Influence of bond angles on the stability of nematic phases of aromatic polyesters

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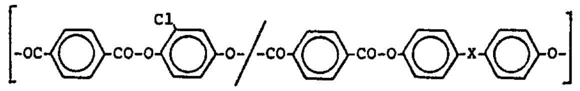
(*Received 8 March 1989; revised 19 May 1989; accepted 29 July 1989*)

Numerous polyesters of phenylthioterephthalic acid were prepared by thermal polycondensation with various acetylated diphenols and 4-acetoxybenzoic acid. The formation and stability of mesophases were determined and compared by differential scanning calorimetry measurements and microscopy. Furthermore, the polyesters of hydroquinone and phenoxy- or naphthyloxyterephthalic acid were compared with the corresponding polyesters of phenylthio- or naphthylthioterephthalic acid. Moreover, the bond angles of diphenyl ethers, benzophenones, diphenylsulphides, diphenylsulphones and bisphenol A from X-ray data of low-molecular-weight models were taken into account. The results indicate that the bond angles are decisive for the stability of mesophases, whereas the bulkiness of substituents is of minor importance. Wide angles in the polymer backbone favour mesophases, yet they are unfavourable in the side-chain.

(Keywords: stability; aromatic polyesters; bond angles; nematic phase)

INTRODUCTION

As described by several authors[1–8] the incorporation of non-linear diphenols, such as 4,4′-dihydroxydiphenylsulphide, 4,4′-dihydroxydiphenylsulphone, 4,4′-dihydroxydiphenylmethane or bisphenol A, into liquid-crystalline main-chain polymers (i.e. thermotropic polyesters) strongly reduces the stability of the nematic phase. In a detailed study of aromatic copolyesters, schematically represented by formulae **a**–**f**, Lenz and Jin[3] reached the conclusion that the steric demands (or bulkiness) of substituents, which affect the lateral distances of neighbouring chains, are mainly responsible for the influence of X on the stability of the nematic phase. This conclusion was partially based on the assumption[3] (no source was given!) that all bond angles of X fall into the narrow range of 105–110°.



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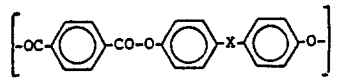
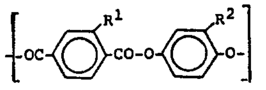
a: X = none
b: X = O
c: X = S
d: X = SO_2
e: X = CH_2
f: X = $C(CH_3)$

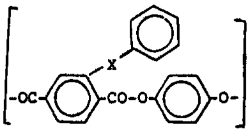
However, if the bulkiness of substituents in aromatic polyesters plays a key role for the stability of nematic phases, it is difficult to understand why polyarylates **2a** and **2b** are completely isotropic above their glass transition temperature (T_g), whereas poly(phenylhydroquinone terephthalate) **3a** and poly(hydroquinone phenylterephthalate) **3b** form a stable nematic melt[9–11]. Furthermore, the polyesters of hydroquinone and phenoxyterephthalic acid **4a**[12], phenylthioterephthalic acid **4b**[13] and naphthylthioterephthalic acid[14] from a nematic phase, whereas **5a** does not. Thus this work has the purpose to reinvestigate the role of bond angles of X in main chains and side-chains of fully aromatic polyesters.



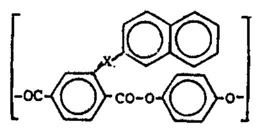
2a,b a: X = SO_2
b: X = $C(CH_3)_2$



3a,b a: R^1 = H, R^2 = C_6H_5
b: R^1 = C_6H_5, R^2 = H



4 a: X = O
b: X = S



5 a: X = O
b: X = S

EXPERIMENTAL

Materials

Thiophenol, dimethylnitroterephthalate and 4,4′-dihydroxydiphenylsulphide were purchased from Aldrich Co. (St Louis, MO, USA). 4,4′-Dihydroxybenzophenone was purchased from Lancaster (Morecambe, Lancs, UK). 4,4′-Dihydroxydiphenyl ether, 4,4′-dihydroxyphenylsulphone, bisphenol A, resorcinol and 4-hydroxybenzoic acid were gifts of Bayer AG (Krefeld-Uerdingen, FRG). All these compounds were used without further purification. All diphenols and 4-hydroxybenzoic acid were acetylated with an excess of acetic anhydride in boiling toluene. Phenylthioterephthalic acid was prepared as described previously[13].

Synthesis of polyester **6**, *poly(phenylthiohydroquinone terephthalate)*

O,O′-Bisacetylphenylthiohydroquinone (m.p. 84–85°C) (50 mmol), terephthalic acid (50 mmol) and magnesium oxide (10 mg) were weighed into a cylindrical glass reactor equipped with stirrer and gas inlet and outlet tubes. The reaction mixture was heated under stirring to 280°C, and the acetic acid was removed under a slow

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Table 1 Yields and properties of polyesters prepared from phenylthioterephthalic acid

Polymer formula	Yield (%)	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	$T_{isotropization}$ (°C)[c] $T_{anisotropization}$ (°C)[c]	Element formula (formula weight)	Element analyses	C	H	S
7	92	insoluble	138	485–495 (dec)	$C_{26}H_{16}O_4S$	Calc.	73.61	3.80	7.55
				–	(424.45)	Found	72.94	3.62	7.24
8	88	0.30	118	only isotropic	$C_{26}H_{16}O_4S_2$	Calc.	68.40	3.53	14.05
					(456.5)	Found	68.28	3.54	14.02
9a	83	0.36	127	only isotropic	$C_{26}H_{16}O_5S$	Calc.	70.89	3.66	7.28
					(440.5)	Found	70.60	3.51	7.05
9b	86	0.70	131	only isotropic	$C_{33}H_{20}O_7S$	Calc.	70.70	3.60	5.72
					(560.6)	Found	70.31	3.55	5.55
9c	91	0.36	12	310–330	$C_{40}H_{24}O_9S$	Calc.	70.57	3.55	4.71
				290–285	(680.7)	Found	69.88	3.56	4.55
9d	88	heterogeneous	128	heterogeneous melt	$C_{47}H_{28}O_{11}S$	Calc.	70.49	3.52	4.00
					(800.8)	Found	69.70	3.30	3.82

[a] Measured with $c=2\,g\,l^{-1}$ in CH_2Cl_2/TFA (4:1 by volume) at 20°C

[b] From d.s.c. measurements with a heating rate of 20°C min^{-1}

[c] Microscopic observation with crossed polarizers, heating or cooling rate 10°C min^{-1}

stream of nitrogen. After 45 min the temperature was raised to 320°C and after 15 min vacuum was applied for an additional 15 min, whereby the reaction mixture solidified. Yield of the crude product was 99%. The polyester was insoluble in CH_2Cl_2 or trifluoroacetic acid (TFA) or mixtures of both solvents. A d.s.c. heating trace measured with a rate of 20°C min^{-1} displayed a glass transition step at 119°C and an endotherm at 370°C. Analyses: calc. for $C_{20}H_{12}O_4S$ (348.38), C 68.95, H 3.47; found, C 68.16, H 3.41.

When the polycondensation was conducted for 3.5 h at 280°C and an additional 0.5 h at 280°C *in vacuo* only a low-molecular-weight product with a T_g of 90°C was obtained.

Synthesis of copolyester **9b** (*typical procedure for all other copolyesters*)

Phenylthioterephthalic acid (40 mmol), bisacetylhydroquinone (41 mmol) 4-acetoxybenzoic acid (80 mmol) and magnesium oxide (10 mg) were weighed into a cylindrical round-bottomed glass reactor equipped with stirrer and gas inlet and outlet tubes. The monomer mixture was rapidly heated to 250°C, where the condensation started. The reaction mixture was then gradually heated to 320°C (within 2 h), and vacuum was then applied for 0.5 h. The liberated acetic acid was removed with a slow stream of nitrogen under stirring. The cold reaction product was dissolved in a mixture of dichloromethane and trifluoroacetic acid (DCM/TFA 4:1 by volume) and precipitated into cold methanol. Finally the polyesters were dried at 60–80°C/12 mbar.

Measurements

The inherent viscosities were measured with an automated Ubbelohde viscosimeter thermostated at 20°C. Solutions of 100 mg polyester in 50 ml of DCM/TFA (4:1 by volume) were used in all cases.

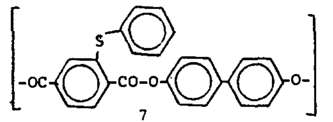
The d.s.c. measurements were conducted with a Perkin-Elmer DSC-4 in aluminium pans at a heating and cooling rate of 20°C min^{-1}.

The WAXS powder patterns were measured with a Siemens D-500 powder diffractometer as described previously[13].

RESULTS AND DISCUSSION

Polymer syntheses

In addition to the previously described polyesters **4a, b** and **5a, b**, which are required for the discussion below, the polyesters **6–11** were synthesized. Phenylthioterephthalic acid was used as monomer for polyesters **7–11**, for the following reasons. First, the phenylthio group significantly lowers the melting point of aromatic polyesters compared with unsubstituted terephthalic acid. Secondly, previous studies have shown that the phenylthio group (e.g. in **4b**) favours the formation of nematic phases more than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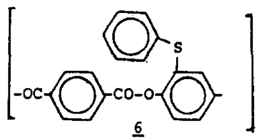
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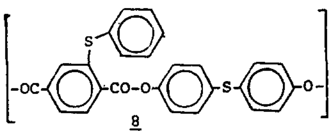
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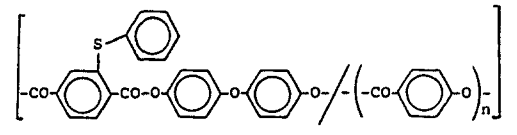
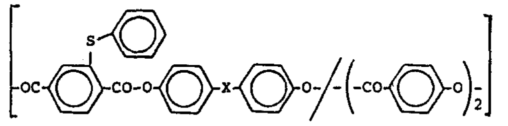

9a-d

a: n = 0
b: n = 1
c: n = 2
d: n = 3


10a-d

a: X = CO
b: X = S
c: SO$_2$
d: C(CH$_3$)$_2$

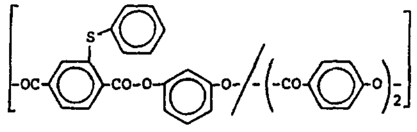

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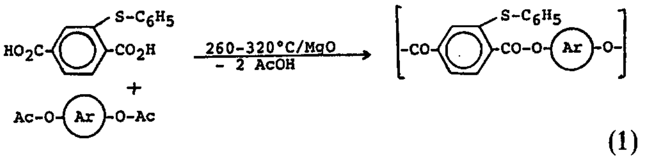
Table 2 Yields and properties of copolyesters prepared from phenylthioterephthalic acid, 4-acetoxybenzoic acid and various acylated diphenols

Polymer formula	Yield (%)	η_{inh}[a] (dl g^{-1})	T_g[b] (°C)	$T_{isotropization}$ (°C)[c] $T_{anisotropization}$ (°C)[c]	Element formula (formula weight)	Element analyses			
							C	H	S
10a	82	0.37	127	330–340 330–325	$C_{41}H_{24}O_9S$ (692.7)	Calc. Found	71.09 70.96	3.49 3.54	4.63 4.39
10b	91	0.43	127	only isotropic	$C_{40}H_{24}O_8S_2$ (696.7)	Calc. Found	68.95 68.17	3.47 3.33	9.20 8.88
10c	92	insoluble	166	only isotropic	$C_{40}H_{24}O_{10}S_2$ (728.7)	Calc. Found	65.93 65.67	3.22 3.36	8.80 8.69
10d	89	0.30	124	only isotropic	$C_{42}H_{30}O_8S$ (706.7)	Calc. Found	73.10 72.53	4.28 4.17	4.54 4.29
11	91	0.28	127	only isotropic	$C_{34}H_{20}O_8S$ (588.7)	Calc. Found	69.37 68.79	3.42 3.28	5.45 5.17

[a] Measured with $c = 2\ g\ l^{-1}$ at 20°C in CH_2Cl_2/TFA (4:1 by volume)
[b] From d.s.c. measurements with a heating rate of 20°C min^{-1}
[c] Microscopic observation with crossed polarizers, heating or cooling rate 10°C min^{-1}

the phenoxy group (e.g. in **4a**)[12,13]. Thirdly, phenylthioterephthalic acid allows the synthesis of aromatic polyesters by thermal condensation with acetylated diphenols according to equation (1)[13]. Aryloxyterephthalic acids are less suited for this simple synthetic method because of side-reactions[15].



(1)

The hitherto unknown polyesters **7–11** were all prepared by thermal condensation of phenylthioterephthalic acid with acetylated diphenols according to equation (1). Their yields and properties are summarized in *Tables 1* and *2*. The polyester **6**, which is isomeric to **4b**, was prepared analogously from terephthalic acid and acetylated phenylthiohydroquinone[16]. Its properties are described in the 'Experimental' part.

The role of bond angles

All polyesters discussed in this work were subjected to d.s.c. measurements conducted with a heating and cooling rate of 20°C min^{-1}. Furthermore, all polyesters were examined under a microscope with crossed polarizers. In several cases, such as **4a, b**, **5a, b**, **7**, **8**, **9** and **10a** WAXS powder patterns were measured.

The d.s.c. measurements of homopolyester **6** display in addition to the glass transition step an endotherm in the heating trace and the corresponding exotherm in the cooling trace (*Figure 1*). The microscopic characterization indicates that this first-order transition is a true melting process, and the WAXS powder pattern proves that the annealed polyester is semicrystalline (*Figure 2*, trace A). The microscopic observation also indicates that a nematic melt is formed above the melting point (T_m), which persists up to temperatures above 450°C where thermal degradation limits further observation. These results demonstrate that the properties of **6** agree largely with those of the isomeric polyester **4b**. Polyester **6** possesses a higher T_m, yet the position of the phenylthio group does not significantly affect the stability of the nematic phase.

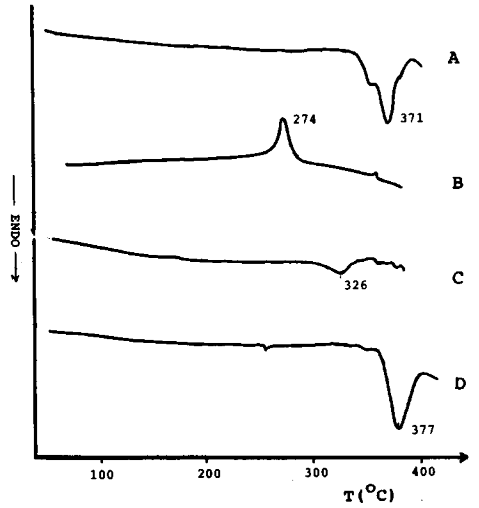


Figure 1 D.s.c. measurements of polyester **6** (heating and cooling rate 20°C min^{-1}): A, first heating after drying at 120°C; B, first cooling; C, second heating; D, third heating after annealing for 20 min at 320°C

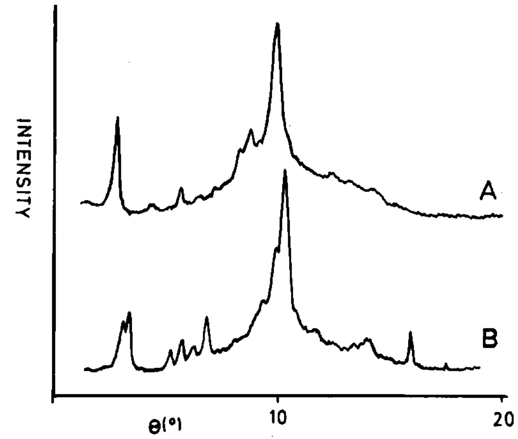


Figure 2 WAXS powder patterns measured at 20°C: A, polyester **6** after annealing at 200°C; B, polyester **7** after annealing at 200°C

As expected polyester **7** is also semicrystalline and forms a stable nematic phase above T_m (*Figure 2*, trace B, and *Figure 3*). In contrast to the crystalline polyesters **6** and **7** all other polyesters synthesized in this work (**8**, **9a–d**, **10a–d** and **11**) are amorphous. Their glass transition temperatures are listed in *Tables 1* and *2*.

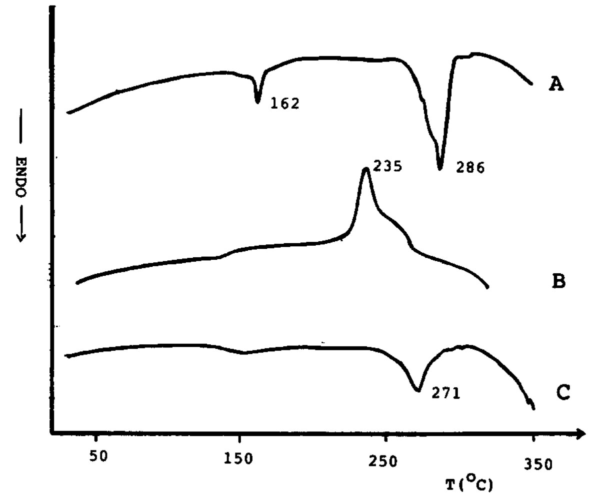


Figure 3 D.s.c. measurements of polyester **7** (heating and cooling rate 20°C min^{-1}): A, first heating after drying at 120°C; B, first cooling; C, second heating

The microscopic characterization of polyesters **8**, **9a**–**d** and **10a**–**d** with crossed polarizers gave the following results. The homopolyesters **8** and **9a** do not form a mesophase in contrast to **4b** and **7**. Even incorporation of one 4-hydroxybenzoic acid (4-Hybe) unit does not suffice to bring about a mesophase as evidenced by **9b**. However, incorporation of two 4-Hybe units yields an amorphous copolyester with a nematic melt that gradually vanishes between 300 and 330°C (*Table 1*). The nematic phase reappears in the form of typical droplets upon slow cooling from the isotropic melt. The texture of this nematic melt is the typical threaded schlieren texture reported many times for nematic main-chain polyesters. Incorporation of three 4-Hybe units (**9d**) yields a heterogeneous material containing a small fraction of crystallites of almost pure poly(4-Hybe). Therefore all other copolyesters (**10a**–**d** and **11**) were prepared with two 4-Hybe units. Microscopic observation revealed a nematic phase for **10a** (*Table 2*), whereas **10b**–**d** proved to be isotropic above T_g.

A consistent interpretation of these results is feasible on the basis of the X-ray data listed in *Table 3*. The listed bond angles of low-molecular-weight models of the diphenols present in **8**, **9a**–**d** and **10a**–**d** indicate that the bond angles of X attached to two benzene rings varies between ~100° and ~125° and not between 105° and 110° as reported by Lenz and Jin[3]. It is worth noting that the bond angles of these model compounds (*Table 3*) agree well with those reported for poly(ether ketone)s (124±1°)[20], poly(phenylene oxide)s (124°)[20] and poly(phenylene sulphide) (110°)[20]. The comparison of **9c** and **10a**–**d** demonstrates that only those diphenols with a relatively wide angle (**9a** and **10a**) can form a mesophase. The comparison of **9a** with **7** illustrates that even the widest bond angle is disadvantageous for the nematic phase, when compared with a stiff, linear building block.

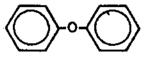
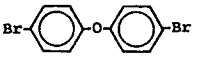
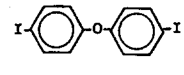
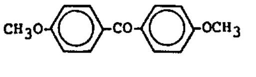
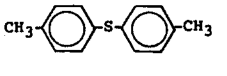
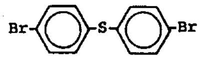
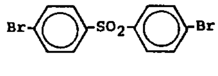
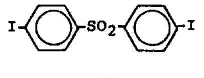
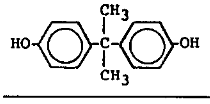
The decisive role of the bond angles also becomes evident when the influence of different substituents is considered. Provided that the steric demands play a key role, one should expect that the polyarylates **2a**, **b** would be thermotropic with broad nematic phases, whereas **3a**, **b** and most polyesters of phenoxy- or phenylthioterephthalic acids would not. Yet the opposite is true; **2a** and **2b** are known to be perfectly isotropic. Furthermore, the stability of the nematic phase should decrease in the order **4a**>**4b**(**5a**)>**5b**. However, the nematic phase of **5b** is more stable than that of **4a**, although the naphthyl group is more space-filling than the phenyl ring and the sulphur more voluminous than the ether oxygen[11]. Obviously, the smaller bond angle of the sulphide group is more compatible with a nearly parallel alignment of side-chain and main chain than the wider angle of aryloxy groups.

Another interesting comparison is that of **3a**, **b** with **4b** and **6**. From the viewpoint of steric demands the nematic phase of **4b** and **6** should be less stable than that of **3a** and **3b**, yet the contrary is true[8,10]. When the bond angles are taken into account the higher melting points of **4b** and **6** and their higher temperatures of isotropization are easy to understand. The phenyl groups of **3a** and **3b** hinder a parallel alignment of neighbouring chains in the solid state and in the nematic phase. The phenyl groups of **4b** and **6** can adopt a conformation parallel to the main chain, so that the steric hindrance for neighbouring main chains is reduced.

A comparison between polyesters **10a** and **11** is of interest because both polyesters contain non-linear diphenols with bond angles close to 120°. However the quasi-linear chain segment between two 'bending points' is shorter by one aromatic ring in the case of **11**. Obviously this difference suffices to suppress the formation of mesophase in agreement with the different properties of **9b** and **9c**.

Finally it is worth mentioning that the 'static bond angle' derived from crystalline materials around room temperature is not necessarily identical with the 'dynamic bond angle' in a nematic melt at 200–400°C. Both vibration in the C–X–C plane and independent rotations

Table 3 Bond angles of model compounds of non-linear diphenols

Structure	Bond angle (deg)	Method	Ref.
	124±5	Dipole moment	17
	123±1	X-ray	17
	122±0.5	X-ray	18
	120.6±0.6	X-ray	19
	109±2	X-ray	17
	109.5±1	X-ray	17
	100±0.5	X-ray	17
	106±2	X-ray	17
	110±1	X-ray and quantum-mechanical calculation	21

of the phenyl rings around the C–X bonds have the tendency to widen the bond angle at X. The assumption of a wider dynamic bond angle may help to understand why, for instance, bisphenol A is less compatible with a mesophase than 4,4′-dihydroxydiphenylmethane[3]. Widening vibrations of the bond angle (and rotations) are more hindered by the methyl groups of bisphenol A than by the central protons of diphenylmethane. Further studies will show to what extent the hypothesis of dynamic bond angles is helpful for a better understanding of structure–property relationships of thermotropic polymers.

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