

Synthesis of Sulfone-Containing Polyamides by Direct Polycondensation with Triphenyl Phosphite

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Synopsis

Several sulfone-containing polyamides were prepared by the direct polycondensation reaction of 4,4'-dicarboxydiphenyl sulfone (DCDPS) with various aromatic diamines by means of triphenyl phosphite in NMP-pyridine solution containing 4 wt % LiCl. DCDPS was synthesized in two steps by the preparation of 4,4'-dimethyldiphenyl sulfone (DMDPS) from toluene and chlorosulfonic acid and subsequent oxidation with an alkaline solution of potassium permanganate. The polyamides were obtained in 85–100% yield and had inherent viscosities in the range 0.42–1.65 dL/g. Their solubility, crystallinity, and thermal properties are also discussed.

INTRODUCTION

Polyamides have found wide commercial acceptance because they can be formed into strong abrasion-resistant fibers and films. High performance sulfonyl polyamides have been prepared^{1,2} via interfacial or solution polymerization by reacting aromatic diacid chlorides with aromatic diamines. The phosphorylation reaction reported by Yamazaki^{3,4} has been found to be a very useful laboratory method for the preparation of wholly aromatic polyamides via the polycondensation of aromatic amino acids or the polycondensation of aromatic diacids with aromatic diamines. This paper describes a successful application of this reaction to the synthesis of high molecular weight sulfone-containing aromatic polyamides from 4,4'-dicarboxydiphenyl sulfone (or 4,4'-sulfonyl dibenzoic acid) and various diamines. Properties of these polymers are described.

EXPERIMENTAL

Materials

Toluene (Hanawa), chlorosulfonic acid (Fluka AG), phosphorus oxychloride (Wako), and potassium permanganate (Fluka AG) were used as received for the preparation of DCDPS. *p*-Phenylenediamine (Wako) was vacuum distilled before use. 4,4'-Oxydianiline (TCI-GR), 3,4'-oxydianiline (Teijin Ltd.), 4,4'-methylenedianiline (TCI-GR), and 4,4'-sulfonyldianiline (TCI-EP) were used without further purification. Reagent-grade triphenyl phosphite (Wako) was purified by vacuum distillation. Commercially obtained anhydrous lithium chloride was dried under vacuum at 150°C for 6 h. Pyridine, *N*-methyl-2-pyr-

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olidone (NMP), and *N,N*-dimethylacetamide (DMAc) were purified by distillation over calcium hydride and stored over 4 Å molecular sieve.

Monomer

4,4'-Dimethyldiphenyl Sulfone (DMDPS)

About 256 mL (2.5 mol) of toluene was refluxed with about 66 mL (1 mol) of chlorosulfonic acid for 30 min. To this solution was added gradually 72 mL (0.8 mol) of phosphorus oxychloride and stirring and refluxing was continued for 10 h. The reaction mixture is then cooled and poured into distilled water. The crude DMDPS obtained was collected by filtration and recrystallized from methanol. Yield: 385 g (78%); mp 156°C. The infrared and NMR measurements confirm the DMDPS formation.

IR(KBr): 1400 and 1450 (CH₃ bending), 1150 and 1300 (SO₂) cm⁻¹.

¹H-NMR(chloroform-*d*₁): δ7.2–7.8 (s, 8H, aromatic) and 2.37 (s, 6H, methyl).

¹³C-NMR(chloroform-*d*₁): δ127.53–143.78 (aromatic) and 21.34 (methyl carbon).

4,4'-Dicarboxydiphenyl Sulfone (DCDPS)

To a boiling and stirred mixture of DMDPS (14 g) and potassium hydroxide (16 g) in pyridine (50 mL), was added a solution of potassium permanganate (117 g in 500 mL water) over a period of 4 h. Refluxing was then continued for 36 h. The precipitated manganese dioxide was filtered, and the filtrate was concentrated and acidified with diluted hydrochloric acid. The precipitated acid was filtered, washed with water, dissolved in sodium carbonate solution, filtered, and reprecipitated with diluted hydrochloric acid. The crude acid obtained was recrystallized from DMF. Yield: 11 g (60%); no melting up to 360°C.

IR(KBr): 3200–2800 (OH), 1680 (C=O), and 1300 and 1160 (SO₂) cm⁻¹.

¹H-NMR(DMSO-*d*₆): δ8.2 (s, 8H, aromatic).

¹³C-NMR(DMSO-*d*₆): δ165.03 (carbonyl carbon) and 143.03–126.99 (aromatic carbons).

ANAL. Calcd for C₁₆H₁₀O₆S: C, 54.89; H, 3.29%. Found: C, 54.77; H, 3.18%.

Polymerization

A typical polymerization procedure is given.

Polymer PA-1 from 4,4'-Oxydianiline (*I*) and DCDPS

A mixture of 1.53 g (5 mmol) of DCDPS, 1.00 g (5 mmol) of 4,4'-oxydianiline, and 3.10 g (0.01 mol) of triphenyl phosphite was heated at 100°C for 3 h under nitrogen in a solvent consisting of NMP (10 mL), pyridine (2.5 mL), and 4 wt % LiCl (0.7 g). After cooling, the reaction mixture was poured into 200 mL of methanol, the precipitated polymer was collected by filtration, washed well with methanol, and dried. The yield was 2.4 g (100%). The inherent viscosity of a 0.5 g/dL polymer solution in DMAc containing 5 wt % LiCl was 1.65 dL/

g at 30°C. The IR spectrum (film) showed absorptions at 3300 (N—H), 1660 (C=O), and 1300 and 1160 (SO₂) cm⁻¹.

All other polymers were prepared in a similar process.

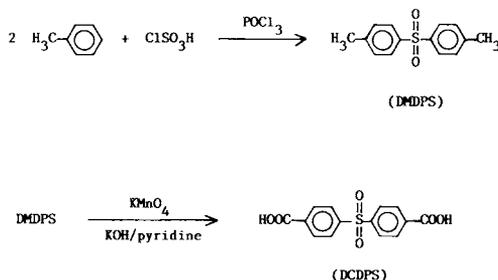
Measurements

A Jasco IRA-2 Grating Infrared Spectrophotometer, a JEOL-JNM-PMX-60 NMR Spectrometer, and a JEOL FX-90Q FT NMR Spectrometer were utilized to identify the structures of monomer and polymer. Inherent viscosities of all polymers were determined at 30°C on solutions of 0.5 g/dL concentrations in DMAc containing 5 wt % LiCl using a Cannon-Fenske viscometer. Qualitative solubility was determined using about 0.2 g of polymer in 2 mL of solvent. X-ray diffraction patterns were obtained on a Rigaku Geiger Flex D-Max IIIa with nickel-filtered CuK α radiations. The scanning rate was 4°/min. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were performed on a DuPont 951 thermogravimetric analyzer and a DuPont 910 differential scanning calorimeter coupled to a DuPont 1090 thermal analyzer.

RESULTS AND DISCUSSION

Monomer

4,4'-Dicarboxydiphenyl sulfone (DCDPS) was prepared in two steps, starting with toluene and chlorosulfonic acid (Scheme 1). In the first step, 4,4'-Dimethyldiphenyl sulfone (DMDPS) was prepared⁵ in 78% yield from toluene, chlorosulfonic acid, and phosphorus oxychloride. In the second step, DMDPS was oxidized to DCDPS in 60% yield with excess alkaline potassium permanganate. Characterization involved IR, NMR, and elemental analysis. The IR spectrum of DCDPS showed absorption bands at 3300–2900 (OH), 1680 (C=O), and 1300 and 1160 (SO₂) cm⁻¹ (see Fig. 1). Figures 2(A) and 2(B) showed the ¹H- and ¹³C-NMR spectra of DCDPS, respectively. Interestingly, the ¹H-NMR spectrum shows a singlet at δ 8.2, indicating the chemical shift equivalence of the aromatic protons. In the ¹³C-NMR spectrum, the absorption peak of carbonyl carbon appears at δ 165.03 and the four peaks in the range δ 143.78–127.53 are peculiar to the aromatic carbons. The complete oxidation of DMDPS was confirmed by absence of the methyl proton signal at δ 2.37 in the ¹H-NMR spectrum and by the disappearance of the methyl carbon signal at δ 21.34 in



Scheme 1. Preparation of DCDPS.

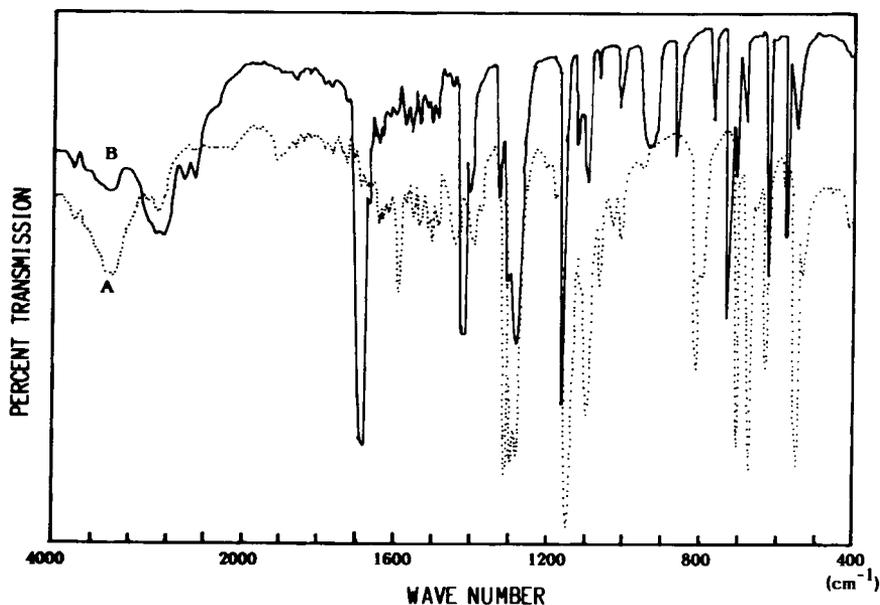


Fig. 1. IR spectra of (A) DMDPS and (B) DCDPS.

the ^{13}C -NMR spectrum. The elemental analysis of DCDPS was in good agreement with the calculated values.

Polymerization

Several polyamides (from PA-1 to PA-5) were directly synthesized from DCDPS and aromatic diamines such as 4,4'-oxydianiline (I), 3,4'-oxydianiline (II), 4,4'-methylenedianiline (III), *p*-phenylenediamine (IV), and 4,4'-sulfonyldianiline (V) using a Yamazaki phosphorylation reaction (Scheme 2). All

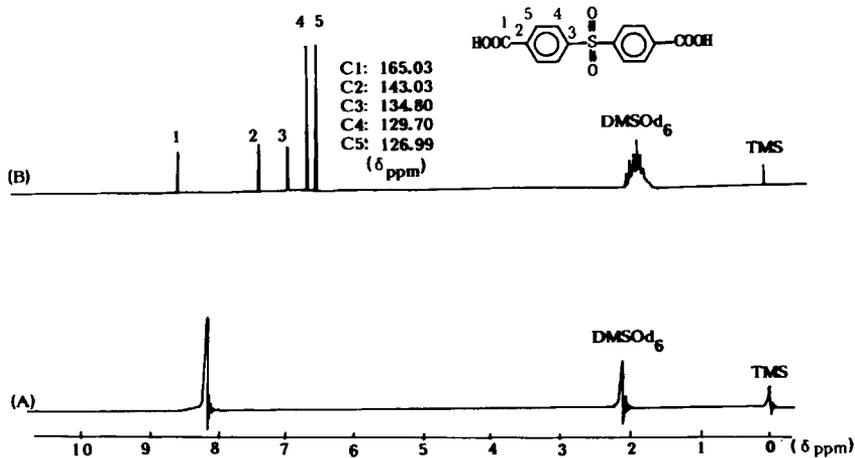
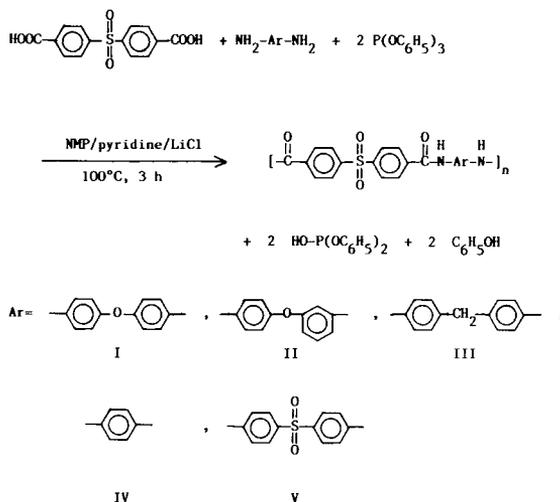


Fig. 2. (A) ^1H - and (B) ^{13}C -NMR spectra of DCDPS measured in dimethyl sulfoxide- d_6 .



Scheme 2.

polymerization reactions were carried out at 100°C for 3 h in NMP-pyridine (4 : 1) solution containing 4 wt % LiCl. The results of the polymerizations are summarized in Table I. The polyamides were obtained in quantitative yield except for PA-5. The typical IR spectrum of these polymers shows the following absorptions: 3250 ± 100 (N-H), 1650 ± 10 (C=O), and 1300 ± 20 and 1160 ± 10 (SO₂) cm⁻¹ (Fig. 3).

Except that of PA-5, the inherent viscosities of all polymers were in the range of 0.92–1.65 dL/g. The less favorable result for PA-5 may be due to the lower reactivity of diamine V which contains negative substitution. A strong and tough film could be cast from PA-1 to PA-3 in DMAc, while the film of PA-4 was embrittled probably due to the more rigid nature of the polymer backbones.

Properties of Polymers

The solubilities of polyamides are listed in Table II. All these polymers were found soluble in DMAc containing 5 wt % LiCl, NMP containing 4 wt % LiCl,

TABLE I
Preparation of Polyamides from DCDPS with Various Diamines by Using TPP
in NMP-Py Solution Containing 4 wt % LiCl^a

Polymer code	Diamine	Yield (%)	η_{inh}^b (dL/g)
PA-1	I	100	1.65
PA-2	II	100	0.92
PA-3	III	100	0.95
PA-4	IV	99	1.34
PA-5	V	85	0.42

^a DCDPS = diamine = 5 mmol, NMP = 10 mL, Py = 2.5 mL, TPP = 3.1 g, LiCl = 0.7 g.

^b Measured in DMAc containing 5 wt % LiCl at 30°C on 0.5 g/dL.

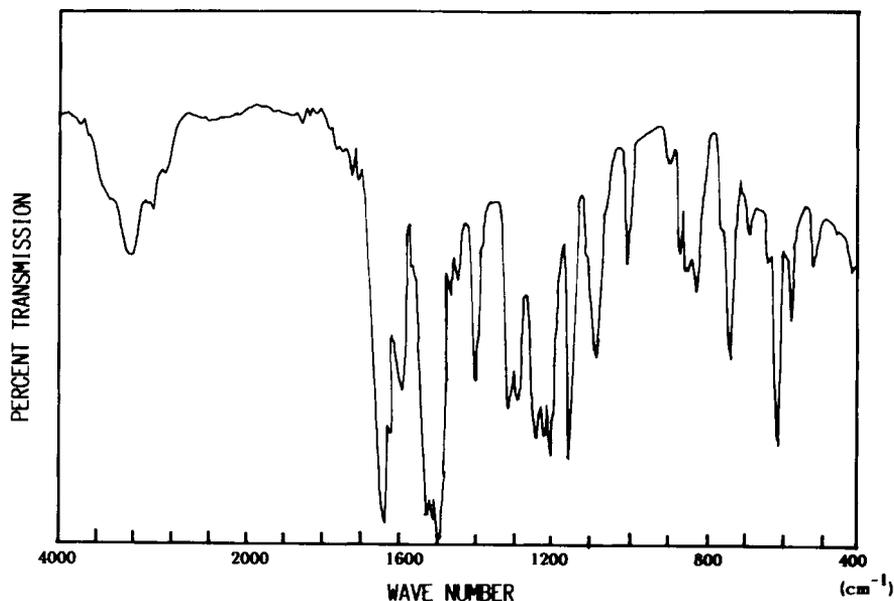


Fig. 3. IR spectrum of polyamide PA-1.

and concentrated sulfuric acid. Some of the polyamides were completely or partially soluble in amide-type solvents such as DMF, DMAc, and NMP. However, they were insoluble in *m*-cresol, chloroform, pyridine, and common organic solvents like benzene, acetone, and ethanol. In general, the introduction of sulfone groups gave a better solubility of polymers than observed on polyamides derived from terephthalic acid or isophthalic acid and aromatic diamines.

The x-ray diffraction patterns of PA-1 to 4 (Fig. 4) indicate that the polymers were essentially amorphous. Some crystallinity was indicated for PA-4 which was derived from *p*-phenylenediamine. All showed an amorphous halo pattern in the region of $2\theta = 10\text{--}30^\circ$. The partially crystalline nature of PA-4 can be attributed to the presence of symmetrical segments in the polymer chains.

The thermal behavior of these polyamides in a nitrogen atmosphere by using thermogravimetric (TG) analysis and differential scanning calorimetry (DSC).

TABLE II
Solubility of Polyamides^a

Polymer	DMF	DMAc	NMP	DMAc + 5 wt % LiCl	NMP + 4 wt % LiCl	<i>m</i> -Cresol chloroform pyridine	Conc. H ₂ SO ₄	Acetone benzene ethanol
PA-1	±	+	+	+	+	-	+	-
PA-2	±	+	+	+	+	-	+	-
PA-3	-	±	+	+	+	-	+	-
PA-4	-	s	s	+	+	-	+	-
PA-5	±	+	+	+	+	-	+	-

^a Note: + soluble, ± partially soluble, - insoluble, s swelling at room temperature.

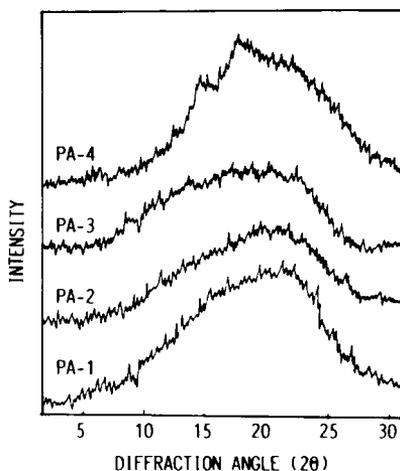


Fig. 4. X-ray diffraction patterns of polyamides.

The TG curves of all these polymers are shown in Figure 5. The temperatures at weight losses of 10, 20, and 30% are given in Table III. This table also presents weight residues at 600°C. These polyamides decompose in the region of 400–450°C. The polymer PA-4 was thermally more stable than the other polymers. This can be attributed to some crystallinity of the polymer chains in the former. The polymer PA-1 with a symmetric 4,4'-diphenyl ether along with the polymer chain showed a better stability than PA-2 with an unsymmetric 3,4'-diphenyl ether along with the polymer backbone. The less stability of PA-5 may be attributed to a lower molecular weight. The glass transition temper-

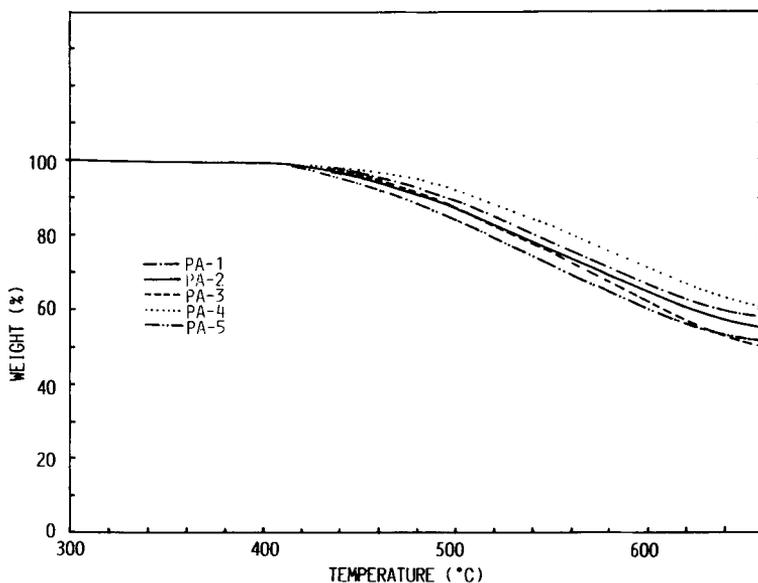


Fig. 5. TG curves of polyamides, with heating rate 10°C/min in nitrogen.

TABLE III
Thermal Behavior Data of Polyamides

Polymer	T_g^a (°C)	Temperature (°C) with following weight loss ^b			Residual wt % at 600°C ^b
		10%	20%	30%	
PA-1	291	523	576	632	74
PA-2	280	512	563	613	72
PA-3	290	512	558	600	69
PA-4	298	542	595	660	78
PA-5	285	497	540	588	67

^a From DSC measurements conducted at a heating rate of 10°C/min in nitrogen.

^b Thermogravimetric analyses conducted at a heating rate of 10°C/min in nitrogen.

ature (T_g) of polyamides are also shown in Table III. All the polymers show glass transition temperatures between 280 and 300°C. The low degrees of crystallinity developed are the main cause for not well defined melting points as observed by DSC.

We are grateful to Dr. T. S. Lin (President of Tatung Institute of Technology) and to the National Science Council of the Republic of China for support of this work. Dr. W. C. Kuo is also appreciated for his assistance in monomer synthesis.

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Received November 30, 1988

Accepted January 8, 1990