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ScienceDirect
Mendeleev Commun., 1993, **3**(**3**), 115–118

Mendeleev Communications

New Polyesters and Copolyesters Derived from 2,5-Dihydroxyterphenyl and 2,5-Dicarboxyterphenyl

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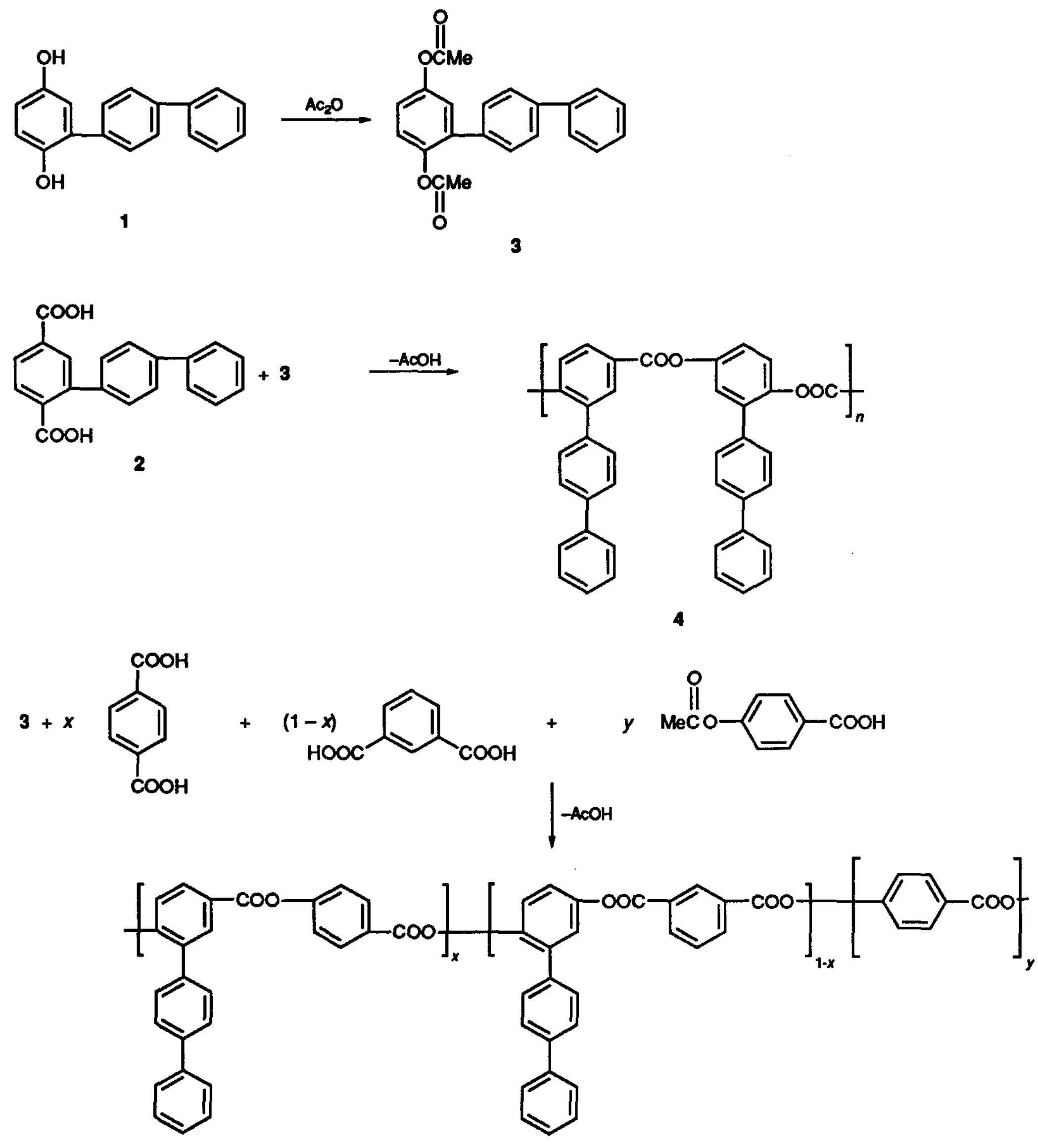
The synthesis and thermal properties of novel (4-diphenyl)-substituted rigid-rod polyesters is described.

Wholly aromatic liquid crystalline (LC) polyesters are the most important commercial class of thermotropic polymers because of their thermal and mechanical properties.[1] However, linear aromatic polyesters, such as poly(*p*-oxybenzoate) and poly(*p*-phenyleneterephthalate), have such high melting temperatures (610 and 600 °C, respectively)[2] that the processing of such polymers is essentially precluded. Several approaches have been used to lower the melting temperatures of aromatic polyesters including the introduction of substituents into the monomer units so as to disrupt lateral packing. According to Dowell[3,4] the introduction into the monomer units of long, rigid side groups should improve



5	x	y
a	1	0
b	0.8	0
c	0.5	0
d	0.5	0.5

both the tractability and the mechanical properties of the polymers.

Recently we described the synthesis of rigid-rod polyesters and polyamides with long rigid side groups linked to the polymer chain *via* an ester bond.[5,6] We found that these polymers were more tractable compared with unsubstituted ones and formed an LC phase. However, transesterification took place at high temperatures leading to polymer cross-linking. In this connection it is interesting to synthesize polyesters in which rigid-rod side groups are connected to the polymer chain *via* a single C–C bond in order to avoid cross-linking. One such promising side group is the (4-diphenyl) group; Heitz[7], who recently described the synthesis of poly[*p*-phenylene(4-diphenyl)terephthalate], observed nematic phase formation in this polymer. The goal of the present work was to synthesize a series of polymers and copolymers based on (4-diphenyl)-substituted hydroquinone and (4-diphenyl)-substituted terephthalic acid and to study their thermal properties.

Transition temperatures and enthalpy changes were measured with a DSC-4 differential scanning calorimeter at a heating rate of 16 °C min^{-1} under argon. Thermogravimetric analysis was carried out at a heating rate of 5 °C min^{-1} in air. Inherent viscosity values (η_{inh}) were determined in 1,1,2,2-tetrachloroethane (TCE) at 25 °C (0.5 cm^3 g^{-1}). 2,5-Dihdroxy-terphenyl **1** and 2,5-dicarboxyterphenyl **2** were prepared as described in refs. 7 and 8, respectively. 2,5-Diacetoxyterphenyl **3** was prepared by refluxing **1** (1 g) in a mixture of CCl_4 (10 ml) and acetic anhydride (3 ml) for 2 h. Solvent was removed under reduced pressure and the residue was recrystallized twice from CCl_4 to give 2,5-diacetoxyterphenyl; yield 82%, m.p. = 123.5–125 °C, elemental analysis: ($C_{22}H_{18}O_4$) Found (%) C 76.21; H 5.01. Calc. (%) C 76.28; H 5.24; IR ν/cm^{-1} 1730 (C=O ester).

Isophthalic acid was recrystallized from propan-2-ol, terepthalic acid was purified *via* the sodium salt, and 4-acetoxybenzoic acid was recrystallized from benzene, m.p. = 189–190 °C. The monomer and polymer synthesis is shown in Scheme 1.

Polymers **4** and **5a–d** were prepared by high-temperature transesterification of diphenol diacetates with aromatic diacids in a melt as follows. In the tube were placed **3**

Table 1 Properties of the polymers synthesized

Polymer	Yield(%)	T_g/°C[a]	$T_{5\%}$/°C[b]	η_{inh}/cm^3 g^{-1}
4	93	163	452	0.92
5a	97	170	461	—
5b	96	165	458	—
5c	96	155	452	0.99
5d	90	165	460	1.12

[a] T_g is the glass transition temperature. [b] $T_{5\%}$ is the temperature at which 5% weight loss occurs.

(0.002–0.01 mol) and an equal quantity of **2** (in the case of polymer **4**) or a mixture of terephthalic and isophthalic acid (molar ratio 100:0 for **5a**, 80:20 for **5b** and 50:50 for **5c**) or a mixture of terephthalic, isophthalic and 4-acetoxybenzoic acid (in the case of **5d**, molar ratio 50:50:50). The tube was rapidly heated under argon to 280 °C to initiate the reaction. The acetic acid liberated was removed by a slow argon stream. The reaction was kept at 280 °C for 30 min, at 320 °C for 30 min and at 340 °C for 1 h, under a vacuum of 2 mm Hg. The polymers formed (**4** and **5c,d**) were dissolved in hot $CHCl_3$, precipitated with acetone and dried *in vacuo*. Polymers **5a,b** were found to be insoluble in common solvents, which prevented their purification due to reprecipitation. The polymer properties are listed in Table 1.

The polymers were tough, slightly coloured solids in appearance. In the IR spectra of the polymers only a carbonyl absorbtion band was observed (1735 cm^{-1}, C=O ester) which suggests a fairly high molecular weight for the polymers. Most of the polymers were soluble in common solvents such as TCE and chloroform in spite of their wholly aromatic nature.

Only polymers **5a,b** were insoluble in common solvents; in addition polymer **5a** remained solid at the end of polycondensation, even when heated to 400 °C. Tough and flexible films could be prepared from solutions of polymers **5c,d** and **4** in $CHCl_3$ or TCE.

Apparently, the rigid (4-biphenyl) substituent strongly increases the solubility of the aromatic polyesters, especially in the case of polymer **4** in which each aromatic core bears a (4-biphenyl) side group. On the other hand, polymer **5a**—which has the same backbone as **4**, but only bears (4-biphenyl) side groups on the hydroquinone residues—is insoluble in common solvents. It is noteworthy that poly[*p*-phenylene(4-biphenyl)terephthalate] is soluble in *p*-chlorophenol[7] while we were not able to dissolve polymer **5a** in any solvent. We may conclude that the disposition of the (4-biphenyl) side group strongly affects the solubility of the poly(*p*-phenyleneterephthalate) backbone.

To increase the processibility of **5a** we introduced comonomers such as isophthalic and 4-hydroxybenzoic acids into the polymer chain to give copolymers **5b–d**. As stated above, polymers **5c–d** were found to be soluble in common solvents; this arises from both the disruption of the chain linearity with isophthalic moieties and the lowering of the structural regularity with 4-(hydroxy)benzoate fragments. To study the thermal properties of the polymers we carried out different scanning calorimetry (DSC) on the polymers. For all polymers except **5a** the first and subsequent heating stages were identical. A glass transition was only obseved in DSC traces of polymers **5b–d** (Table 1). Annealing at 180 °C for 20 h had little effect on the thermal behaviour of polymers **5b–d**. In the case of **5a** an exotherm was observed on the first heating (ΔH=2.8 kJ mol^{-1}) at 215 °C but it disappeared on the second and subsequent heating, Fig. 1. Taking into consideration the fact that the exotherm was observed just after the glass transition (Table 1), we attribute that exotherm to crystallization. This conclusion is also confirmed by the increase in birefringence of **5a** above 200 °C. On the other hand, there was no birefringence in the samples of polymers **5b–d**, which suggests an amorphous nature for these copolymers.

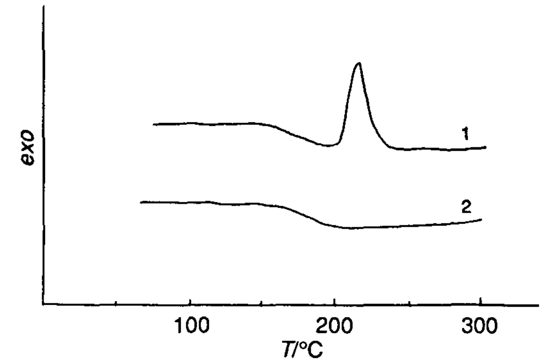


Fig. 1 DSC traces of polymer **5a**. 1:first heating scan; 2:second heating scan.

The thermal stability of polymers **4** and **5a–d** was tested by TGA (Table 1). The polymers presented have good thermal stability (the temperature at which 5% loss of weight took place was above 450 °C in air) which, along with their good tractability, makes them promising materials for technical applications. As stated above we were not able to observe an LC phase in any of the polymers. We could explain the amorphous nature of polymer **4** by the presence of bulky side groups that hindered the packing of polymer chains parallel with each other. Polymers **5b–d** have *m*-phenylene moieties incorporated into the polymer chain that disrupt the chain linearity; this might in principle prevent LC phase formation. However, it is known that linear aromatic polyesters containing up to 50 mol% of *m*-phenylene moieties exhibit an LC phase,[9] so we have to conclude that the (4-biphenyl) substituent in **5b–d** also hinders the lateral packing of the polymer chains, preventing LC phase formation. On the other hand, poly[*p*-phenylene(4-biphenyl)terephthalate] (PPBT) exhibits an LC nematic phase[7] while polymer **5a** does not, though their structures are very similar to each other. The difference between them is that the (4-biphenyl) group is attached to the terephthalic moiety in PPBT and to the hydroquinone moiety in polymer **5a**. Such a difference in their thermal properties is as yet unclear. To solve this problem it is necessary to perform detailed X-ray investigations on the above-mentioned polymers. Meanwhile, it has already been mentioned[10] that the presence of a side group on the hydroquinone moiety in the poly(*p*-phenyleneterephthalate) chain is unfavourable for LC phase formation.

In conclusion, we have synthesized a series of new, wholly aromatic rigid polyesters and copolyesters containing (4-biphenyl) side groups. The introduction of the (4-biphenyl) side group has enhanced polymer processibility, and in addition their thermostability has remained at a high level characteristic of linear rigid-rod aromatic polyesters. It is noteworthy that all the polymers except **5a** are amorphous in nature; this might be the result of lateral packing disruption by the bulky, rigid (4-biphenyl) group.

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Received: Moscow, 29th September 1992
Cambridge, 8th January 1993; Com. 2/05428K