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New aromatic polyamide materials containing sulfone, ether and ketone linkages

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Several aromatic polyamides were prepared from 4,4′-[sulfonyl bis(*p*-benzoyl)(*p*-phenyleneoxy)]dibenzoic acid with various diamines by the phosphorylation route. The polymers were characterized by elemental analysis, thermogravimetric analysis, differential scanning calorimetry and infra-red analysis. The polyamides, obtained in quantitative yield, possessed inherent viscosities in the range 0.3–1 $\mathrm{dl\,g^{-1}}$ and 10% weight loss in nitrogen and air were above 460 and 440°C, respectively. Most of the polymers were soluble in aprotic solvents. The effect of the structure on properties such as solubility and thermal behaviour were also studied. Copyright © 1996 Elsevier Science Ltd.

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Introduction

Wholly aromatic polyamides (aramides) possess thermal stability, chemical resistance, low flammability and have excellent mechanical properties as fibres. However, they are difficult to process because of limited solubility and high glass transition (T_g) or melt (T_m) temperature, due to chain-stiffness and intermolecular hydrogen-bonding between amide groups[1–3].

Many papers can be found in the literature describing the synthesis of new aromatic polyamide materials containing sulfone and ketone or ether groups[4–17]. In fact, such polymers often show the advantages of poly(ether ether ketone) (PEEK, Imperial Chemical Industries) and aramides in properties such as processability, better thermomechanical properties and good hydrolytic and thermo-oxidative stability. In particular, the introduction of sulfone groups is attractive. Sulfonyl aromatic polyamides have been reported to have potential for commercial utility, because fibres and films of these polymers not only possess excellent physical properties at room temperature, but retain their strength and excellent response to in-service loading at elevated temperatures for prolonged periods of time[18].

The goal of the present work was the preparation and characterization of new polyamides containing ether, sulfone and ketone groups in the same chain. The combination was considered potentially attractive because the anticipated polymers were expected to exhibit a favourable balance of properties.

Experimental

Materials. *N*-methyl-2-pyrrolidone (NMP) was refluxed over CaH_2 for 8 h and distilled under reduced pressure. It was then refluxed in the presence of P_2O_5 and freshly distilled before use. Triphenyl phosphite (TPP) was purified by fractional distillation under vacuum. Pyridine (Py) was refluxed in an inert atmosphere in the presence of NaOH for 6 h, distilled and stored over 4 Å molecular sieves. LiCl (Aldrich Co.) was dried for 16 h at 180°C under vacuum. Reagent grade aromatic diamines (Aldrich Co.) such as *p*-phenylenediamine (PPD), *m*-phenylenediamine (MPD) and 4,4′-oxydianiline (ODA) were purified by sublimation; 4,4′-methylenedianiline (MDA) was crystallized twice from benzene and 4,4′-diaminodiphenylsulfide (AS) was crystallized from ethanol/water. 4,4′-Sulfonyl dianiline (DAS) and 1,5-diaminonaphthalene (DAN) were crystallized from ethanol. Methyl-4-hydroxybenzoate (Aldrich Co.) was used as received. 4,4′-Difluorobenzoyl diphenylsulfone (DFDKS) was synthesized according to the literature[19].

Instrumental methods. Inherent viscosities ($\eta_{inh} = \ln \eta_r / C$ at polymer concentration $C = 0.5\,\mathrm{g\,dl^{-1}}$) were measured with an Ostwald viscometer at 30°C using NMP as solvent.

Qualitative solubility was determined using about 0.2 g of polymer in 2 ml of solvent.

Differential scanning calorimetry (d.s.c.) analyses were carried out using a Mettler DSC 20 with Al pans at a heating rate of 20°C $\mathrm{min^{-1}}$ under nitrogen. Thermogravimetric analyses (t.g.) were performed with a Mettler M3 thermobalance at a heating rate of 10°C $\mathrm{min^{-1}}$ in nitrogen (25 ml $\mathrm{min^{-1}}$) and in air atmosphere; the decomposition temperature (T_d) was taken at the 10% weight loss. The char yields (C_y) were calculated as the percentage of solid residue after heating from room temperature to 700°C under nitrogen.

Infra-red (i.r.) spectra were measured with a Perkin–Elmer FT-1725-X spectrophotometer on a pressed mixture with KBr. Elemental analyses were conducted on a Carlo Erba Elemental Analyser-Mod 1106.

*Monomer synthesis. Synthesis of 4,4′-[sulfonyl bis(*p*-benzoyl)(*p*-phenyleneoxy)]dibenzoic acid.* To 9.24 g of DFDKS (0.02 mol) in 60 ml of NMP was added 7.59 g of methyl-4-hydroxybenzoate potassium salt (0.04 mol).

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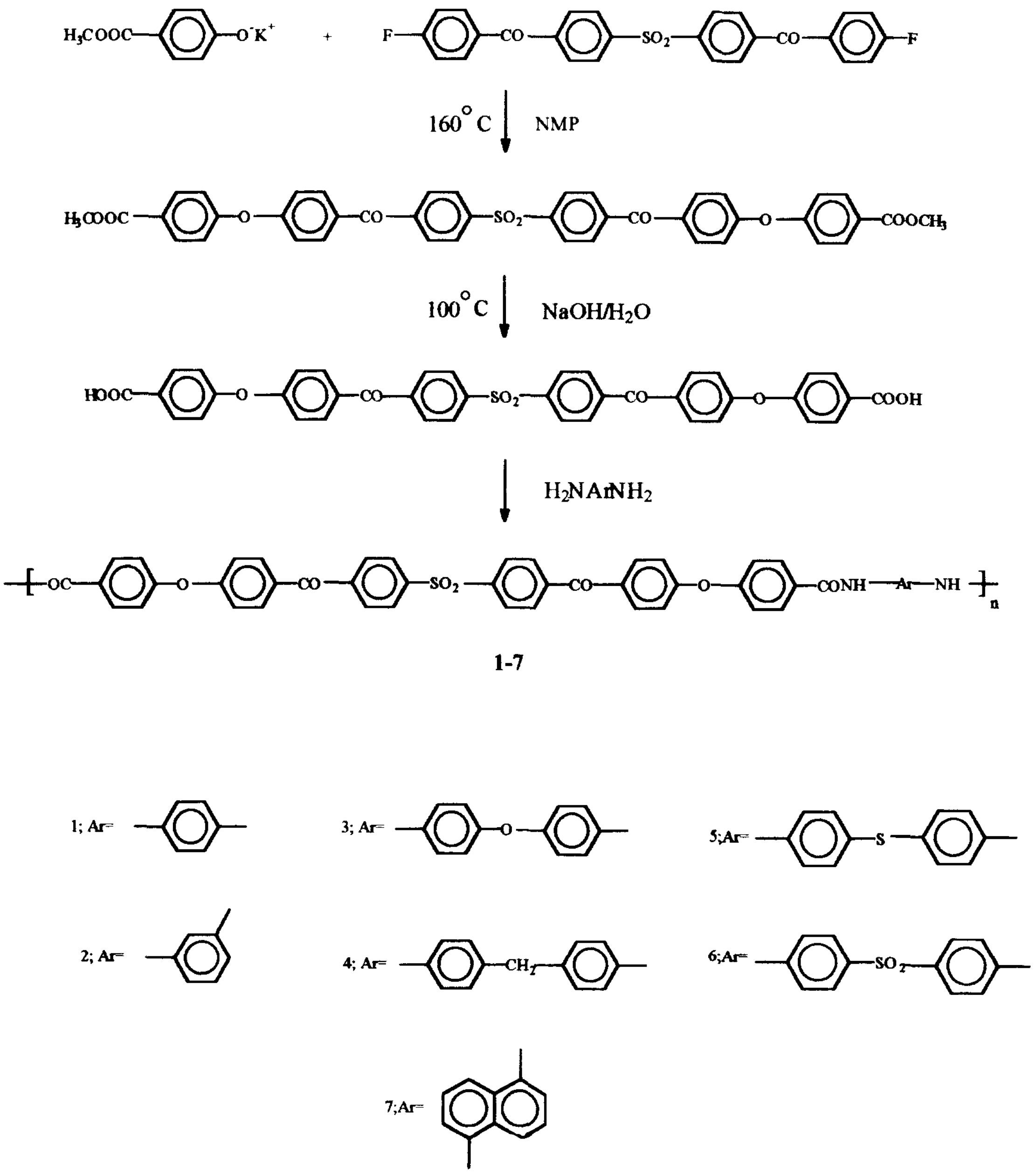
The mixture was stirred and heated in a nitrogen atmosphere at 160°C for 6h. After cooling, 60ml of 10% aqueous sodium hydroxide was added and the mixture was then heated at 110°C for 2h. The cooled solution was diluted to 1 litre with water and acidified with dilute sulfuric acid to pH 2. The slurry was stirred for 2h and then filtered. The white precipitate was washed with water, dried and crystallized from dioxane/H_2O, m.p. 301°C (75% yield).

The i.r. spectrum showed absorbances at 1684 and 1658 cm^{-1} (C=O), 1385–1164 cm^{-1} (SO_2) and 1248 cm^{-1} (COC). Elemental analysis calcd for $C_{24}H_{26}O_{10}S$ (698.69): C, 68.76; H, 3.75; S, 4.58. Found: C, 68.37; H, 3.96; S, 4.68.

Polymer synthesis. A typical example of solution polymerization is as follows: A solution of NMP (5ml) and Py (1.25ml) containing 8wt% LiCl (0.5g) was added to a mixture of diacid (0.8735g, 0.00125mol), ODA (0.2503g, 0.00125mol) and TPP (0.7757g, 0.0025mol). The mixture was maintained under stirring and in nitrogen atmosphere at 105°C for 3h. The resulting reaction mixture, after cooling, was poured into methanol (200ml), and the precipitated polymer was separated by filtration and extracted with methanol overnight. The collected polymer was dried under vacuum for 12h at 100°C. The yield was 98% and η_{inh} of the polymer in NMP was 0.75 dl g^{-1}.

Results and discussion

Monomer synthesis. 4,4′-[Sulfonyl bis (*p*-benzoyl) (*p*-phenyleneoxy)]dibenzoic acid was synthesized by reacting the potassium salt of methyl-4-hydroxybenzoate with DFDKS, followed by hydrolysis of the resulting diester (*Scheme 1*). The diacid was characterized by i.r. and elemental analysis.



Scheme 1

Table 1 Elemental analysis and i.r. data for polymers 1–7

		Elemental analysis[a]				I.r. data (cm^{-1})	
Polymer	Formula	C	H	N	S	NH	CO
1	$(C_{46}H_{30}N_2O_8S)_n$	71.67	3.92	3.63	4.16	3348–3075	1665
	$(770.81)_n$	(69.75)	(3.82)	(3.45)	(4.05)		
2	$(C_{46}H_{30}N_2O_8S)_n$	71.67	3.92	3.63	4.16	3366–3066	1665
	$(770.81)_n$	(70.05)	(3.85)	(3.55)	(4.08)		
3	$(C_{52}H_{34}N_2O_9S)_n$	72.38	3.97	3.25	3.71	3370–3070	1660
	$(862.90)_n$	(70.05)	(3.88)	(3.11)	(3.55)		
4	$(C_{53}H_{36}N_2O_8S)_n$	73.94	4.21	3.25	3.72	3362–3057	1660
	$(860.94)_n$	(71.85)	(4.15)	(3.13)	(3.61)		
5	$(C_{52}H_{34}N_2O_8S_2)_n$	71.05	3.89	3.19	7.29	3374–3066	1660
	$(878.97)_n$	(69.47)	(3.75)	(3.03)	(7.12)		
6	$(C_{52}H_{34}N_2O_{10}S_2)_n$	68.56	3.76	3.07	7.04	3366–3084	1669
	$(910.97)_n$	(67.25)	(3.68)	(2.94)	(6.92)		
7	$(C_{50}H_{32}N_2O_8S)_n$	73.16	3.93	3.41	3.90	3360–3066	1660
	$(820.87)_n$	(71.68)	(3.79)	(3.33)	(3.81)		

[a] Found values are reported in parentheses

Polymer synthesis. The direct polycondensation of dicarboxylic acid with aromatic diamines using tri-phenyl phosphite and pyridine as condensing agents[20,21] is a convenient method for the preparation of amides on a laboratory scale. The reactions have been carried out in NMP solution of the diacid with PPD, MPD, ODA, MDA, AS, DAS and DAN (polymers **1**–**7** respectively), in the presence of 8% by weight of LiCl, in a nitrogen atmosphere and at a temperature of 105°C (*Scheme 1*). The temperature was carefully controlled because its increase beyond this value causes a drop in polymer viscosity, probably due to the decrease of interactions between Py and TPP in a range close to the boiling temperature of Py. In order to achieve high molecular weights, other factors were found to affect the low-temperature condensation; in particular, the solubility of the forming polymer in the polymerization medium plays an important role favouring the formation of higher molecular weight chains. An optimization of this reaction was then attempted taking into account the effects of monomer and salt concentration and metal salts. These effects were studied for the polyamide derived from 4,4′-[sulfonyl bis (*p*-benzoyl)(*p*-phenyleneoxy)]dibenzoic acid and ODA. The highest values were found for a monomer concentration of 0.2 mol l^{-1}. The viscosity reaches a maximum as a function of the concentration of the solution. In fact, if the concentration is too high, the reaction mixtures are too viscous to enable good stirring and gelation or precipitation may occur, with the consequent production of low molecular weights. On the contrary, lower monomer concentration can yield lower viscosities due to competitive side reactions[20]. Metal salts may contribute to the improvement of the solubility of the resulting polyamide: the addition of about 8 wt% of LiCl, instead of $CaCl_2$, produced the maximum η_{inh} of 0.75 dl g^{-1}. All the polymerizations proceeded in homogeneous solution, the yields of the polymers were quantitative and the polyamides thus obtained had inherent viscosities of 0.3–1 dl g^{-1}.

Table 2 Solubility of polyamides[a]

Polymer	DMAc	NMP	DMF	H_2SO_4	THF MeOH Acetone
1	+	+	+/–	+	–
2	+	+	+	+	–
3	+	+	s	+	–
4	+	+	+	+	–
5	s	s	s	+	–
6	+	+	+	+	–
7	–	–	–	–	–

[a] +, Soluble; +/–, partially soluble; –, insoluble; s, swelling at room temperature

Table 3 Solution viscosities and thermal characterization of polymers 1–7

Polymer	η_{inh}[a]	T_d[b] (°C)	T_d[c] (°C)	T_g (°C)	C_y[d]
1	0.41	461	455	–[e]	64.6
2	0.45	477	450	–[e]	64.5
3	0.75	500	465	–[e]	59.6
4	0.33	470	462	240	67.7
5	0.62	497	440	–[e]	67.8
6	0.44	495	480	260	59.7
7	1.00[f]	500	470	–[e]	67.5

[a] Measured in NMP
[b] Temperature of 10% weight loss determined in nitrogen atmosphere
[c] Temperature of 10% weight loss determined in static air
[d] Char yield
[e] Not detectable by d.s.c.
[f] Measured in NMP/8 wt% LiCl

Concerning the elemental analyses values of these polymers (*Table 1*), hydrogen and nitrogen analyses were in good agreement with theory but several of the analyses of carbon were observed to be somewhat lower than the calculated value. This situation is not unusual for aromatic polyamides: the cause of the low values could be traced to the difficulty in combustion of the char formed by these thermally stable polymers which give high char yields[16].

The i.r. spectra of the polymers (*Table 1*), showed absorptions near 3400–3060 cm^{-1} and 1655 cm^{-1},

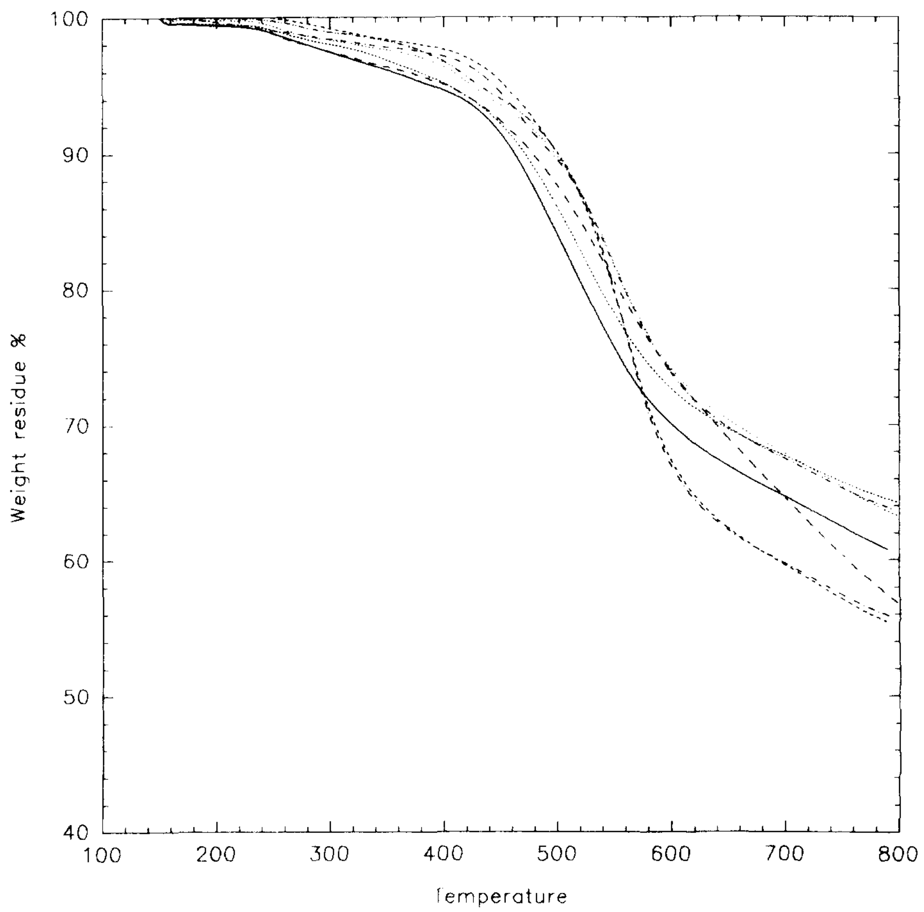


Figure 1 T.g. curves in nitrogen of polymers: ——, **1**; ——, **2**; ——, **3**; - - - - -, **4**; · · · · · ·, **5**; · - · -, **6**; · · · · –, **7**

corresponding to the amino and carbonyl groups, respectively.

Properties of polymers. All polymers (*Table 2*), except polymer **7**, were soluble in a variety of solvents such as dimethyl acetamide (DMAc), dimethyl formide (DMF), NMP and sulfuric acid; all were insoluble in tetrahydrofuran (THF), methanol (MeOH) and acetone. The poor solubility of polymer **7** may be due to its rigid structure and high crystallinity[22].

The thermal behaviour and T_g of polymers were evaluated by t.g. and d.s.c., respectively. The values of T_g, T_d and C_y are summarized in *Table 3*. The T_ds for these polymers are in the range 460–500°C in nitrogen (*Figure 1*) and 440–480°C in air, the T_d in nitrogen atmosphere being 5–30°C higher than that in air. It should be noted that the amount of carbonized residue of polyamides at 700°C in nitrogen was above 59% and reached 68%.

D.s.c. analyses detected a T_g only for polymers **4** and **6**, while in all cases there was no evidence of T_m. These results can be rationalized by taking into account the structure of the studied polymers. In designing the structure of our polymers we considered that the goal of improving the processability could be reached introducing sulfone groups in the chains. The introduction of these groups in polymers such as poly(ether ketone)s produces higher solubility and lower crystallinity because of the disruption of the polymer chain planarity due to different bond angles (105° for Ar–SO$_2$–Ar, with respect to 124° for Ar–CO–Ar and Ar–O–Ar)[23], resulting in a lower interaction between the chains. For our polyamides the moiety containing the sulfone group is not sufficient to promote a drop of crystallinity and subsequent detection of a T_g. But when the repeat unit contains other groups having the same effect (another sulfone such as in polymer **6**, or a methylene group such as in polymer **4**), the result is the presence of a T_g due to the increase of amorphous domains. Although it was difficult to believe that the sulfone group did not disrupt the crystallinity, we have previously found evidence of the same for similar systems[19,24]. In any case, the lack of an observed T_g may be related to molecular constraints arising from the crystallized region which effectively smear out the T_g process and the d.s.c. instrument used not being sensitive enough to detect it. No T_m was detected for any polymer, indicating that degradation occurs before melting.

Further work is in progress to better understand the influence of sulfone-containing monomers on the degree of crystallinity of polyamides.

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