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Synthesis and characterization of *meta*-linked polyamides containing sulfone, ether and ketone linkages

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High molecular weight aromatic polyamides were obtained from 4,4′-bis[(3-carboxyphenoxy)(*p*-benzoyl)]phenyl sulfone, by direct polycondensation reaction in N-methyl-2-pyrrolidone with various aromatic diamines, using triphenyl phosphite and pyridine as condensing agents. The polymers were characterized by solution viscosities, elemental analysis, thermogravimetric analysis, differential scanning calorimetry and infrared analysis. The polymers, obtained in 92–95% yield, possessed inherent viscosities in the range 0.56–1.35 dl g^{-1}, glass transition temperatures between 210 and 228°C, and 10% weight loss temperatures in nitrogen and air above 490 and 460°C respectively. The effect of the different structures on properties such as solubility, molecular weight, T_g and thermal behaviour were also studied. © 1997 Elsevier Science Ltd.

(Keywords: aramides; poly(ether ketone sulfone)amides; direct polycondensation)

INTRODUCTION

Aromatic polyamides are of commercial importance and academic interest[1]. They exhibit high thermal stability and excellent mechanical properties. However, they are generally difficult to process into fibres and films because of their insoluble nature or limited solubility in organic solvents and their high softening or melting temperatures. The processing of these polymers by thermoplastic methods has been difficult because they tend to degrade before or at the softening or melting temperature[2].

To make aromatic polyamides more processable, various attempts have been made to reduce their melting temperature or improve their solubility. The introduction in the polymer chain of ether linkages improves the solubility because of the enhancement of chain flexibility. A similar effect, but to a lower extent, is shown by the presence of ketone groups. The improvement of solubility without extreme loss of thermal stability can also be reached by introducing sulfonyl groups[3–5] that are more active than ether or ketone groups in disrupting chain stiffness[6]. We have already reported[7] that polymers containing ether, carbonyl, sulfonyl and amide groups connected by aromatic rings, linked in all *para* fashion within the polymeric backbone, exhibit a favourable balance of properties. These polyamides, synthesized starting from 4,4′-bis[(4-carboxyphenoxy)(*p*-benzoyl)]phenyl sulfone, showed high solubility and lower crystallinity but the moiety containing the sulfone group was not sufficient to promote a drop of crystallinity and subsequent detection of a T_g for all polymers. As it is recognized that chain symmetry can affect the T_g, the solubility and the crystallinity of the polymers, in this work we describe the synthesis and characterization of polyamides obtained starting from 4,4′-bis[(3-carboxyphenoxy)(*p*-benzoyl)]phenyl sulfone; the influence of the incorporation of the *meta* linkage into the polymer backbone on the thermal properties of the polymers is also studied.

EXPERIMENTAL

Materials

N-methyl-2-pyrrolidone (NMP; Aldrich) was refluxed under vacuum in the presence of CaH_2 for 8 h and distilled in the same conditions. Then it was refluxed under vacuum in the presence of P_2O_5 for 6 h and distilled. Triphenyl phosphite (TPP; Aldrich) was purified by fractional distillation under vacuum. Pyridine (Py; Aldrich) was refluxed in an inert atmosphere in the presence of NaOH for 6 h and distilled. LiCl (Aldrich) was dried for 16 h at 180°C under vacuum. Reagent grade aromatic diamines were commercial materials (Aldrich): *p*-phenylenediamine, *m*-phenylenediamine and 4,4′-oxydianiline were purified by sublimation; 4,4′-methylenedianiline was crystallized from benzene; 4,4′-sulfonyldianiline and 1,5-diaminonaphthalene were crystallized from ethanol. Methyl 3-hydroxybenzoate (Aldrich) was used as received and 4,4′-bis(*p*-fluorobenzoyl)phenyl sulfone was synthesized according to the literature[8].

Instrumental methods

Infrared spectra (i.r.) of the polymers were recorded using a Perkin–Elmer FT-1725-X spectrophotometer over the range 4000–600 cm^{-1} on a pressed mixture with KBr. Elemental analyses were conducted on a Carlo Erba Elemental Analyzer, model 1106. The determination of glass transition temperature (T_g) by differential scanning calorimetry (d.s.c.) was carried out using a Mettler DSC 30 with Al pans at a heating rate of 20°C min^{-1} under N_2. Thermogravimetric analyses (t.g.a.) were performed with a

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Mettler M3 thermobalance at a heating rate of 10°C min^{-1} in nitrogen (25 ml min^{-1}) and in air atmosphere.

Ostwald viscometers were used to determine inherent viscosities, η_{inh} ($= \ln \eta_r/C$), of polymer solutions having concentration $C = 0.5\,\mathrm{g\,dl}^{-1}$. A constant temperature bath was maintained at 30°C. Quantitative solubility was determined using 0.2 g of polymer in 2 ml of solvent.

*Monomer synthesis: synthesis of 4,4′-bis[(3-carboxyphenoxy)(*p*-benzoyl)]phenyl sulfone*

To 6.16 g of 4,4′-bis(*p*-fluorobenzoyl)phenyl sulfone (0.013 mol) in 40 ml of NMP was added 5 g of methyl 3-hydroxybenzoate potassium salt (0.026 mol). The mixture was stirred and heated in a nitrogen atmosphere at 160°C for 6 h. After cooling, 60 ml of 10% aqueous sodium hydroxide was added and the mixture was then heated at 110°C for 2 h. The cooled solution was diluted to 1 litre with water and acidified with dilute sulfuric acid to pH 2. The slurry was stirred for 2 h and then filtered. The crude solid was washed with water, dried and crystallized from acetic acid and charcoal to yield (70%) a white solid, m.p. 240°C. The i.r. spectrum showed absorptions at 1680 and 1655 cm^{-1} (C=O), 1398–1161 cm^{-1} (SO_2) and 1235 cm^{-1} (COC). Elemental analysis calculated for $C_{40}H_{26}O_{10}S$ (698.69): C, 68.76; H, 3.75; S, 4.58. Found: C, 68.58; H, 3.71; S, 4.61.

Polymer synthesis

Diacid (0.8735 g, 0.001 25 mol), diamine (0.00 125 mol) and TPP (0.7757 g, 0.002 50 mol) were mixed into 5 ml of NMP and 1.25 ml of Py containing 0.5 g of LiCl (8 wt%). The mixture was maintained under stirring, in nitrogen atmosphere, for 3 h at 105°C. After cooling, it was poured into 200 ml of methanol and the precipitated polymer was collected by filtration, extracted with methanol overnight and dried under vacuum for 14 h at 80°C.

RESULTS AND DISCUSSION

Monomer synthesis

4,4′-bis[(3-carboxyphenoxy)(*p*-benzoyl)]phenyl sulfone was synthesized according to *Scheme 1* by the aromatic nucleophilic displacement of fluorine from an activated substrate by the potassium salt of methyl 3-hydroxybenzoate, in NMP solution at 160°C for 6 h. The diacid, obtained from hydrolysis of the resulting diester, was characterized by i.r. and gave satisfactory results in elemental analysis.

Polymer synthesis

Polyamides **2a–f** were prepared by direct polycondensation of the aromatic dicarboxylic acid (**1**) with diamines (**a–f**) via the phosphorylation route by the procedure described by Yamazaki *et al.*[9] in the presence of 8% by weight of LiCl, in a nitrogen atmosphere. All the polymerizations proceeded in homogeneous solution and, at the end, the viscosity of the solution was very high; the yields were in the range 92–95%. The properties of the polyamides are summarized in *Table 1*. The polymers possessed η_{inh} in the range 0.56–1.35 dl g^{-1}: the values for the *meta*-linked polyamides are higher than those of the *para*-linked polyamides[7]. From structural considerations the opposite could be expected, but we have to take into account that, to achieve high molecular weights, many factors affect low-temperature condensation. In particular, the solubility of the growing polymer in the polymerization medium plays an important role: the higher solubility of *meta*-polyamides (*Table 2*), with respect to the *para*-phenylene ones, gives rise to polymers with higher molecular weight[9]. The elemental analysis values for carbon, hydrogen and nitrogen are in close agreement with the calculated values. I.r. spectra of all the compounds show N–H stretching in the range 3435–3415 cm^{-1}. The presence of absorption bands at 1660 cm^{-1}, due to amide C=O, at 1580 cm^{-1}, due to N–H bend, and at 1420 cm^{-1}, due to amide C–N stretch, confirm the structure of the polyaramides.

Table 1 Properties of polyamides **2a–f**

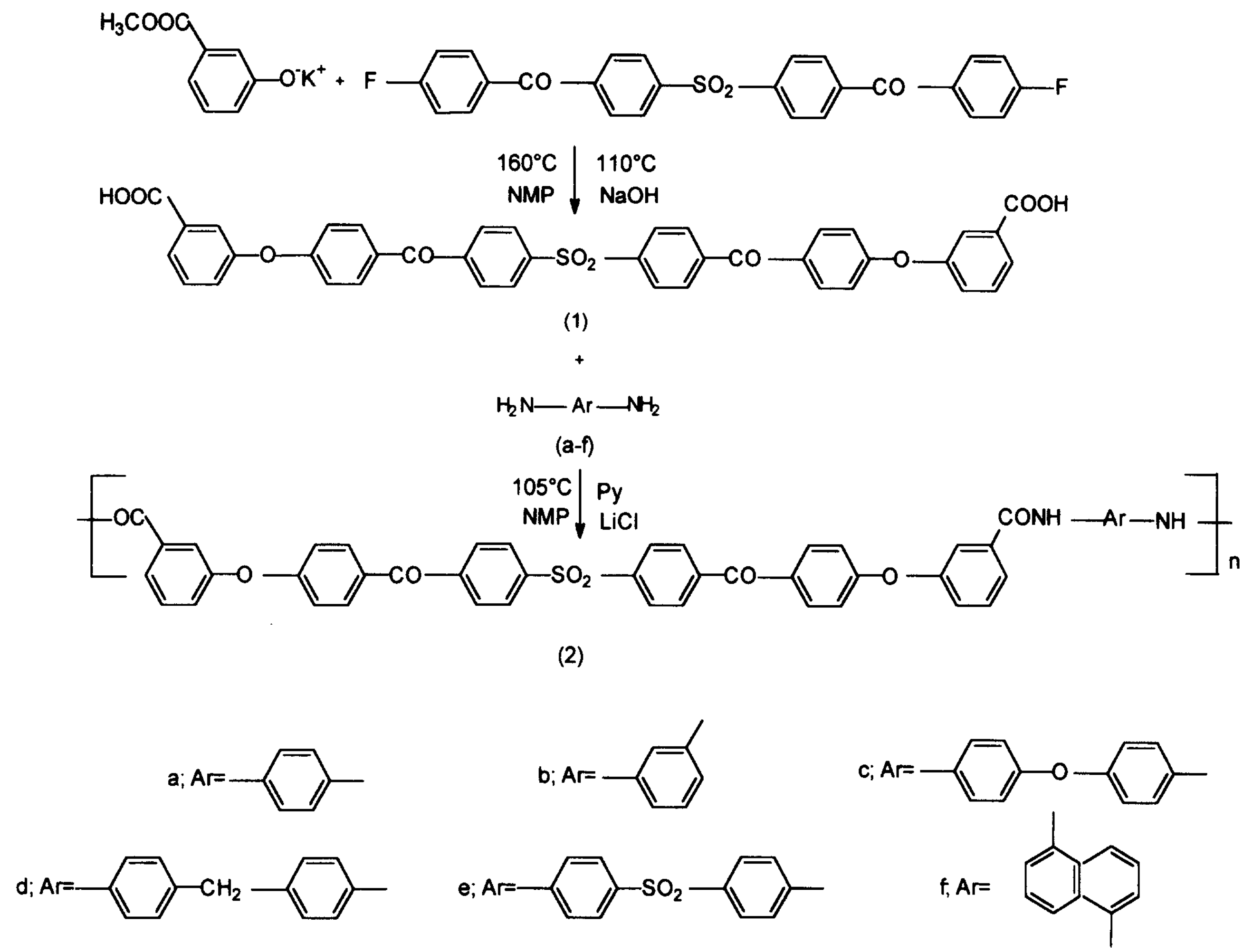
			Elemental analysis[b]			
Polymer	η_{inh}^{a}	Formula	C	H	N	S
2a	0.89	$(C_{46}H_{30}N_2O_8S)_n$ $(770.81)_n$	71.15 (71.68)	3.85 (3.92)	3.70 (3.63)	4.25 (4.16)
2b	0.96	$(C_{46}H_{30}N_2O_8S)_n$ $(770.81)_n$	71.25 (71.68)	4.05 (3.92)	3.75 (3.63)	4.07 (4.16)
2c	0.56	$(C_{52}H_{34}N_2O_9S)_n$ $(862.90)_n$	72.45 (72.38)	4.08 (3.97)	3.34 (3.25)	3.65 (3.71)
2d	1.06	$(C_{53}H_{36}N_2O_8S)_n$ $(860.93)_n$	73.75 (73.94)	4.28 (4.21)	3.35 (3.25)	3.65 (3.72)
2e	0.91	$(C_{52}H_{34}N_2O_{10}S_2)_n$ $(910.96)_n$	68.48 (68.56)	3.82 (3.76)	3.10 (3.08)	7.11 (7.04)
2f	1.35	$(C_{50}H_{32}N_2O_8S)_n$ $(820.87)_n$	72.95 (73.16)	3.86 (3.93)	3.46 (3.41)	3.85 (3.90)

[a] Measured in NMP.
[b] Calculated values are reported in parentheses.

Table 2 Solubility of polyamides **2a–f**[a]

Polymer	DMAc	NMP	DMF	H_2SO_4	*m*-cresol
2a	+	+	+	+	–
2b	+	+	+	+	±
2c	+	+	+	+	±
2d	+	+	+	+	±
2e	+	+	+	+	+
2f	+	+	+	+	±

[a] +, soluble on heating; ±, partially soluble on heating; –, insoluble.



Scheme 1

Table 3 Thermal characterization of polymers **2a–f**

Polymer	T_d (°C)^a	T_d (°C)^b	T_g (°C)	C_y^c
2a	500	470	222	64
2b	510	460	220	66
2c	520	480	212	64
2d	490	460	210	61
2e	500	460	228	62
2f	515	470	225	67

[a] Temperature of 10% weight loss determined in nitrogen atmosphere.

[b] Temperature of 10% weight loss determined in static air.

[c] Char yield calculated as the percentage of solid residue after heating from room temperature to 700°C under nitrogen.

All the polymers are soluble in concentrated H_2SO_4 and in aprotic polar solvents such as NMP, DMAc, DMF etc. (*Table 2*). Polymer **2f**, obtained starting from the *meta*-diacid and 1,5-diaminonaphthalene, was soluble also in these solvents, although the same polyamide prepared from the *para*-diacid was insoluble. In *m*-cresol only the polymers with more flexible chains were partially or completely soluble, so polymer **2a**, with a rigid structure, remained insoluble in this solvent. These results clearly show that the introduction of *meta* structures increases the solubility and leads to better processability.

The thermal behaviour of the polymers was investigated by t.g.a. and d.s.c. (*Table 3*). All the polymers are stable up to 490 and 460°C in nitrogen and air atmosphere, respectively. The T_ds are in the range 490–520°C in nitrogen (*Figure 1*) and 460–480°C in air. Polyamides from the *meta*-diacid show greater thermal stability than all *para*-linked polyamides[7]: these results are in agreement with the data reported in the literature for similar systems[4,10,11]. The high thermal stability of these polyamides is confirmed by the high C_y values determined at 700°C, which were always above 61% and reached a maximum value of 67%. The T_gs were determined by d.s.c.: samples were heated to 250°C for 30 min at a heating rate of 20°C min^{-1}, allowed to cool slowly to room temperature and subsequently re-run to obtain the T_g. For all polymers it was possible to detect T_g near 220°C; as expected, *para*-linked polyamides[7] exhibit, when it was possible to detect them, T_gs higher than those of the corresponding *meta*-linked polyamides, which may be due to the parallel alignment of the chain when the aromatic rings are linked in all *para* fashion within the polymeric backbone[11]. The T_gs and therefore the end-use temperatures are in all cases high (210–228°C range).

In conclusion, the introduction of *meta* linkage in the polymer backbone influences the properties of the obtained polymers with respect to the same polymers where the groups are connected by aromatic rings linked in all *para* fashion. The polyamides derived from *meta*-diacid show higher η_{inh}, greater solubility and therefore better processability, lower, but still high, T_gs and greater thermal stability than all *para*-linked polyamides.

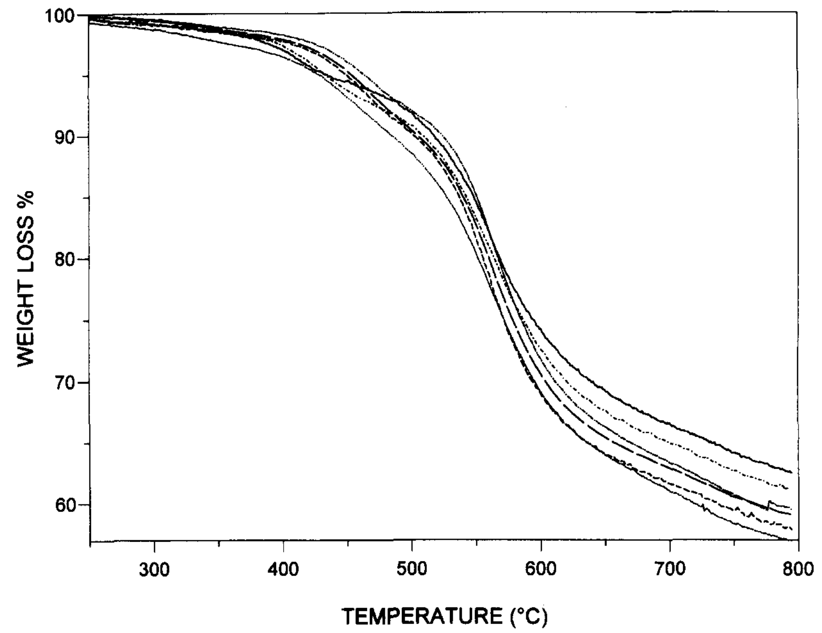


Figure 1 T.g.a. curves in nitrogen of polymers: **2a** (—— ——); **2b** (– · –); **2c** (–·· –); **2d** (· · ·); **2e** (- - -); **2f** (———).

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