Poly(p-phenylene sulfone)

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Received June 25, 1993; Revised Manuscript Received September 20, 1993[⊕]

ABSTRACT: The title polymer has been synthesized in moderate molecular weight by the self-condensation of sodium 4-halobenzenesulfinate at 175 °C in dimethyl sulfoxide. The use of a small amount of 4-fluorophenyl sulfone served to greatly increase the yield of polymer, presumably by acting as an initiator for a chain–type polymerization. The title polymer is highly crystalline (>85%) and poorly soluble in all solvents attempted. The number-average degree of polymerization was estimated to be 10–16 by elemental analysis. No thermal transitions below 500 °C were detected by DSC. The polymer exhibited extremely high and unusual thermal stability when studied by TGA; the onset of significant mass loss occurred at 517 °C in nitrogen and at 555 °C in air. The polymer was characterized by IR and solid-state ^{13}C NMR spectroscopy and by X-ray diffraction. Analogous model compounds for the trimer and tetramer were prepared and used to confirm the structure of the polymer.

Introduction

Aromatic sulfone-containing polymers are widely used in high-performance applications, but until now the parent compound poly(p-phenylene sulfone) (PPSO2, 1) has not been reported.

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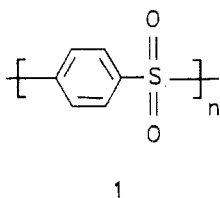
Formally, PPSO2 is simply the oxidation product of poly(p-phenylene sulfide) (PPS), a well-known commercial material. However, any kind of chemical modification of PPS is difficult because PPS is highly insoluble and most reagents cannot penetrate the solid. In fact, the high chemical resistance of PPS allows its use in aggressive environments. Under oxidative conditions, PPS is reported[1] to undergo cross-linking reactions rather than conversion to PPSO2.

As an extension of our work in sulfone chemistry,[2,3] we realized that linear poly(p-phenylene sulfone) might be effectively synthesized by the self-condensation (via aromatic nucleophilic substitution) of 4-halobenzenesulfinate salts (Scheme I). This idea is closely related to the work of Lenz et al.[4] and Lovell and Still,[5] who studied the self-polymerization of 4-halothiophenoxides to produce linear poly(p-phenylene sulfide) (PPS). However, the sulfone group present in a growing PPSO2 chain is much more strongly activating toward aromatic nucleophilic substitution than the sulfide group in PPS synthesized in an analogous way. Therefore, the polymerization reaction to form PPSO2 should be more facile. Aromatic nucleophilic substitution of halogen by sulfinate has been reported previously for small molecules.[3,6–11] The reaction was extended to macromolecules by Sato and co-workers, who synthesized polysulfones by the condensation of disodium 4,4′-oxydibenzenesulfinate with strongly activated dihalides.[12–14] Similarly, Reuter disclosed that m-benzenedisulfinate salts react with p-dinitrobenzene via double nitrite displacement to form alternating para- and meta-poly(phenyl sulfone).[15] Other aromatic polysul-

fones, including poly(biphenylene sulfone), were prepared by Vogel using Friedel–Crafts chemistry.[16]

An aromatic halogen should be much more strongly activated toward nucleophilic displacement by a para-sulfone group than by a negatively charged para-sulfinate group. Sodium 4-halobenzenesulfinate monomer should react more rapidly with a growing chain end (activated by a sulfone) than with a second molecule of itself (activated by a sulfinate). Therefore, under suitable conditions, the polymerization may proceed mainly by a chain mechanism (Scheme I, Path B), with only minor contributions from a step mechanism (Scheme I, Path A). The situation in which reaction between two monomer molecules is possible, but the principal reaction involves addition to a growing chain, has been termed "preferential polymer formation" by Lenz,[4] although examples other than PPS are rare.[17]

We reasoned that the polymerization reaction could be assisted by supplying a small amount of the reactive equivalent of the growing chain, specifically 4-fluorophenyl sulfone, which is essentially a dimeric species of the polymer (Scheme I, Path B). In this way, a reactive core of the growing polymer chain would be present to initiate the chain mechanism of polymerization. This paper reports on our successful preparation of poly(p-phenylene sulfone) by this method and its physical characterization.

Experimental Section

Materials and Methods. Sodium 4-fluorobenzenesulfinate (Parish) and sodium 4-chlorobenzenesulfinate (Columbia) were dried by azeotropic distillation with toluene for 18 h with continuous separation of water employing a Dean–Stark apparatus. The toluene was then removed at reduced pressure. Sodium benzenesulfinate (Parish) was used without further drying. Dimethyl sulfoxide (DMSO) and sulfolane were dried by distillation from calcium hydride at reduced pressure. 4-Fluorophenyl sulfone (Aldrich) was purified by sublimation at reduced pressure.

Infrared spectra were obtained on a Nicolet Model 60SX Fourier transform spectrometer. ^{1}H NMR spectra were obtained on a GE QE-300 instrument, operating at 300 MHz. Solid-state ^{13}C NMR spectra were obtained on a Brucker Model CXP-100 spectrometer, operating a magic angle spinning probe from Doty Scientific. The operating frequency was 25.1 MHz for ^{13}C, with a 90° pulse width of 4.0 μs. All chemical shifts are reported in ppm referenced to tetramethylsilane. TGA data were obtained on a Perkin-Elmer TGS-II system. X-ray diffraction was performed on a Rigaku RU-300 diffractometer using Cu Kα radiation, a diffracted beam monochromator, and a scintillation detector. The sample was passed through a 100-mesh sieve and front-loaded into a polycarbonate sample holder. Field-desorp-

Scheme I. Preferential Polymer Formation of PPSO2
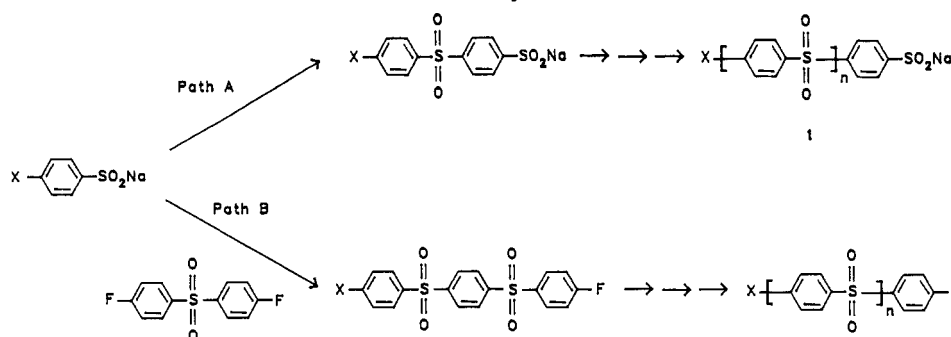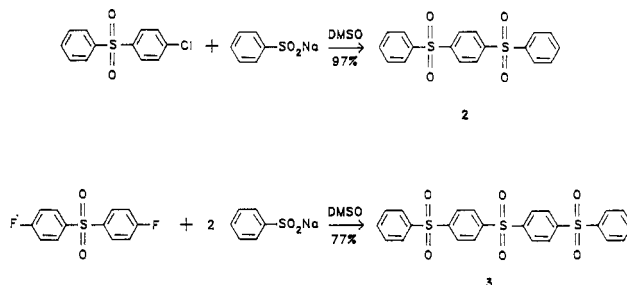
tion mass spectroscopy (FD-MS) was performed on a Varian MAT Model 731 instrument. Elemental analyses other than fluorine were performed by Analytical Technology Division, Eastman Kodak Co. Fluorine elemental analysis was performed by Galbraith Laboratory, Knoxville, TN. Melting points were measured by differential scanning calorimetry (DSC) and are reported as the temperature of the peak of the melting endotherm.

1,4-Bis(phenylsulfonyl)benzene (2). A mixture of 25.3 g (0.100 mol) of 4-chlorophenyl phenyl sulfone and 18 g (0.11 mol) of sodium benzenesulfinate was dissolved in 75 mL of dry DMSO under nitrogen and heated at 130 °C for 16 h. After cooling, the solution was poured onto 200 g of ice, precipitating the product. The crude solid was recrystallized from *N*-methylpyrrolidinone and then washed successively with methanol and with pentane to give 34.7 g (97%) of a white solid: mp (DSC) 223 °C (lit.[1] mp 228–230 °C); ^{1}H NMR ((CD$_3$)$_2$SO) δ 7.62 (m, 6 H), 7.95 (m, 4 H), 8.16 (s, 4 H). Anal. Calcd for C$_{18}$H$_{14}$O$_4$S$_2$: C, 60.32; H, 3.94; S, 17.89. Found: C, 60.10; H, 3.89; S, 17.78.

4,4′-Bis(phenylsulfonyl)phenyl Sulfone (3). Into 100 mL of dry DMSO was dissolved 12.7 g (0.050 mol) of 4-fluorophenyl sulfone and 18 g (0.110 mol) of sodium benzenesulfinate, and the solution was heated, under nitrogen, at 130 °C for 16 h. After cooling, the mixture was poured onto 200 g of ice, precipitating the product. The crude solid was recrystallized from *N*-methylpyrrolidinone and then washed successively with methanol and with pentane to give 18.8 g (77%) of a white solid: mp 312 °C (DSC) (lit.[11] mp 309–312 °C); ^{1}H NMR ((CD$_3$)$_2$SO) δ 7.59 (m, 4 H), 7.69 (m, 2 H), 7.93 (m, 4 H), 8.16 (m, 8 H); FD-MS *m/e* 498 (M$^+$).

Poly(*p*-phenylene sulfone) (1). Typical Procedure. Sodium 4-fluorobenzenesulfinate dihydrate (10.0 g, 45.8 mmol) was dried as described above, and then 0.24 g (0.92 mmol) of 4-fluorophenyl sulfone and 50 mL of dry DMSO were added. The resulting mixture was stirred and heated to 175 °C under nitrogen. All solids dissolved initially, but a white precipitate began to form within a few hours. After 24 h of heating, the reaction mixture was cooled to 23 °C and poured into 500 mL of vigorously stirred water. The resulting finely divided white solid was filtered and was washed successively with water, methanol, and dichloromethane. The polymer was dried for 24 h at 100 °C at reduced pressure: yield 6.4 g (100%). Anal. Calcd for C$_6$H$_4$O$_2$S: C, 51.42; H, 2.88; S, 22.88. Found: C, 48.92; H, 2.86; S, 22.35. The low value obtained for the carbon analysis may be caused by the difficulty in fully combusting this highly thermally stable polymer. The above procedure was repeated, but 4-fluorophenyl sulfone was omitted. A 9% yield of insoluble polymer was obtained.

Results and Discussion

Model Compounds. To test the efficacy of the proposed polymerization reaction and to prepare model compounds for comparison with the title polymer, we first synthesized the trimer (2) and the tetramer (3) by reacting sodium benzenesulfinate with 4-chlorophenyl phenyl sulfone and with 4-fluorophenyl sulfone, respectively (Scheme II). In these model reactions, conditions were developed that were later used for polymerization. The two model compounds were fully characterized by NMR

Scheme II. Model Compound Synthesis

and MS. Both 2 and 3 exhibited high melting points, but these compounds were soluble in dipolar, aprotic solvents.

Polymer Synthesis and Mechanism. Sodium 4-fluorobenzenesulfinate and sodium 4-chlorobenzenesulfinate were polymerized by heating with a small amount (1–2 mol %) of 4-fluorophenyl sulfone in a dipolar, aprotic solvent at 170–180 °C for 24–48 h. The polymer was isolated by pouring the cooled reaction mixture into excess water, filtering the insoluble product, and washing well with water followed by organic solvents. As expected, sodium 4-fluorobenzenesulfinate gave better yields of PPSO2 than sodium 4-chlorobenzenesulfinate. Under the best conditions (fluorine leaving group, DMSO solvent, 2 mol % initiator, 175 °C for 24 h), the yield of poly(*p*-phenylene sulfone) was quantitative. Much poorer results were obtained when the starting materials and solvent were not purified and dried rigorously.

The efficacy of 4-fluorophenyl sulfone as an initiator was clearly demonstrated by the high yields of polymer obtained in its presence. In its absence, lower and inconsistent yields of 1 were achieved, possibly reflecting variations in the time required to build up a significant quantity of sulfone-activated species. Other activated aromatic halogen (or related[15]) compounds would probably work equally well as initiators, but we did not explore these variations.

DMSO was found to be the best solvent for the polymerization reaction. Sulfolane could also be used, but yields were lower. Attempts to use *N*-methylpyrrolidinone (NMP) led to dark brown, apparently decomposed products. Even under the best conditions, the polymer precipitated during the course of the reaction, and the isolated product was not soluble. Acetone, dichloromethane, chloroform, tetrahydrofuran, *p*-cresol, pyridine, *N,N*-dimethylformamide, dimethyl sulfoxide, and molten diphenyl sulfone (at 200 °C) were tried. Therefore, the attainable molecular weight (see below) of PPSO2 synthesized in this way may be limited by its poor solubility in the reaction medium and could possibly be improved by judicious choice of reaction solvent and conditions.[18]

The high yields obtained in the presence of 4-fluorophenyl sulfone are not consistent with the rather low molecular weights estimated by elemental analysis (see

## Scheme III. Chain Transfer to Polymer via Sulfinate Exchange
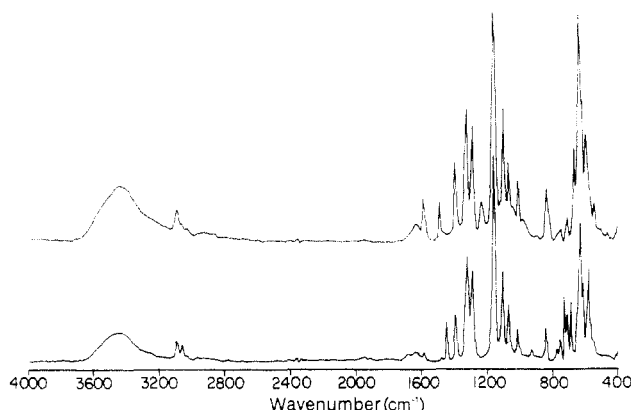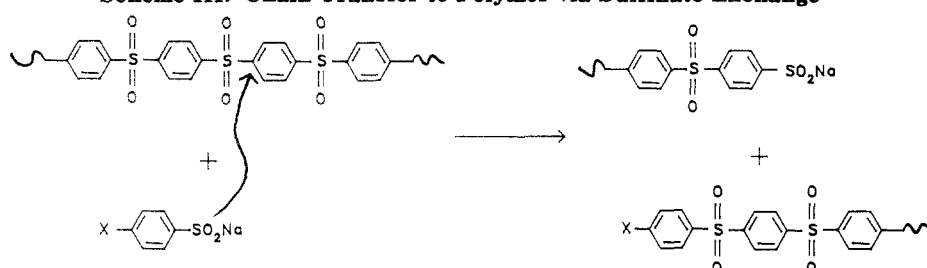
Figure 1. IR spectra of model compound 3 (upper) and poly-(*p*-phenylene sulfone) (1) (lower).

below). (That is, if the reaction proceeded to quantitative yield exclusively according to Path B, the mechanism has elements of living polymerization. A 2 mol % initiator charge would have given a degree of polymerization of 50, which is higher than found.) The actual polymerization mechanism is probably quite complicated. Both Paths A and B may be operating, and, in addition, it is likely that chain transfer to polymer occurs[19] (Scheme III), thereby increasing the number of growing chains.

Apparently the reaction of sodium 4-halobenzenesulfinate with another molecule of itself is very slow. When the two monomers do combine, the dimer that forms is much more reactive (Path A, preferential polymer formation). This process should accelerate as sulfone-activated end groups are formed. The initiator provides a nucleus for polymer growth (Path B) without the induction period caused by the sluggish reaction of two monomers.

Physical Properties and Molecular Weight. Poly-(*p*-phenylene sulfone) was isolated as an off-white powder. Its structure was established by elemental analysis and by comparison of IR and solid-state ^{13}C NMR spectra with those of the model compound 3 (Figures 1 and 2). Clearly, there is good agreement between the spectral features of the polymer and its model.

The molecular weight of the polymer could be estimated from elemental analysis, but the results depend on unproven assumptions concerning the identity of the end groups and polymer purity. Typical fluorine contents for PPSO2 samples prepared from sodium 4-fluorobenzenesulfinate in DMSO were ca. 2.3 wt %. If the polymer is terminated at both ends with 4-fluorophenyl groups, this result corresponds to approximately 11 repeat units. However, if there is only one fluorine atom per chain, only 6 repeat units are required to fit the data. In an attempt to clarify this matter, the residual sodium content of the samples was determined to be ca. 0.5 wt %, a value inconsistent with a significant concentration of sodium sulfinate end groups. It is possible that the residual sodium content is due to occluded NaF in the polymer, in which
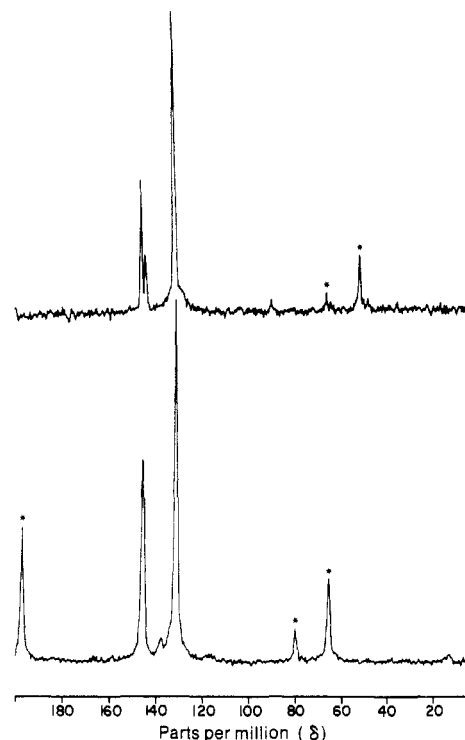
Figure 2. Solid-state (CP-MAS) ^{13}C NMR spectra of model compound 3 (upper) and poly(*p*-phenylene sulfone) (1) (lower). The peaks marked with asterisks are artifacts (spinning sidebands).

case the upper estimate for the degree of polymerization becomes approximately 16.

The positive identification of the end groups in PPSO2 is impractical because of its extreme insolubility. However, the tetramer 3 *is soluble in DMSO*, a fact that supports a considerably higher degree of polymerization for the PPSO2 samples. In addition, a moderately high degree of polymerization is consistent with the CP-MAS ^{13}C NMR results, in which only two distinct carbon atoms were detectable. Signals attributable to end groups were not present.

X-ray powder diffraction (Figure 3) indicated that PPSO2 was highly crystalline (ca. 90%), with only slight diffuse scattering due to amorphous components. Eleven diffraction peaks at angles between 3° and 50° were detected (Table I). This high degree of crystallinity is the likely cause of the poor solubility behavior. The polymer showed no thermal transitions by DSC up to 500 °C, above which point decomposition occurred. The very high melting point of the polymer is not surprising, considering that the model tetramer 3 already melts at 312 °C.

PPSO2 displayed very high and unusual thermal stability when examined by DSC (Figure 4). The onset of decomposition in nitrogen was found to be 517 °C, with a residue of 35% at 1000 °C. The onset of decomposition in air was slightly *higher* (555 °C), although decomposition was much more precipitous and the residue at 1000 °C was, of course, much lower (3%). This effect was repro-
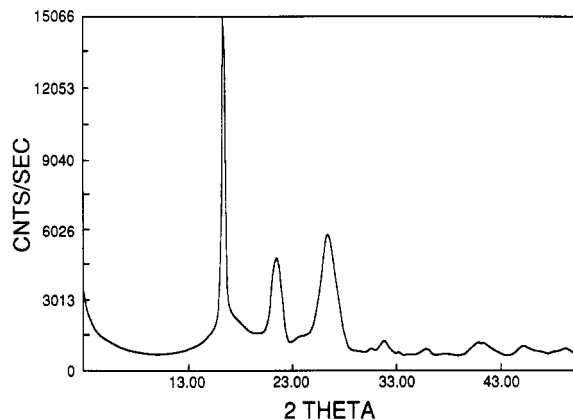
Figure 3. Powder X-ray diffraction pattern from poly(*p*-phenylene sulfone) (1).

Table I. Powder X-ray Diffraction Peaks of Poly(p-phenylene sulfone) (1)[a]

2θ (deg)	d-spacing (Å)	2θ (deg)	d-spacing (Å)
5.74	15.40	35.88	2.503
16.42	5.40	38.00	2.368
21.52	4.13	40.97	2.203
26.47	3.367	45.18	2.007
30.61	2.921	49.23	1.851
31.81	2.813		

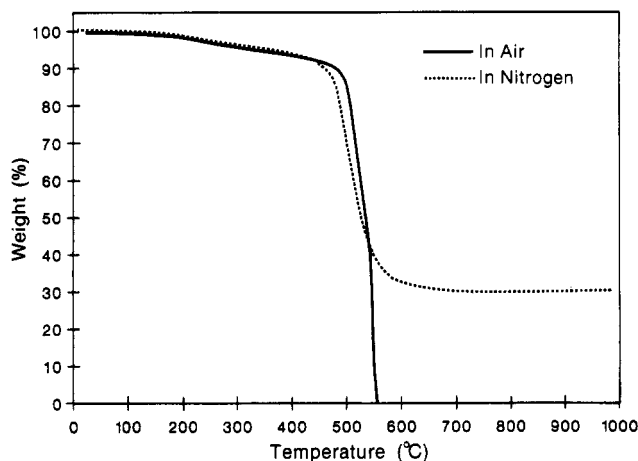[a] Cu Kα radiation. (See Figure 4.)

Figure 4. Thermogravimetric traces of polymer 1 in air (solid line) and in nitrogen (dotted line).

ducible with different batches of 1. The slightly higher decomposition point in air compared to nitrogen may be caused by oxidative cross-linking reactions in the polymer.

The TGA behavior of materials obtained with and without initiator was similar, indicating that essentially the same polymer had formed in both cases.

An attempt to melt-press a pellet of PPSO2 at 300 °C was unsuccessful.

Conclusions

Poly(*p*-phenylene sulfone) has been successfully synthesized for the first time, albeit in only moderate molecular weight. The polymer exhibits extreme thermal stability for a fully organic material, but its possible uses are limited by its intractability.

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