

Synthesis and characterization of poly(arylene ether sulfone amide)s

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SUMMARY:

Methyl-substituted or unsubstituted aromatic dicarboxylic acids and diamines containing ether and sulfone linkages between phenylene units were used alone or in combination with *p*-phenylenediamine, *m*-phenylenediamine, terephthalic acid, and isophthalic acid to prepare flexible or semirigid aromatic polyamides by direct polycondensation activated by triphenyl phosphite and pyridine. The inherent viscosities of the obtained polymers ranged from 0.40 to 1.01 dL/g. The wholly flexible polyamides are amorphous, are readily soluble in *N,N*-dimethylacetamide, dimethyl sulfoxide, and *m*-cresol, and can afford transparent, flexible, and tough films by solution-casting. The polyamides prepared from *p*-phenylenediamine or terephthalic acid are partially crystalline and melt around 410°C. Differential scanning calorimetry shows glass transition temperature in the 202–255°C range for the wholly flexible polyamides. All the polyamides are thermally stable in excess of 400°C. The methyl-substituted polyamides had higher glass transition temperatures, but lower initial decomposition temperatures, than the corresponding unsubstituted polyamides.

Introduction

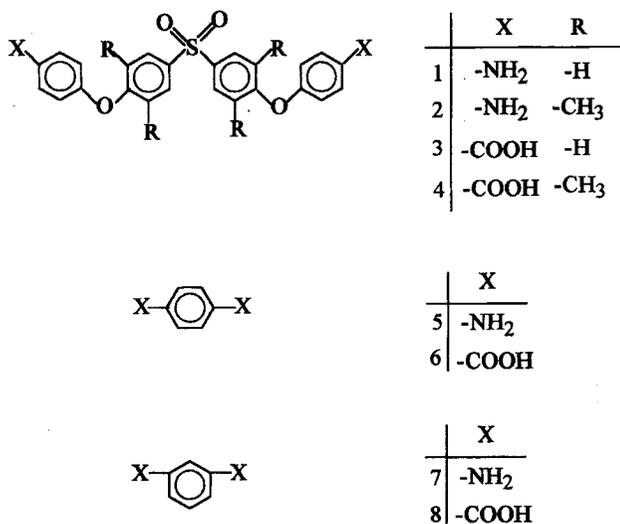
Aromatic polyamides (aramids) have been noted for their unique property combinations^{1,2}. They can be formed into strong abrasion-resistant fibers with very high modulus, good thermal stability and high solvent resistance. Traditionally these materials have been infusible and only soluble in strongly acidic media, consequently potential applications have been limited. Therefore, several modifications of the chemical structure have been used in order to lower the transition temperatures and to increase the solubility of aramids.

One approach to increase the solubility and processability of aramids is the introduction of kinked and flexible bridging units into the polymer chain^{3–11}. A number of kinked bridging units can be incorporated between aromatic units to reduce the chain rigidity. Among the commonly used kinked links are: —O—, —CO—, —CH₂—, —C(CH₃)₂—, —C(CF₃)₂—, —S—. The linkages not only create bent bonds in the polymer chain, but also permit the rotation of aromatic units. Unfortunately, the loss of thermal stability and significant decrease in tensile strength on heating are almost always a consequence of the reduced chain stiffness. On the other hand, the insertion of sulfone (—SO₂—) groups into the macromolecular chain generally leads to an enhanced solubility, together with interesting properties such as increased *T_g* and higher thermo-oxidative stability. Hence, the goal of better solubility, together with retained higher thermal stability, could be achieved in preparing poly-

amides containing both sulfone and flexible groups like ether. Some of aromatic polyamides with both aryl ether and aryl sulfone links between amide groups have been prepared by polymerization of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dianiline (diamine **1** as shown in Scheme 1) with the carboxylic acid derivatives^{12,13} or by reacting the acyl chloride of 4,4'-[sulfonylbis(1,4-phenyleneoxy)]dibenzoic acid (diacid **3** in Scheme 1) with aromatic diamines¹⁴. Aramids of this general structure are of interest since they possess enhanced tractability and solubility characteristics, together with moderately high T_g .

Scheme 1:

Structures of monomers:



The presence of methyl substituents on a ring unit at *ortho* positions to the ether linkage generally increased T_g of the polymers, due to the hindrance effect of the chain rotation^{15,16}. Furthermore, the methyl-substituted aromatic poly(ether ketone)s were found to crosslink by radiation of ultraviolet light due to the presence of a sensitizing benzophenone structure^{15,16}. In addition, some methyl-substituted polysulfones were found to exhibit more favorable gas separation properties, when compared to their unsubstituted counterparts¹⁷.

The goal of the present work was the preparation and characterization of new polyamides having ether and sulfone in the main chain, together with methyl substituents on the aromatic units. The combination was considered potentially attractive because the anticipated polymers were expected to exhibit a favourable balance of properties. For comparison, related polyamides without methyl substitution were also prepared and characterized.

Experimental part

Materials

Reagent grade 4,4'-sulfonyldiphenol (Sigma) and 4,4'-sulfonylbis(2,6-dimethylphenol) (Aldrich) were used as received. *N*-Methyl-2-pyrrolidone (NMP) and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) (Fluka) was purified by distillation under reduced pressure. Calcium chloride was dried *in vacuo* at 180 °C for 10 h. *p*-Phenylenediamine (Wako) was purified by sublimation, and *m*-phenylenediamine (Janssen) was vacuum-distilled prior to use.

Preparation of diamine monomers

4,4'-[Sulfonylbis(1,4-phenyleneoxy)]dianiline (**1**) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline (**2**) were prepared according to reported procedures¹⁸. A detailed procedure for the preparation of diamine **2** is as follows.

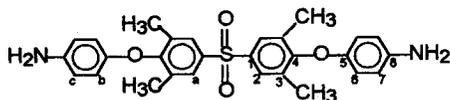
4,4'-Sulfonylbis(2,6-dimethylphenol) (61.2 g, 0.2 mol) and 63.0 g (0.41 mol) of *p*-chloronitrobenzene were dissolved in 200 mL of anhydrous *N,N*-dimethylformamide (DMF) in a 500-mL flask with stirring. Then, 56.7 g (0.41 mol) of anhydrous potassium carbonate was added, and the suspension mixture was refluxed at 160 °C for 10 h. The mixture was allowed to cool and subsequently poured into 300 mL of 1:1 (v/v) methanol-water to precipitate a yellow solid which was collected by filtration and dried. The crude product was recrystallized from DMF to give pure bis[4-(4-nitrophenoxy)-3,5-dimethylphenyl] sulfone with a melting point of 228–230 °C in 88% yield (96.3 g). A mixture of 20 g (0.036 mol) of the obtained dinitro compound, 0.24 g of 10% Pd/C, and 700 mL of ethanol was heated to reflux. Into the suspension solution 120 mL of hydrazine monohydrate were added dropwise over a period of 1 h. After the addition was complete, the reaction was continued at reflux temperature for additional 20 h. The mixture was then filtered to remove Pd/C. After cooling, the precipitated colorless flakes of diamine **2** were isolated by filtration and dried in vacuum; m.p. = 186–188 °C. Yield: 14.5 g (81.5%).

C ₂₈ H ₂₈ N ₂ O ₄ S (488.6)	Calc.	C 68.83	H 5.77	N 5.73
	Found	C 68.43	H 5.68	N 5.69

IR(KBr): 3452, 3356 (—NH₂), 1280, 1137 (—SO₂—), 1224 cm⁻¹ (C—O—C).

¹H NMR (DMSO-*d*₆): δ = 7.79 (s, H_a, 2H), 6.49 (d, H_b, 4H), 6.44 (d, H_c, 4H), 4.75 (s, —NH₂, 4H), 2.11 ppm (s, —CH₃, 12H).

¹³C NMR (DMSO-*d*₆): δ = 155.74 (C⁴), 147.71 (C⁵), 143.62 (C⁸), 137.10 (C¹), 132.91 (C³), 128.21 (C²), 115.17 (C⁶), 115.08 (C⁷), 18.67 ppm (methyl carbon).



The diamine **1** was prepared starting from 4,4'-sulfonyldiphenol and *p*-chloronitrobenzene by a similar procedure; m.p. = 188–189 °C (lit.¹³) 189–191 °C).

C ₂₄ H ₂₀ N ₂ O ₄ S (432.50)	Calc.	C 66.65	H 4.66	N 6.48
	Found	C 66.38	H 4.69	N 6.40

Preparation of diacid monomers

4,4'-[Sulfonylbis(1,4-phenyleneoxy)]dibenzoic acid (**3**) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dibenzoic acid (**4**) were prepared according to a reported procedure³. A detailed procedure for the preparation of diacid **4** is described as follows.

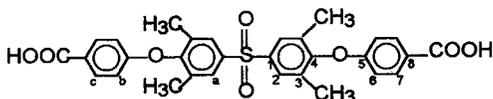
4,4'-Sulfonylbis(2,6-dimethylphenol) (15.3 g, 0.05 mol) and potassium carbonate (13.8 g, 0.1 mol) were suspended in a mixture of 100 mL of DMF and 60 mL of toluene and heated with stirring at reflux temperature using a Dean-Stark trap to remove the water. After complete removal of the water, the residual toluene was distilled off. Then, 12.1 g (0.1 mol) of *p*-fluorobenzonitrile was added, and heating was continued at 150°C for 6 h. After cooling, the reaction mixture was poured into 600 mL of water. The precipitated product was filtered off and dried (yield 23.7 g; 93.2%), and recrystallized from ethanol to afford colorless needles of 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]-dibenzonitrile with a melting point of 197–199°C in 77% (19.5 g) yield. A suspension of the intermediate dinitrile (19 g, 0.0374 mol) in 500 mL of 1:1 volume mixture of water and ethanol containing 56 g (1.0 mol) of potassium hydroxide was refluxed for 24 h. The resulting clear solution was acidified to pH = 2–3, and the white precipitate was filtered off, washed with water to neutral and dried to give 19.0 g (95% yield) of diacid **4**; m. p. = 312–315°C.

C ₃₀ H ₂₆ O ₈ S (550.63)	Calc.	C 65.92	H 4.79
	Found	C 65.36	H 4.72

IR (KBr): 2400–3600 (O–H str.), 1688 (C=O str.), 1282, 1150 (–SO₂– str.), 1232 cm⁻¹ (C–O–C str.).

¹H NMR (DMSO-*d*₆): δ = 8.01 (s, H_a, 4H), 8.00 (d, H_c, 4H), 6.90 (d, H_b, 4H), 2.20 (s, –CH₃, 12H).

¹³C NMR (DMSO-*d*₆): δ = 167.43 (C=O), 160.50 (C⁵), 154.90 (C⁴), 138.88 (C¹), 133.59 (C⁷), 132.72 (C³), 129.35 (C²), 125.68 (C⁸), 115.27 (C⁶), 16.75 ppm (methyl carbon).



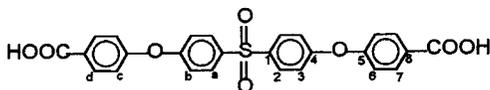
The diacid **3** was prepared starting from 4,4'-sulfonyldiphenol in a similar procedure; m. p. = 288–290°C (DSC 292°C) (lit.¹⁹ 292–295°C).

C ₂₆ H ₁₈ O ₈ S (490.49)	Calc.	C 63.67	H 3.70
	Found	C 63.62	H 3.86

IR (KBr): 2400–3600 (O–H str.), 1680 (C=O str.), 1300, 1150 (–SO₂– str.), 1247 cm⁻¹ (C–O–C str.).

¹H NMR (DMSO-*d*₆): δ = 8.02 (s, H_d, 4H), 8.01 (d, H_a, 4H), 7.30 (d, H_b, 4H), 7.20 (d, H_c, 4H).

¹³C NMR (DMSO-*d*₆): δ = 166.58 (C=O), 160.16 (C⁴), 158.61 (C⁵), 136.08 (C¹), 131.85 (C⁷), 130.04 (C²), 127.10 (C⁸), 119.34 (C³), 118.67 ppm (C⁶).



Typical polymerization procedure

Polymers were synthesized according to literature procedures^{20,21}. A mixture of 1.25 mmol of diacid, 1.25 mmol of diamine, 0.2 g calcium chloride, 0.9 mL (2.5 mmol) of triphenyl phosphite, 0.8 mL of pyridine, and 1.5 mL of NMP was heated with stirring at 110 °C for 3 h. The viscosity of the solution drastically increased during the reaction. The obtained polymer solution was slowly added to 400 mL of stirred methanol, producing a stringy precipitate which was washed thoroughly with methanol and hot water, collected by filtration and dried. Yields were usually quantitative.

Measurements

The infrared spectra were obtained on a Jasco FT/IR-7000 Fourier-transform infrared spectrometer. Elemental analyses were performed using a Perkin-Elmer C, H, N, 2400 elemental analyzer. The ¹H NMR and ¹³C NMR spectra were recorded at 30 °C using a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-*d*₆) as an external reference, working at 400 and 100 MHz, respectively.

The inherent viscosities were measured on a Cannon-Fenske viscometer at 30 °C in DMAc-5 wt.-% LiCl (*c* = 0.5 g/dL).

Wide-angle X-ray diffraction patterns were recorded at room temperature on a Rigaku Geiger Flex D-Max III_a X-ray diffractometer, using Ni-filtered Cu-*K*_α radiation (1.5418 Å). The scanning rate was 2°/min over a 2θ range of 5–40°.

The thermal behavior was investigated by a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller at a heating rate of 20 °C/min in flowing nitrogen. Thermogravimetry (TG) was carried out by means of a Rigaku Thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were performed with 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 20 °C/min. The measurements were taken after an initial 250 °C/5 min drying step.

Results and discussion

Synthesis and characterization

The monomers used to prepare the polyamides are shown in Scheme 1. Diamine **1** and diacid **3** have been widely used to improve the processability of rigid aromatic polymers such as polyimides, polyamides, and poly(amide-imide)s²². Little is known about the polymers based on the methyl-substituted diamine **2** and diacid **4**. Diamines **1** and **2** were prepared by catalytic hydrazine reduction of the corresponding dinitro compounds, obtained from nucleophilic chlorine substitution of *p*-chloronitrobenzene with the potassium phenolate of 4,4'-sulfonyldiphenol and 4,4'-sulfonylbis(2,6-dimethylphenol), respectively. Diacids **3** and **4** were synthesized by alkaline hydrolysis of the corresponding dinitriles, obtained by nucleophilic flourine displacement of *p*-fluorobenzonitrile with 4,4'-sulfonyldiphenol and 4,4'-sulfonylbis(2,6-dimethylphenol), respectively, in the presence of a base such as potassium carbonate. The elemental analyses and spectroscopic data listed in the *Experimental part* confirm the structure of these monomers.

The direct polycondensation of dicarboxylic acids with aromatic diamines using triphenyl phosphite and pyridine as condensing agents²³ is a convenient method for

the preparation of polyamides on a laboratory scale. The polymerization reactions have been carried out in NMP in the presence of CaCl_2 at a temperature of 110°C . In general, the viscosity of reaction solutions increased significantly approximately 40 min after starting the reaction. Due to insolubility, polymers PA-3 and PA-4 precipitated out of reaction in an early stage, and further addition of NMP and CaCl_2 failed to redissolve the precipitated products. In other cases, the polymerization reaction proceeded homogeneously throughout the reaction. As included in Tab. 1, all the polymers were obtained in almost quantitative yield, with inherent viscosities

Tab. 1. Inherent viscosity, solubility, and film quality of poly(arylene ether sulfone amide)s

Polymer code	Monomer	$\eta_{\text{inh}}^{\text{a)}$ dL/g	Solubility ^{b)} in			Film quality ^{c)}
			DMAc	DMSO	<i>m</i> -cresol	
PA-1	6 + 1	0.96	+	-	-	brittle
PA-2	6 + 2	0.87	+h	-	-	brittle
PA-3	3 + 5	0.62	-	-	-	- ^{d)}
PA-4	4 + 5	0.52	-	-	-	- ^{d)}
PA-5	1 + 8	0.78	+	+	+	flexible
PA-6	2 + 8	0.59	+	+	+	flexible
PA-7	3 + 7	0.74	+	+	+	flexible
PA-8	4 + 7	1.01	+	+	+	flexible
PA-9	1 + 3	0.58	+	+	+	flexible
PA-10	2 + 3	0.79	+	+	+	flexible
PA-11	1 + 4	0.40	+	+	+	flexible
PA-12	2 + 4	0.75	+	+	+	flexible

a) Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt.-% LiCl dissolved.

b) +: Soluble; +h: soluble on heating; -: insoluble even on heating. DMAc: *N,N*-dimethylacetamide; DMSO: dimethyl sulfoxide.

c) Films were cast by slow evaporation of polymer solutions in DMAc.

d) Insoluble in suitable solvents for film casting.

in the 0.40–1.01 dL/g range. Except for polyamides PA-3 and PA-4, all polyamides were soluble in DMAc and afforded free-standing films by solution-casting. The films made from PA-1 and PA-2 were noncreasable, and the others were flexible and tough.

The IR spectra of all the polyamides exhibit carbonyl stretching band near 1650 cm^{-1} and the stretching band of hydrogen bonded N—H near 3350 cm^{-1} . Other characteristic absorptions include C—O—C stretching near 1245 cm^{-1} , S(=O)₂ stretching near 1300 and 1150 cm^{-1} , and aromatic C=C skeletal stretching at 1600 and 1500 cm^{-1} .

Properties of polymers

The solubility behavior of the prepared polyamides was tested qualitatively in DMAc, DMSO, and *m*-cresol. The results are also summarized in Tab. 1. Polymers PA-1 to 4, containing the terephthalic or the *p*-phenylenediamine moiety, showed limited solubility; only PA-1 and PA-2 were soluble in DMAc at room temperature or on heating. Incorporation of *m*-phenylene units, such as in PA-5 to 8, or more kinked linkers, such as in PA-9 to 12, into the polymer main chain led to significantly increased solubility.

The less solubility of PA-1 to 4 compared to the other polyamides might be due to their higher level of crystallinity. As evidenced by wide-angle X-ray diffraction measurements, polymers PA-1 to 4 show partially crystalline patterns, while the other polymers are amorphous (Fig. 1). By comparing the diffraction peak positions and amorphous halo, it can be seen that methyl substitution such as in PA-2 and PA-4 not only increased the polymer crystallinity, but also altered the crystalline structure significantly. Changing the *p*-phenylene group to *m*-phenylene, or terephthalamide to isophthalamide, for example, polyamides PA-5 to 8, all reduced the polymer crystallinity drastically. The polyamides PA-9 to 12 show completely amorphous X-ray diffraction patterns as the kinked and flexible links are present in both the diacid and diamine moieties.

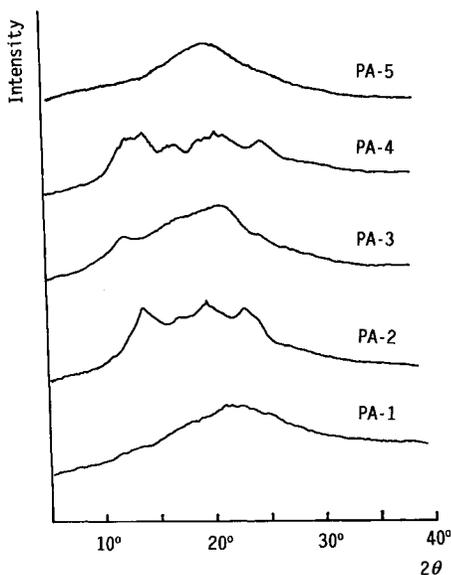


Fig. 1. X-ray diffraction patterns of some poly(arylene ether sulfone amide)s

The thermal behavior of the prepared polyamides was evaluated by differential scanning calorimetry (DSC) and thermogravimetry (TG), and the data are reported in Tab. 2. The polyamides were quenched from elevated temperature at approximately 400 °C to form predominantly amorphous samples, and thus, distinct glass

Tab. 2. Thermal properties of poly(arylene ether sulfone amide)s

Polymer code	$T_g^a)$ °C	$T_d^c)/°C$		Residue (in %) at 800 °C in N ₂
		in N ₂	in air	
PA-1	-(312) ^{b)}	489	485	52.3
PA-2	-(389)	419	423	51.3
PA-3	-(300)	489	480	52.7
PA-4	-(352)	445	425	39.8
PA-5	219	499	494	54.0
PA-6	255	433	427	59.7
PA-7	217	484	484	55.8
PA-8	228	433	427	59.1
PA-9	202	507	499	45.8
PA-10	244	453	444	56.6
PA-11	222	443	440	52.8
PA-12	247	444	430	58.8

- a) Baseline shifts in the second DSC heating traces, with a heating rate of 20 °C/min.
 b) Values in the parentheses are the onset temperatures of the sharp endotherms appearing in the first heating DSC curves.
 c) Decomposition temperatures at which 10% weight loss was recorded by TG at a heating rate of 20 °C/min.

transitions generally could be observed on the subsequent heating DSC traces. The semicrystalline polyamides PA-1 to 4 exhibited broad endotherms centred around 410 °C in the first heating DSC traces, and no discernible glass transitions could be observed on their second heating DSC traces after rapid cooling. All the amorphous polyamides (PA-5 to 12) showed clear glass transitions centered in the range of 202–255 °C. As expected, the methyl-substituted polyamides exhibited higher T_g 's than the corresponding unsubstituted polyamides due to the hindrance effect of the chain rotation in the methyl-substituted polymers.

Dynamic thermogravimetry confirms the high thermal stability of the prepared polyamides. All the polymers were stable up to 400 °C in both air and nitrogen atmospheres. It is quite reasonable that the methyl-substituted polyamides began to decompose at lower temperatures compared with the unsubstituted polymers.

Conclusion

High-molar-mass methyl-substituted poly(arylene ether sulfone amide)s on the basis of 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dibenzoic acid and/or 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenyleneoxy)]dianiline were successfully synthesized by means of triphenyl phosphite-pyridine. The poly(arylene ether sulfone amide)s synthesized from the new methyl-substituted monomers had higher T_g 's and increased chain rigidity but lower initial decomposition temperatures compared to those of the corresponding unsubstituted polymers.

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