New thermotropic polyesters with quinoline units in the chain

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New aromatic polyesters with rigid quinoline units in the chain have been synthesized in order to investigate the possibility of generating materials that exhibit liquid crystalline behaviour in the melt. Similar materials containing 2,6-naphthalene units in the chain have also been prepared and compared with the quinoline polymers.

(Keywords: polyesters; quinoline; naphthalene)

Introduction

Polyquinolines with a wide range of chain stiffness, which can be altered from relatively flexible polymers with a low glass transition temperature (T_g) to rod-like macromolecules with a high T_g, have been reported in the literature[1]. The synthetic route used is the Friedlander reaction, under a variety of base- or acid-catalysed conditions, between an aromatic bis-*o*-aminoketone and an aromatic diketone. All the polymers show excellent thermal stability, with initial weight losses occurring between 500 and 600°C in air.

Most of the materials are soluble in common organic solvents and have a low degree of crystallinity[2,3], except for rigid polyquinoline ($T_g = 415°C$, melting temperature (T_m) = 552°C, crystallinity > 60%).

The introduction of such quinoline units into the polymer backbone of other aromatic polymers could influence the degree of crystallinity, the T_m and the thermal stability, and hence in the past we have successfully synthesized new quinoline monomers such as quinoline-2,6-dicarboxylic acid and 6-aminoquinoline-2-carboxylic acid[4]. In our approach the quinoline ring is formed in the monomer synthesis, rather than in the polymerization. The synthesis of polyamides and poly(arylene)ethers, containing such quinoline units in the chain, has been reported previously[5,6].

We have now synthesized new aromatic polyesters with rigid quinoline units in the chain, in order to investigate the possibility of generating materials that exhibit liquid crystalline behaviour in the melt, i.e. thermotropic liquid crystals. Similar materials containing 2,6-naphthalene units in the chain have also been synthesized and compared with the quinoline polymers.

In fact, the desired lower thermal transitions can be obtained by molecular structural modifications of the systems, which would diminish interchain association by disrupting interchain correlations.

Results and discussion

Polymers **1–14** (*Scheme 1*) were synthesized in 96–100% yield by the direct formamide-catalysed polycondensation method using tosyl chloride in pyridine, following the procedure reported for similar systems[7].

The data relating to inherent viscosities (η_{inh}), thermomechanical and thermogravimetric analyses (t.m.a. and t.g.a.) and polarization microscopy are reported in *Table 1*. The decomposition temperatures (T_Ds) of all polymers are, as expected, in the range of 350–450°C.

Among the polymers that exhibit thermotropic behaviour, polymer **1**, containing only 20% of quinoline units, showed a liquid crystalline transition as low as 140–170°C. The crystalline transition temperatures are generally higher or absent when the percentage of quinoline units in the chain is increased (samples **2**–**5**, **7**, **8** and **10**). The substitution of the quinoline units by the naphthalene rings did not introduce remarkable variations in the range of mesophase.

Other approaches to reducing intermolecular interactions by using methyl-substituted hydroquinone[8,9] (polymers **9**, **10**, **13** and **14**) or biphenol monomers (polymer **5**) were also exploited. The results indicate no remarkable variations with respect to the other polymers.

Experimental

Starting materials. Tosyl chloride was purified by double recrystallization from n-hexane, m.p. 68–69°C. Pyridine (b.p. 115.5°C) was vacuum distilled under argon in the presence of KOH pellets, and stored under 3 Å molecular sieves. Quinoline-2,6-dicarboxylic acid was prepared as previously reported[4].

The other starting materials were either purchased or prepared by literature procedures.

Polymers. The polymers were prepared in 96–100% yield by following literature procedures[7].

A typical synthesis for polymer **7** (*Scheme 1*) is as follows. A solution of pure tosyl chloride (1.235 g, 0.0065 mol) in dry pyridine (10 ml), stirred at room

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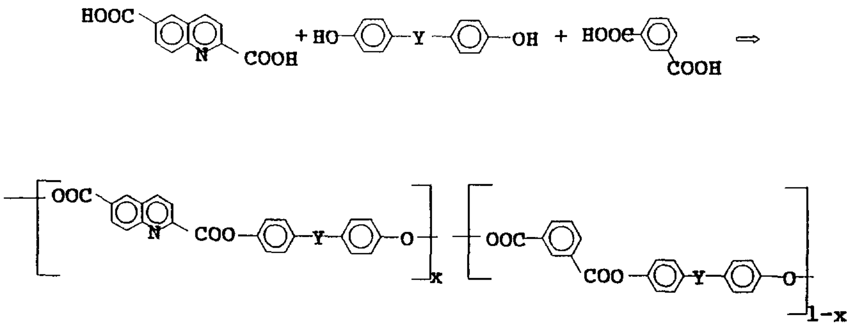

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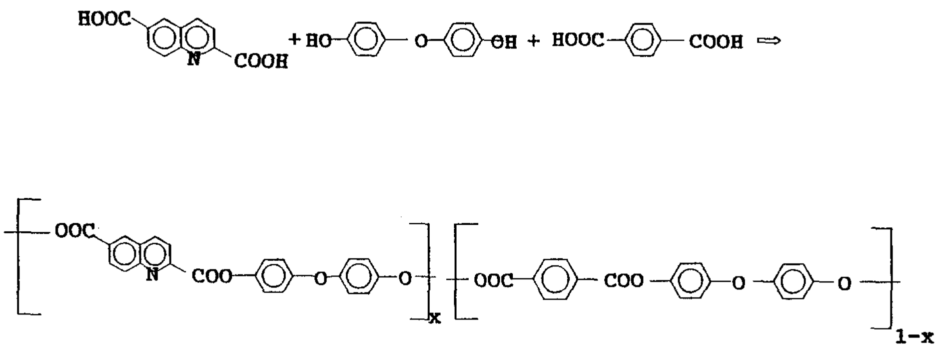

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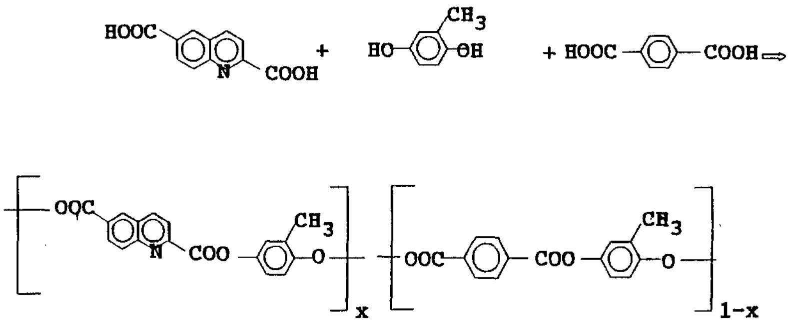

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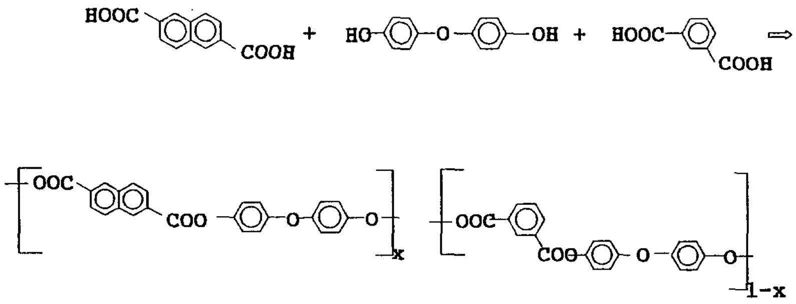

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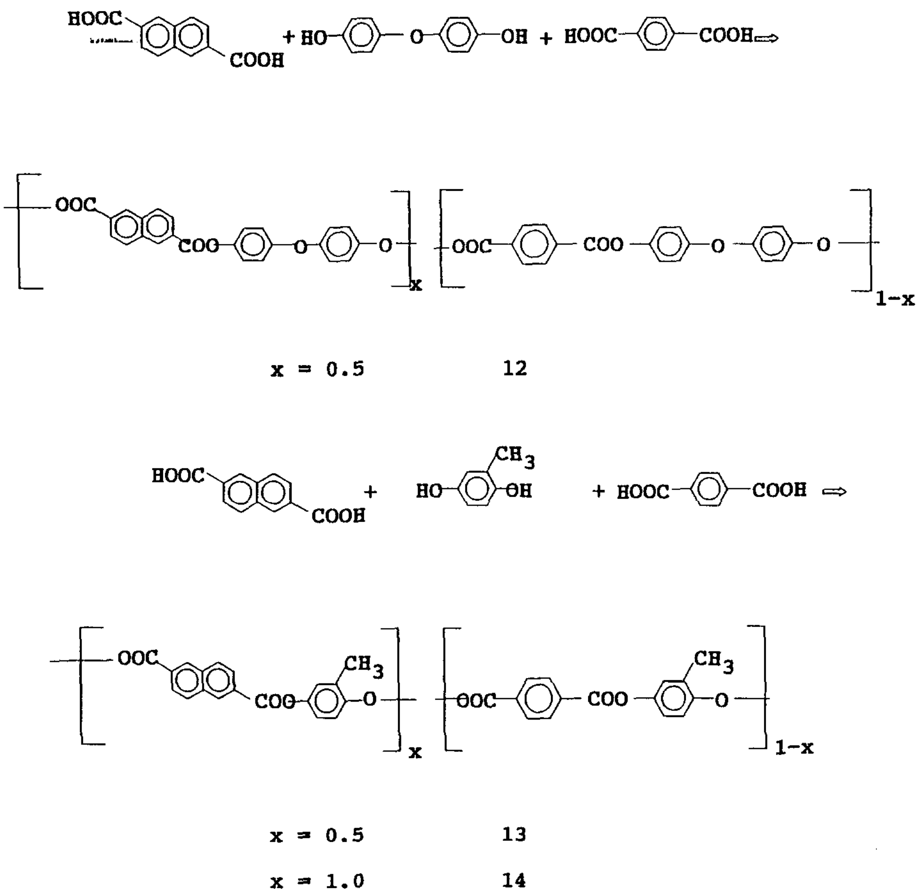

Scheme 1

Table 1 Data obtained from solution viscometry, t.m.a., t.g.a. and polarization microscopy

Polymer[a]	η_{inh}[b] (dl g^{-1})	T_g[c] (°C)	T_D[d] (°C)	Range of mesophase[e] (°C)
1	0.36	140	400	140–170
2	0.42	150	350	210–230
3	0.48	180	350	–
4	0.30	300	350	–
5	–[f]	320	400	–
6	0.52	160	400	160–300
7	0.87	170	400	210–280
8	0.59	190	350	–
9	1.13	140	380	170–280
10	–[f]	190	300	–
11	–[f]	240	420	190–240
12	–[f]	300	450	200–300
13	0.55	160	380	170–250
14	–[f]	210	300	–

[a] All elemental analyses confirmed the proposed structures of the polymers

[b] Measured in $CF_3COOH{:}CH_2Cl_2$ (1:4 by volume)

[c] Determined from thermomechanical curves at a heating rate of 15°C min^{-1} and a load of 0.8 kg cm^{-2}

[d] Determined by t.g.a. curves at a heating rate of 5°C min^{-1} in air (10% weight loss)

[e] The phase behaviour was investigated by polarization microscopy with crossed polarizing filters with heating and cooling rates of 8°C min^{-1}

[f] Insoluble

temperature for 30 min, was added dropwise over 30 min to a hot solution of terephthalic acid (0.1038 g, 0.00125 mol) in dry pyridine–dimethylformamide (1:1; 20 ml) preheated at 125°C for 5 min. The resulting mixture was stirred under argon at 120°C for 2 h. The polymer solution was then poured into methanol to precipitate the polymer. (When the copolyesters precipitated from the reaction media during the polymer synthesis, the suspension was diluted with methanol.) The polymer was isolated by filtration, washed with methanol and dried under vacuum at 40°C.

Instrumental methods. The softening temperature was determined from thermomechanical curves on a Tseitlin apparatus at a heating rate of 15°C min^{-1} and a load of 0.8 kg cm^{-2}, and taken from the intersection of the tangents to the branches of the thermomechanical curves in the area of initial flow. The temperature at which 10% weight loss of polyesters occurred (T_D) was determined from t.g.a. curves taken on a Derivatograph Q-1500 D (System F. Paulik, Hungary) at a heating rate of 5°C min^{-1} in air. Phase behaviour was investigated by polarizing microscopy with crossed polarizing filters on MIN-8 apparatus (Russia); the heating and cooling rate was 8°C min^{-1}.

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