than those of corresponding quasiplanar chains containing COMCO units. Although the available experimental evidence is very limited (*Table 5*), it is in agreement with this conclusion.

CONCLUSIONS

Calculation of chain moduli of aromatic polyesters containing randomly distributed *m*-phenylene rings is presently manageable only for quasiplanar conformations, where the ester groups, *m*-phenylene rings and virtual bonds representing *p*-phenylene rings are confined to a plane. When at least one oxygen atom of an ester group is adjacent to the *m*-phenylene ring, as is the case for *m*-oxybenzoyl (OMCO) and *m*-phenylenedioxy (OMO) units, the quasiplanar conformations are not feasible. Whilst this rules out the evaluation of chain moduli, the lack of planarity will have in itself a detrimental effect on chain modulus. The use of such disruptor units is therefore undesirable.

In contrast, when the *m*-phenylene rings are incorporated into the chain through the carbon atoms of the ester groups, as is the case for isophthaloyl (COMCO) units, the quasiplanar conformations are feasible. From comparison of the observed WAXS features of the poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) fibres with those obtained from two kinds of quasiplanar models, it was concluded that the extended '*trans*' conformations are realistic. This is also the case for poly(*p*-phenylene isophthalate) and for the corresponding rigid-chain homopolymer poly(*p*-phenylene terephthalate),

but not for poly(*p*-oxybenzoate) where the '*cis*' conformation occurs in reality.

The calculations of moduli for quasiplanar chains revealed the dominant role of the angle opening contributions, which depend on the departures of the chain from the line of action. This explains why the chain modulus of '*trans*' poly(*p*-phenylene terephthalate) is about 50% higher than that of '*cis*' poly(*p*-oxybenzoate). For the same reason the moduli of copolymer chains with a given concentration of COMCO units are strongly influenced by chain regularity and length.

There is no simple relationship between the concentration of COMCO units and chain modulus. Indeed, the modulus of '*trans*' poly(*p*-phenylene isophthalate) is higher than that of some copolymer chains with a lower content of disruptor units and it also exceeds the modulus of the '*cis*' poly(*p*-oxybenzoate) chain. Thus, the intuitive notion employed in the design of thermotropic polymers, that the fewer disruptor units the better, is clearly a misconception.

In spite of certain necessary simplifications in the approach adopted in this work it was possible to appreciate the role of partial replacement of *p*-phenylene rings in aromatic polyesters by *m*-phenylene rings. A similar approach can be applied to polymers containing other angular disruptors, such as ether oxygen. It should be possible to use it in a predictive manner for the design of thermotropic polymers.

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