

# Synthesis and Characterization of Poly(imide-Sulfonamide)s

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## Synopsis

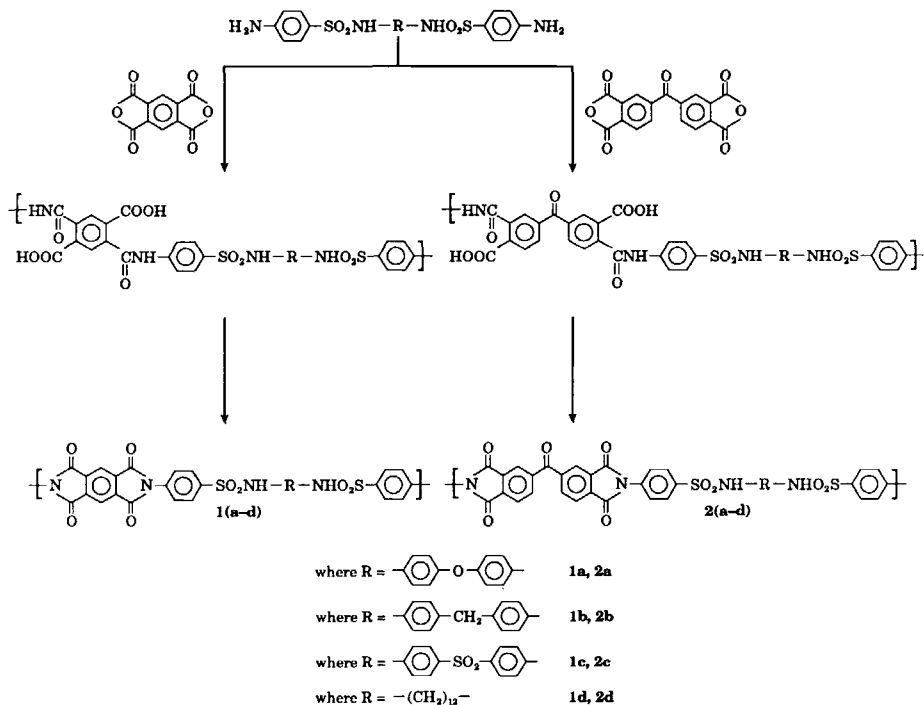
Eight novel poly(imide-sulfonamide)s have been prepared by reacting pyromellitic dianhydride and benzophenone tetracarboxylic acid dianhydride with variously substituted dianilines containing preformed sulfonamide linkages. Inherent viscosities of the prepared polymers ranged from 0.13 to 0.53 dL/g. Four of the polymers formed tough, transparent yellow, flexible films. Glass transition temperatures, determined by differential scanning calorimetry, ranged from 103 to 249°C. Thermogravimetric analyses of the polymers showed that they have moderate thermal stability with weight losses ranging from 6.8 to 42% at 400°C.

## INTRODUCTION

A large number of polyimides have been prepared by the direct reaction of various aliphatic and aromatic diamines with carboxylic acid dianhydrides,<sup>1-5</sup> utilizing solution polymerizations. The initial reaction forms a soluble poly(amic acid) that can be cyclo-dehydrated chemically or thermally to form the polyimide structure. Polyimides derived from aromatic diamines are commercially important because of their outstanding thermal and thermo-oxidative stabilities. Polyimides have been modified by incorporating various functional moieties into the polymer backbone. In this way, properties of both functional groups are incorporated into the final structure and an inflexible, insoluble polyimide is modified. Imai and Okunoyama<sup>6</sup> prepared a new class of poly(imide-sulfonamide)s by reacting various diamines with 4-chlorosulfonyl phthalic anhydride. High molecular weight polymer was achieved using low-temperature solution polymerizations with *N,N*-dimethyl acetamide as a solvent and an acid acceptor. Poly(imide-sulfonamide) films obtained from thermally cured poly(amic acid sulfonamide) films cast from solution were generally transparent, yellow, and brittle. As might be expected, aromatic poly(imide-sulfonamide)s showed properties intermediate between those of polysulfonamides and polyimides.

The objective of this work was to synthesize and characterize a series of novel poly(imide-sulfonamide)s with general structures **1** and **2**, where R is 4,4'-oxydianiline, 4,4'-methylene dianiline, 4,4'-diaminodiphenyl sulfone, and 1,12-diaminododecane, respectively. Variously substituted dianilines containing preformed sulfonamide linkages were prepared and reacted with pyromellitic dianhydride and benzophenone tetracarboxylic acid dianhydride using low-temperature solution techniques to produce poly(amic acid sulfonamide)s. Poly(amic acid sulfonamide)s were thermally cured to give the polymer struc-

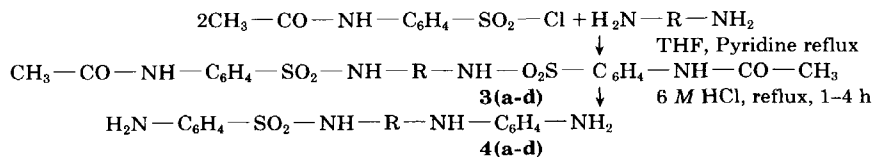
tures. These polymers are expected to have good mechanical and thermal properties.



## DISCUSSION OF RESULTS

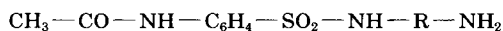
The strategy of the synthesis of the title polymers involved (1) the synthesis of a diacetanilide containing a preformed sulfonamide linkage, (2) a deblocking reaction that converted the diacetanilide to a dianiline monomer containing preformed linkages, (3) the solution polymerization of the dianiline monomers with either pyromellitic dianhydride or benzophenone tetracarboxylic dianhydride to give the poly(amic acid sulfonamide), and (4) thermal curing of the poly(amic acid sulfonamide) to produce the poly(imide-sulfonamide).

The diacetanilides, **3a-d**, were prepared by reacting various diamines with 2 molar equivalents of *N*-acetyl sulfanilyl chloride. A simple acid hydrolysis removed the acetyl blocking groups on the diacetanilides to give the dianilines **4a-d**. The reaction sequence for the synthesis of the dianilines **4a-d** is



Initially, synthesis of these novel diacetanilides was attempted by reacting various diamines with *N*-acetyl sulfanilyl chloride using glacial acetic acid as a

solvent and anhydrous sodium acetate as an acid acceptor.<sup>7</sup> The diamines used were 4,4'-oxydianiline, 4,4'-methylene dianiline, 4,4'-sulfonyl dianiline, and 1,12-diaminododecane. Approximately 80% yields of crude products were obtained. Thin layer chromatography analysis of the product showed the desired diacetanilide, **3**, contaminated with unreacted *N*-acetyl sulfanilyl chloride and a monoacetanilide. The structure of the monoacetanilide is shown below and results from the 1 : 1 molar reaction of *N*-acetyl sulfanilyl chloride with the diamine.



Attempts to purify these products by recrystallization were unsuccessful. It was believed that poor mixing and high reactant concentrations during the reaction caused the formation of mixtures.

To minimize the formation of these mixtures, reaction conditions were changed. The solvent was changed to tetrahydrofuran in which both reactants were soluble. Anhydrous pyridine was used as an acid acceptor. Low concentrations of reactants, large volumes of tetrahydrofuran, order of addition, and vigorous mechanical stirring, which ensured good mixing, resulted in the formation of the desired diacetanilides. Yields were relatively high and ranged from 75 to 90%. TLC analysis showed minor contamination by unreacted *N*-acetyl sulfanilyl chloride. The diacetanilides could be purified by recrystallization.

The deblocking reaction of the diacetanilides **3a–d** proved to be straightforward. A simple reflux with 6 *M* hydrochloric acid for 1–4 h led to the formation of the dianiline monomers **4a–d** having preformed sulfonamide linkages. TLC was used to monitor the progress of the hydrolysis. Yields varied from 80 to 95%. The dianiline monomers were purified by column elution chromatography. The properties of the dianilines are summarized in Table I.

The diamines retained 5–14% water by weight and had to be dried over phosphorus pentoxide and refluxing toluene for several hours before use in

TABLE I  
Properties of Dianilines

Dianiline	mp (°C) <sup>a</sup>	<i>R</i> <sub>f</sub> <sup>b</sup>	Elemental analysis				
				C	H	N	S
<b>4a</b>	179–180	0.57	Calcd.	56.46	4.34	10.97	12.55
			Found	56.43	4.45	10.75	12.05
<b>4b</b>	222–223	0.41	Calcd.	59.04	4.77	11.01	12.60
			Found	59.37	4.68	11.03	12.84
<b>4c</b>	171–173	0.39	Calcd.	51.60	3.97	10.03	17.22
			Found	52.03	3.89	9.74	17.50
<b>4d</b>	175–176	0.69	Calcd.	56.44	7.52	10.97	12.56
			Found	56.67	7.23	10.62	12.38

<sup>a</sup> Melting points were determined on dianilines purified by column chromatography.

<sup>b</sup> Dianilines were chromatographed on Eastman Chromagram Silica Gel with fluorescent indicator using a solvent mixture of ethyl acetate–hexane (3 : 1 by volume).

polymerization reactions. The observed elemental analyses correspond favorably to calculated values. Infrared spectra (KBr) showed absorptions at 3480 and 3380  $\text{cm}^{-1}$ , which confirm the presence of primary amine groups. The loss of an absorption at 1680  $\text{cm}^{-1}$  confirms that the hydrolysis of the acetyl group was successful.

Eight novel poly(imide-sulfonamide)s having the structures **1a–d** and **2a–d** have been synthesized using low-temperature polymerization techniques. Dianilines **4a–d** were reacted with pyromellitic dianhydride and benzophenone tetracarboxylic acid dianhydride to produce poly(amic acid sulfonamide)s, which were thermally cured to yield polymer structures **1** and **2**, respectively.

Polymerizations were carried out using pure dianiline monomers, anhydrous *N,N*-dimethyl acetamide, oven-dried apparatus assembled while hot and a reaction temperature of 0°C. Poly(amic acid sulfonamide)s were cured at 280°C for 3 h to yield the title polymers. Initial polymerization attempts led to the formation of brittle poly(amic acid sulfonamide)s having low inherent viscosities. Even though the dianiline monomers showed one spot upon TLC analysis, their purity was suspect. Thermal gravimetric analysis of the dianiline monomers showed 4–14% solvent entrapment, more than enough impurity to prevent the formation of a high molecular weight polymer.

A second series of polymerizations carried out using dianiline monomers purified by column elution chromatography and dried over phosphorus pentoxide and refluxing toluene led to the formation of polymers having higher inherent viscosities. The prepared polymers were characterized by infrared spectroscopy, dilute solution viscosity, differential scanning calorimetry, and thermogravimetric analysis. Their properties are characterized in Table II.

The infrared spectra obtained for the prepared polymers are consistent with the poly(imide-sulfonamide) structures. All showed absorptions at 3200–3310 (broad) and 1690–1800  $\text{cm}^{-1}$  corresponding to the sulfonamide and imide absorptions, respectively.

Inherent viscosities of the prepared poly(amic acid sulfonamide)s ranged from 0.13 to 0.53 dL/g and were determined in *N,N*-dimethyl acetamide at

TABLE II  
Properties of Poly(imide-Sulfonamide)s

Polymer	Inherent viscosity <sup>a</sup>	TGA <sup>b</sup>	T <sub>g</sub> <sup>c</sup> (°C)
<b>1a</b>	0.53	8.9	182
<b>1b</b>	0.32	19.0	194
<b>1c</b>	0.21	24.0	132
<b>1d</b>	0.13	42.0	105
<b>2a</b>	0.49	12.7	249
<b>2b</b>	0.36	6.8	248
<b>2c</b>	0.23	34.0	214
<b>2d</b>	0.19	42.0	103

<sup>a</sup> Inherent viscosities determined in *N,N*-dimethyl acetamide at 25°C and a concentration of 0.5 g/dL.

<sup>b</sup> Percent weight loss at 400°C in nitrogen at a heating rate of 20°C/min.

<sup>c</sup> Observed by differential scanning calorimetry at a heating rate of 20°C/min in nitrogen.

25°C using concentrations of 0.5 g/dL. Polymers **1a**, **1b**, **2a**, and **2b** had inherent viscosities of 0.53, 0.32, 0.49, and 0.36 dL/g, respectively, and formed tough, transparent yellow films. These polymers clearly showed the best film-forming properties. Polymers **1c** and **2c**, containing the 4,4'-sulfonyl diphenylene moiety, had inherent viscosities of 0.21 and 0.23 dL/g and formed brittle films. Polymers **1d** and **2d**, containing the dodecamethylene group, had even lower inherent viscosities and did not form films.

Glass transition temperatures of the prepared polymers were determined by differential scanning calorimetry and ranged from 103 to 249°C. These data are summarized in Table II. Polymers **2a–c**, containing the benzophenone moiety showed the highest  $T_g$  of the polymer series prepared and were significantly higher than those polymers derived from the pyromellitic dianhydride. Ordinarily, polymers derived from pyromellitic dianhydride have higher  $T_g$  values. These high glass transition temperatures indicate a high degree of order in the polymer backbones and may be accounted for by hydrogen bonding between the sulfonamide N–H and the carbonyl grouping in the benzophenone moiety. Moreover, when hydrogen bonding occurs, the benzene rings adjacent to the sulfonamide and the benzene of the benzophenone linkage may align resulting in greater  $\pi$ – $\pi$  cloud overlap. Polymers **1a**, **1b**, **2a**, and **2b** utilizing R equal to diphenyl ether and diphenyl methylene show similar values, changing only with the dianhydride moiety used. This can be attributed to similar flex and bulk characteristics of these linkages. In polymers **1c** and **2c** with R equal to diphenyl sulfone, a bulkier and more rigid grouping, the  $T_g$  is lower. Polymers **1d** and **2d** containing the 1,12-dodecamethylene moiety, a flexible grouping, were not affected by the change in dianhydride structure.

The thermal stability of the prepared poly(imide-sulfonamide)s was measured by thermogravimetric analysis. All the polymers showed a 0.5–1.5% weight loss at 150°C, which was attributed to the loss of entrapped solvent. The thermogravimetric weight loss at 400°C is summarized in Table II. Polymers **1a** and **2b** showed the highest thermal stability and showed no weight loss until major decomposition occurred at 400°C. Polymers **1b** and **2a** showed a weight loss at 200°C, which was attributed to incomplete imidization. Polymers **1c**, **1d**, **2c**, and **2d** began to degrade at 350°C followed by major decomposition at 400°C. The low thermal stabilities of these polymers were attributed to low molecular weight. The incorporation of a sulfonamide linkage into a polyimide structure does not appear to improve thermal stabilities of the resulting poly(imide-sulfonamide)s, and, in fact, it may be the thermal weak link in the structure. Aromatic polysulfonamides, regardless of structure, are known to degrade between 345–395°C (air) and 380–400°C (nitrogen).<sup>8</sup>

## EXPERIMENTAL

### General Information

Reagent grade chemicals and solvents were purchased from Aldrich Chemical Company or Eastman Kodak Company and were used without further purification unless specified. *N,N*-dimethyl acetamide was distilled from calcium hydride under reduced pressure and stored over molecular sieves.

Elemental analyses were run by Baron Consulting Company, Orange, CT. Diamines were dried *in vacuo* over phosphorus pentoxide in a drying pistol with refluxing toluene. Infrared spectra were run on a Perkin-Elmer 681 Spectrometer. All solids were run as potassium bromide pellets. Melting points were run on a Mettler FP-5 apparatus and are uncorrected. Inherent viscosities of poly(amic acid sulfonamide)s were determined as dilute solutions, concentration 0.5 g/dL in *N,N*-dimethyl acetamide using a Ubbelohde viscometer at a constant temperature of 25°C. Thermal gravimetric analyses were determined on a Perkin-Elmer TGS-2 Thermogravimetric Analyzer. Sample were heated at a rate of 20°C/min in a nitrogen atmosphere. Glass transition temperatures,  $T_g$ , were determined on a Perkin-Elmer DSC-4 Differential Scanning Calorimeter. Thin-layer chromatography was run on Eastman Kodak Chromagram silica gel 13181 sheets with fluorescent indicator. Column elution chromatography was carried out using Woelm silica gel as the stationary phase and ethyl acetate-hexane (3 : 1 by volume) as the mobile phase.

#### **General Procedure for the Preparation of Blocked Diamine Monomers**

*N*-acetyl sulfanilyl chloride, 256.7 g, (0.11 mol, 10% excess), 250 mL tetrahydrofuran, and 9.7 mL pyridine were placed in a 2.0-L round-bottom flask fitted with condenser, mechanical stirrer, and pressure equalizing addition funnel. To this refluxing mixture was added a solution of 0.050 mol of diamine in 250 mL of tetrahydrofuran over a period of 2 h. A viscous oil formed during the addition period. After cooling, the tetrahydrofuran was decanted from the oil. The oil was slowly poured over ice water to form a precipitate. The precipitate was filtered, washed with water, and dried *in vacuo* for several hours.

#### **General Deblocking Procedure for the Preparation of Diamine Monomers**

The 4,4'-[oxybis(*p*-phenylene sulfonamido)]diacetanilide, 0.05 mol, and 120 mL 6 *M* hydrochloric acid were added to a round-bottom flask fitted with condenser and magnetic stirring bar. The mixture was refluxed for 1 h, cooled, and transferred to a beaker containing three times the reaction solution volume of water. The resulting solution was made basic by small additions of sodium carbonate. The precipitate formed upon neutralization was filtered, washed with water, and dried *in vacuo* for several hours at 30°C.

#### **General Polymerization Procedure for the Preparation of Poly(imide-Sulfonamide)s**

All polymerizations were carried out using ultra pure monomers, anhydrous solvents, and dry apparatus.

Freshly distilled *N,N*-dimethyl acetamide, 3.0 mL, was placed in a 50-mL round-bottom flask fitted with drying tube and magnetic stirrer. The solvent was cooled to 0°C in an ice-water bath and the dianhydride (5 mmol) added in one portion. Once the dianhydride dissolved, the diamine monomer (5 mmol) was added. The mixture was stirred for 6 h, poured into 250 mL distilled water, the precipitate collected by filtration, washed several times with water, and

dried *in vacuo* for 6 h at 100°C. A 20% by weight solution of the poly(amic acid sulfonamide) in *N,N*-dimethyl acetamide was cast as a film on a tempered glass plate and cured at 280°C to give the poly(imide-sulfonamide).

*Preparation of 4,4'-[Oxybis(p-Phenylene Sulfonamido)]Diacetanilide 3a*

Using the general procedure, 4,4'-oxydianiline, 11.68 g (0.05 mol) was reacted with 25.0 g (0.11 mol) *N*-acetyl sulfanilyl chloride to produce 23.76 g, 80% yield, of **3a**. Recrystallization from methanol : chloroform (30 : 70 v/v) gave a white powder, mp 238–240°C.

*Preparation of 4,4'-[Methylenebis(p-Phenylenesulfonamido)]Diacetanilide 3b*

Using the general procedure, 4,4'-methylenedianiline, 9.95 g (0.05 mol) was reacted with 25.0 g (0.11 mol) of *N*-acetyl sulfanilyl chloride to produce 26.70 g, 90% yield, of **3b**. Recrystallization from methanol : chloroform (30 : 70 v/v) gave a white powder, mp 148–152°C.

*Preparation of 4,4'-[Sulfonylbis(p-Phenylenesulfonamido)]Diacetanilide 3c*

Using the general procedure, 4,4'-sulfonyldianiline, 12.40 g (0.05 mol) was reacted with 25.0 g (0.11 mol) of *N*-acetyl sulfanilyl chloride to produce 24.23 g, 75% yield, of **3c**. Recrystallization from methanol : chloroform (30 : 70 v/v) gave a tan powder, mp 161–162°C.

*Preparation of 4,4'-[Dodecamethylenebis(p-Phenylene Sulfonamido)]Diacetanilide 3d*

Using the general procedure, 1,12-diaminododecane, 10.0 g (0.05 mol) was reacted with 25.0 g (0.11 mol) of *N*-acetyl sulfanilyl chloride to produce 26.17 g, 88% yield, of **3d**. Recrystallization from methanol : chloroform (30 : 70 v/v) gave a white powder, mp 152–154°C.

*Preparation of 4,4'-[Oxybis(p-Phenylenesulfonamido)]Dianiline 4a from 3a*

Using the general deblocking procedure, 10 g (17 mmol) of **3a** was treated with 80 mL of 6 *M* hydrochloric acid to produce 7.60 g, 80% yield of dianiline monomer **4a**. Purification by column elution chromatography gave material having a mp of 179–180°C.

*Preparation of 4,4'-[Methylenebis(p-Phenylenesulfonamido)]  
Dianiline 4b from 3b*

Using the general deblocking procedure, 10.0 g (16.9 mmol) of **3b** was treated with 80 mL of 6 *M* hydrochloric acid to produce 7.54 g, 87% yield of dianiline monomer **4b**. Purification by column elution chromatography gave material having mp of 222–223°C.

*Preparation of 4,4'-[Sulfonylbis(p-Phenylenesulfonamido)]  
Dianiline 4c from 3c*

Using the general deblocking procedure, 10.0 g (15 mmol) of **3c** was treated with 80 mL of 6 *M* hydrochloric acid to produce 7.81 g, 93% yield of dianiline

monomer **4c**. Purification by column elution chromatography gave a material having a mp of 171–173°C.

*Preparation of 4,4'-[Dodecamethylenebis(p-Phenylenesulfonamido)]  
Dianiline **4d** from **3d***

Using the general deblocking procedure, 10 g (17 mmol) of **3d** was treated with 80 mL of 6 M hydrochloric acid to produce 8.16 g, 95% yield of dianiline monomer **4d**. Purification by column elution chromatography gave a material having a mp of 175–176°C.

*Polymerization of Dianiline Monomer **4a** with Pyromellitic Dianhydride*

Using the general polymerization procedure, 1.8796 g (3 mmol) of dianiline monomer **4a**, was reacted with 0.7313 g (3 mmol) of pyromellitic anhydride to produce 2.48 g, 95% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.53 dL/g. A solution of this poly(amic acid sulfonamide), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **1a**.

*Polymerization of Dianiline Monomer **4b** with Pyromellitic Dianhydride*

Using the general polymerization procedure, 0.6708 g (1 mmol) of dianiline monomer **4b** was reacted with 0.2619 g (1 mmol) of pyromellitic dianhydride to produce 0.9047 g, 97% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.32 dL/g. A solution of this poly(amic acid sulfonamide), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **1b**.

*Polymerization of Dianiline Monomer **4c** with Pyromellitic Dianhydride*

Using the general polymerization procedure, 2.3357 g (4.5 mmol) of dianiline monomer **4c** was reacted with 0.9120 g (4.5 mmol) to produce 3.1181 g, 96% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.21 dL/g. A solution of this poly(amic acid sulfonamide), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **1c**.

*Polymerization of Dianiline Monomer **4d** with Pyromellitic Dianhydride*

Using the general polymerization procedure, 0.8790 g (1.7 mmol) of dianiline monomer **4d** was reacted with 0.3754 g (1.7 mmol) of pyromellitic dianhydride to produce 1.2295 g, 98% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.13 dL/g. A solution of this poly(amic acid sulfonamide), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **1d**.

*Polymerization of Dianiline Monomer **4a** with Benzophenone  
Tetracarboxylic Acid Dianhydride*

Using the general polymerization procedure, 0.8339 g (1.5 mmol) of dianiline monomer **4a** was reacted with 0.4793 g (1.5 mmol) of benzophenone tetracar-



boxylic acid dianhydride to produce 1.2511 g, 95% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.49 dL/g. A solution of this poly(amic acid sulfonamide), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **2a**.

*Polymerization of Dianiline Monomer 4b with Benzophenone  
Tetracarboxylic Acid Dianhydride*

Using the general polymerization procedure, 0.4012 g (0.7 mmol) of dianiline monomer **4b** was reacted with 0.2311 g (0.7 mmol) of benzophenone tetracarboxylic acid dianhydride to produce 0.6133 g, 97% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.36 dL/g. A solution of this poly(amic acid sulfonamide), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **2b**.

*Polymerization of Dianiline Monomer 4c with Benzophenone  
Tetracarboxylic Acid Dianhydride*

Using the general polymerization procedure, 2.8470 g (5.1 mmol) of dianiline monomer **4c** was reacted with 1.6423 g (5.1 mmol) of benzophenone tetracarboxylic acid dianhydride to produce 4.4011 g, 98% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.23 dL/g. A solution of this poly(amic acid sulfonamide), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **2c**.

*Polymerization of Dianiline Monomer 4d with Benzophenone  
Tetracarboxylic Acid Dianhydride*

Using the general polymerization procedure, 0.6515 g (1.3 mmol) of dianiline monomer **4d** was reacted with 0.4111 g (1.3 mmol) of benzophenone tetracarboxylic acid dianhydride to produce 1.009 g, 95% yield, of poly(amic acid sulfonamide) having an inherent viscosity of 0.119 dL/g. A solution of this poly(amic acid dianhydride), 20% by weight in *N,N*-dimethyl acetamide, was cast as a film and cured for 3 h at 280°C to produce poly(imide-sulfonamide) **2d**.

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