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Synthesis of Aromatic Poly(ether sulfone)s by Nickel-Catalyzed Coupling Polymerization of Aromatic Dichlorides

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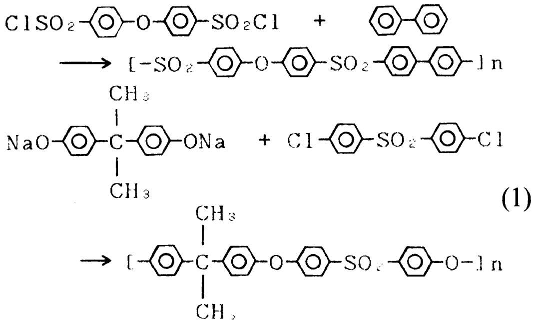
ABSTRACT: Aromatic poly(ether sulfone)s were prepared by the nickel-catalyzed coupling polymerization of aromatic dichlorides containing ether sulfone structures. Polymerizations were carried out in *N*,*N*-dimethylacetamide (DMAc) in the presence of nickel chloride, zinc, triphenylphosphine, and bipyridine and produced aromatic poly(ether sulfone)s with inherent viscosities up to 0.38 dl g^{-1} under mild conditions. The effects of various factors, such as amount of catalyst, ligand, zinc and solvent, reaction temperature, and sonication, were studied. The thermogravimetry of the aromatic poly(ether sulfone)s showed 10% weight loss in air and in nitrogen at 525—565 and 530—570°C, respectively.

KEY WORDS Nickel / Coupling Polymerization / Aromatic Dichloride / Poly(ether sulfone) /

Poly(phenylene ether sulfone)s have been developed into commercial products because of their excellent thermal oxidative stability and mechanical properties. Recently, these polymers have been investigated as thermoplastic matrices in fiber-reiforced composites using glass, carbon, or Kevlar fibers as reinforcement.

A number of synthetic routes for producing poly(phenylene ether sulfone)s have been described in the literatures.[1] They can be prepared by two major methods, by electrophilic (Friedel-Crafts) or aromatic nucleophilic substitution reactions (eq 1).



(1)

The commercially available poly(phenylene ether sulfone)s have been prepared by the both methods.

In the previous paper,[2] we reported a successful synthesis of poly(phenylene either sulfone) by direct polycondensation of sodium 4-phenoxybenzenesulfonate using phosphorus pentoxide methanesulfonic acid (PPMA) as condensing agent and solvent.

A number of routes to the poly(phenylene ether sulfone) stated above are available, but alternative procedures are always of interest. Recently, we showed that nickel-catalyzed coupling polymerization of aryl dichlorides containing ether–ketone structures is a very useful method for the synthesis of aromatic poly(ether ketone)s.[3] In order to expand the preparative utility of this method, it was applied to the synthesis of aromatic poly(ether sulfones)s. Quite recently, the synthesis of aromatic poly(ether sulfone)s by nickel-catalyzed coupling of aryl dichlorides has been reported.[4]

This article describes a successful synthesis of aromatic poly(ether sulfone)s by nickel-catalyzed coupling of aromatic dichlorides containing ether sulfone structures.

EXPERIMENTAL

Materials

Reagent grade anhydrous $NiCl_2$ was dried at 220°C under vacuum. Triphenylphosphine (PPh_3) was purified by recrystallization from hexane. Powdered (400 mesh) zinc was purifies by stirring with acetic acid, filtering, washing throughly with ethyl ether, and drying under vacuum. All slovents such as *N*,*N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrolidone (NMP), and *N*,*N*-dimethylformamide (DMF) were stirred over powdered calcium hydride overnight, then distilled under reduced pressure, and stored over 4-Å molecular sieves.

1,1′-Sulfonylbis[4-(4-chlorophenoxy)benzene] (**3a**)

In a two-necked flask equipped with nitrogen inlet, Dean-stark trap, and a condenser, *p*-chlorophenol (12.8 g, 0.1 mol), K_2CO_3 (16.58 g, 0.12 mol), DMAc (120 ml), and toluene (50 ml) were added. The mixture was refluxed for 48 h. Water was removed azeotropically with toluene. Then, to this mixture, the solution of bis(4-chlorophenyl)sulfone (12.9 g, 0.045 mol) in toluene (30 ml) was added. The mixture was refluxed for 6 h. Upon cooling, the solution was poured into water. The product was filtered, washed with water, and dried. The yield 18.0 g (85%). Recrystallization from water–methanol afforded white needles. mp 134—135°C. IR (KBr): 1320, 1140 (ν SO_2), 1230 cm^{-1} (ν C–O–C). *Anal.* Calcd for $C_{24}H_{16}O_4SCl_2$: C, 61.16%; H, 3.42%. Found: C, 59.98%; H, 3.38%.

1,1′-Sulfonylbis[4-(3-chlorophenoxy)benzene] (**3b**)

This compound was prepared from *m*-chlorophenol and bis(4-chlorophenyl)sulfone as described above. The yield was 18.4 g (87%). Recrystallization from water–methanol gave white needles. mp 127—128°C. IR (KBr): 1320, 1140 (ν SO_2), 1230 cm^{-1} (ν C–O–C). *Anal.* Calcd for $C_{24}H_{16}O_4SCl_2$: C, 61.16%; H, 3.42%. Found: C, 61.24%; H, 3.47%.

1,1′-Oxybis[4-(4-chlorophenylsulfonyl)benzene] (**3c**)

To a mixture of 4,4′-oxydiphenyldisulfonyl chloride (9.1 g, 0.03 mol), chlorobenzene (6.8 g, 0.06 mol) and nitrobenzene (100 ml) in a 500 ml flask equipped with a stirrer and a condenser with a dry tube was slowly added anhydrous ferric chloride (5.0 g, 0.031 mol). The reaction mixture was refluxed for 40 h. The mixture was then distilled with steam to remove nitrobenzene. The residue was extracted with chloroform. The organic solution was dried (Na_2SO_4), and the solvent was removed under reduced pressure. The yield was 6 g (38%). Recrystallization from toluene produced white crystals. mp 210—213°C. IR (KBr): 1320, 1155 (ν SO_2), 1240 cm^{-1} (C–O–C). *Anal.* Calcd for $C_{24}H_{16}O_5SCl_2$: C, 55.50%; H, 3.10%. Found: C, 55.81%; H, 3.17%.

4,4′-Dimesylbiphenyl (**2**)

(4-Chlorophenyl)methyl sulfone (**1**) was prepared by the Friedel-Crafts reaction of methanesulfonyl chloride with chlorobenzene.

In a 25 ml two-necked round bottomed flask were placed $NiCl_2$ (13.0 mg, 0.10 mmol), PPh_3 (262 mg, 1.0 mmol), bipyridine (bpy) (15.6 mg, 0.10 mmol), zinc (200 mg, 3.0 mmol), and I (381 mg, 2.0 mmol). The flask was evacuated and filled with nitrogen three times. Then, dry DMAc (1.5 ml) was added *via* syringe through the serum cap. The mixture was stirred at 90°C for 6 h. The mixture was diluted with NMP (2 ml) and poured into a HCl/methanol solution. The precipitate was washed with methanol and dried. The yield was 0.308 g (99%). Recrystallization from acetophenone yielded white plates. mp 308°C (lit.[5] 302°C). IR (KBr): 1305, 1145 cm^{-1} (ν SO_2). *Anal.* Calcd for $C_{14}H_{14}O_4S_2$: C, 54.17%; H, 4.55%.

Found: C, 54.31%; H, 4.53%.

Polymer Synthesis

A typical example of the polymerization is as follows.

Polymer (**4c**) *from* (**3c**). In a 25 ml two-necked round bottomed flask were placed $NiCl_2$ (3.24 mg, 0.025 mmol), PPh_3 (157 mg, 0.6 mmol), bipyridine (bpy) (3.91 mg, 0.025 mmol), zinc (101 mg, 1.55 mmol), and I (259 mg, 0.5 mmol). The flask was evacuated and filled with nitrogen three times. Then, dry DMAc (0.5 ml) was added *via* syringe through the serum cap. The mixture was stirred at 95°C for 2 h. The resulting viscous mixture was diluted with NMP (2 ml) and poured into a large amount of HCl–methanol (1 : 9). The polymer was collected, washed with methanol and dried *in vacuo* at 80°C for 24 h. The yield was 214 mg (95%). The inherent viscosity of the polymer in NMP was $0.38\,\mathrm{dl\,g^{-1}}$, measured at a concentration of $0.5\,\mathrm{g\,dl^{-1}}$ at 30°C. IR (film): 1320, 1150 (ν SO_2), $1245\,\mathrm{cm^{-1}}$ (ν C–O–C). *Anal.* Calcd for $(C_{24}H_{16}O_5S_2)_n$: C, 64.27%; H, 3.60%. Found: C, 63.89%; H, 3.72%.

Measurement

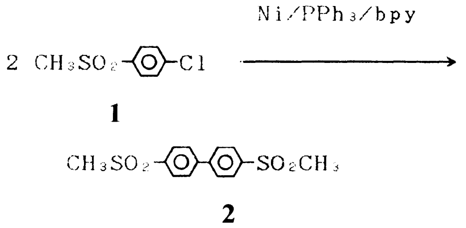
The infrared spectra were recorded on a Hitachi I-5020 FT-IR spectrometer, and the NMR spectra on a Hitachi R-22 (90 MHz) instrument. Thermogravimetry (TGA) and differential thermal analysis (DTA) of powder polymer samples were performed on a Seiko SSS 5000 thermal analyzer at a heating rate $10\,°\mathrm{C\,min^{-1}}$. The glass transition temperature was determined on a Seiko SSS 5000 differential scanning calorimetry (DSC) at a heating rate of $10\,°\mathrm{C\,min^{-1}}$ in nitrogen.

RESULTS AND DISCUSSION

Model Reaction

Detailed reaction conditions for the nickel-catalyzed coupling of aryl chlorides in the presence of reducing metals have examined and coupling products of aryl chlorides with various substituents have also been prepared. The limitations for the aryl chlorides were described, for example, nitro groups completely inhibited the reaction, and acidic substituents, such as phenolic hydroxyl and carboxylic acids, caused reduction to arene.[6] However, no couplings of aryl chlorides with sulfone groups have been reported. Therefore, model compound work was performed to determine if the desired model compounds were formed in quantitative yields to constitute a polymer-forming reaction.

The coupling reaction of (4-chlorophenyl)methyl sulfone (**1**) was studied (eq 1).



(1)

The results are shown in Table I. The reaction proceeded at 90°C and gave 4,4′-dimesylbiphenyl (**2**) quantitatively in the presence of bpy.

Polymer Synthesis

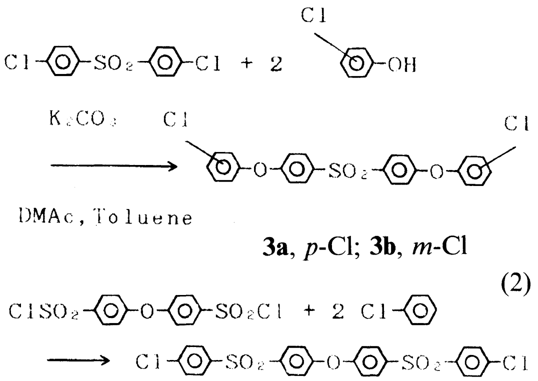
As polymer forming monomers, three aryl dichlorides containing ether–sulfone structures such as 1,1′-sulfonylbis[4-(4-chlorophenoxy)benzene] (**3a**), 1,1′-sulfonylbis[4-(3-chlorophenoxy)benzene (**3b**), and 1,1′-oxybis[4-(4-chlorophenylsulfonyl)benzene] (**3c**) were pre-

Table I. Preparation of 4,4′-dimesylbiphenyl **2**[a]

Reaction conditions			Product **2**
PPh_3/mmol	bpy/mmol	Temp./°C	Yield/%
0.76	—	80	—
0.76	—	80	83
1.0	—	90	85
1.0	0.1	90	99

[a] Reaction conditions: (4-chlorophenyl)methyl sulfone (2.0 mmol), $NiCl_2$ (0.10 mmol), Zn (3.06 mmol), DMAc (1.5 ml), 6 h.

pared by the nucleophilic substitution reaction of bis(4-chlorophenyl) sulfone with chlorophenol and the Friedel-Crafts reaction of 4,4′-oxydiphenyldisulfonyl chloride with chlorobenzene, respectively (eq 2).

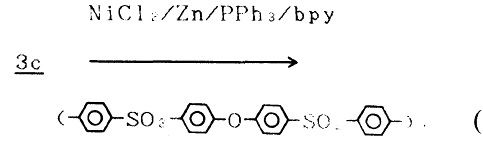


3a, *p*-Cl; **3b**, *m*-Cl

(2)

3c

On the basis of results on the model reaction and the synthesis of poly(ether ketone)s by nickel-catalyzed coupling polymerization of aromatic dichlorides, the polymerization was carried out in DMAc in the presence of zinc, triphenylphosphine, and bipyridine (bpy) (eq 3), in which monomer **3c** was used as electron-withdrawing groups tend to favor the coupling reaction. To determine optimal conditions for polymerization, the following factors that influence the reaction were studied: amount of catalyst, ligand, zinc and solvent, reaction temperature, and sonication.



(3)

(4c)

The influence of reaction temperature on the inherent viscosity of the resulting polymer was examined between 80 and 110°C. The polymerization was found to be highly dependent on temperature and the highest viscosity was attained at 95°C. At a lower temperature of 80°C, the reaction rate was so slow that polymer **4c** remained in low molecular weight. Raising the temperature to 110°C gave inferior results probably due to transfer of aryl groups from triarylphosphine. These results are summarized in Table II.

Table II. Effect of reaction temperature on polymerization[a]

Temperature	Polymer	
(°C)	Yield/%	η_{inh}/dl g^{-1} [b]
80	86	0.03
85	94	0.15
90	99	0.22
95	99	0.30
100	99	0.28
110	4	—

[a] Reaction conditions: monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), TPP (0.3 mmol), Zn (1.55 mmol), bpy (0.025 mmol), DMAc (0.5 ml), 2 h.

[b] Measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C.

Table III. Effect of amount of solvent on polymerizatin[a]

Amount of solvent	Polymer	
ml	Yield/%	η_{inh}/dl g^{-1} [b]
0.4	100	0.26
0.5	99	0.30
0.7	99	0.24
1.0	99	0.22

[a] Reaction conditions: monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), TPP (0.3 mmol), Zn (1.55 mmol), bpy (0.025 mmol), 95°C, 2 h.

[b] Measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C.

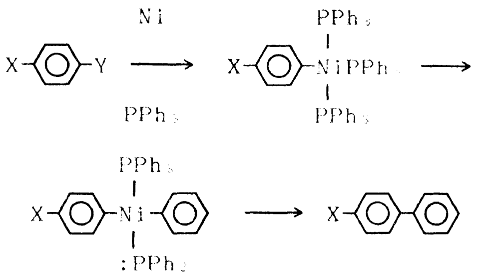
Next, the effect of the amount of solvent on the polymerization was studied (Table III). The amount of DMAc found to be appropriate for the reaction on a 0.5 mmol scale was 0.5 ml.

With consideration of the coupling mechanism in which the methathesis of the arylnickel species I is very slow (eq 4),[6] the minimum amount of Ni catalyst that minimizes the formation of the arylnickel species I after all of the aryl chloride end group of the polymer is consumed is preferable to obtain higher molecular weights of polymer.

$$\underset{\mathrm{I}}{2\mathrm{ArNi^{I}L_3}} \xrightarrow[\text{slow}]{-\mathrm{L}} \overset{\mathrm{Ar}}{\mathrm{ArNi^{II}L_2}} + \mathrm{Ni^{0}L_3} \xrightarrow[\text{fast}]{+\mathrm{L}} \mathrm{Ar\text{-}Ar} + \mathrm{Ni^{0}L_3} \qquad (4)$$

The effect of amount of catalyst on the polymerization where a bpy/$NiCl_2$ ratio was kept constant at 1 : 1, is summarized in Table IV. The inherent viscosity of the polymer reached its highest value with 7 mol% of the catalyst based on the monomer.

One of the main side reaction in the nickel-catalyzed coupling of aryl chlorides is the transfer of aryl groups from triphenylphosphine to metal, which reaction is suppressed by using bipyridine and excess amount of triphenylphosphine to $NiCl_2$ (eq 5).



(5)

The effect of amount of TPP on the polymerization, is shown in Table V. A large excess of TPP was required to obtain higher molecular weights of polymer. This results are quite different from that for the synthesis of poly(ether ketone)s, where 7 times the molar quantity of TPP to $NiCl_2$ was enough to obtain high molecular weights of polymer.

Table IV. Effect of amount of catalyst on polymerization[a]

Reaction conditions	Polymer	
Cat. ($NiCl_2$/bpy = 1) mol/%	Yield/%	η_{inh}/dl g^{-1} [b]
2.0	82	0.08
2.5	92	0.17
5.0	99	0.30
7.0	100	0.32
10.0	98	0.21
15.0	97	0.19

[a] Reaction conditions: monomer (0.5 mmol), TPP (0.3 mmol), Zn (1.55 mmol), DMAc (0.5 ml), 95°C, 2 h.

[b] Measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C.

Table V. Effect of amount of tiphenylphosphine on polymerization[a]

Reaction conditions	Polymer	
PPh_3 mol/%	Yield/%	η_{inh}/dl g^{-1} [b]
0.05	96	0.20
0.1	97	0.21
0.2	98	0.23
0.3	99	0.30
0.4	99	0.37
0.6	98	0.38
0.8	99	0.34

[a] Reaction conditions: monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), Zn (1.55 mmol), bpy (0.025 mmol), DMAc (0.5 ml), 95°C, 2 h.

[b] Measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C.

As the rate-determinig step was reported to be a reduction process involving nickel and zink metal in the presence of excess aryl chloride,[6] the effect of the ratio of zinc to nickel catalyst on the polymerization was investigated. As shown in Table VI, a large excess of zinc was required to obtain higher molecular weights of polymer.

Numerous organometallic reactions are accelerated by ultrasound. It is speculated that the rate enhancement is due not only to reduced particle size but, more importantly, to the sweeping away of reacted species from the metal surface, exposing a fresh surface for reaction.[7] Therefore, the polymerization of **3c** was carried out with sonication (Table VII). No discernible effect on the inherent viscosity

Table IV. Effect of amount of zinc on polymerization[a]

Reaction conditions	Polymer	
Molar ratio of Zinc/$NiCl_2$	Yield/%	η_{inh}/dl g^{-1} [b]
31	96	0.15
62	99	0.30
124	98	0.27

[a] Reaction conditions: monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), TPP (0.6 mmol), bpy (0.025 mmol), DMAc (0.5 ml), 95°C, 2 h.

[b] Measured at a concentration of 0.5 g dl^{-1} in NMP at 30°C.

Table VII. Effect of ultrasonic irradiation on polymerization[a]

Polymerization conditions		Polymer	
Temp/°C	Sonication	Yield/%	η_{inh}/dl g^{-1} [b]
60	on	99	0.19
70	on	98	0.15
80	on	99	0.19
95	on	100	0.19
70	off	—	—
80	off	99	0.13
95	off	98	0.23

[a] Reaction conditions: monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), TPP (0.3 mmol), bpy (0.025 mmol), DMAc (0.5 ml), 2 h.

[b] Measured at a concentration of 0.5 d gl^{-1} in NMP at 30°C.

of the polymer observed, but even at 60°C where the polymerization does not start without using sonication, the polymer with inherent viscosity of 0.19 dl g^{-1} was obtained quantitatively.

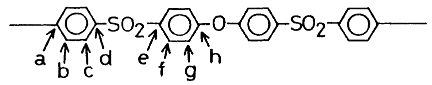
In spite of the detailed studies of conditions for polycondensation, a high molecular weight poly(ether–sulfone) was not obtained. This is probably due to some side reactions, such as the reduction of aryl chlorides to ArH in the presence of acidic substituents or contaminants such as water and the transfer of aryl groups from triphenylphosphine to metal (eq 5).

Table VIII. Preparation of aromatic poly(ether sulfone)s **4**[a]

Monomer	Polymer		
	Type	Yield/%	η_{inh}/dl g^{-1} [b]
3a	**4a**	100	0.26
3b	**4b**	98	0.23
3c	**4c**	98	0.38

[a] Reaction conditions: monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), TPP (0.6 mmol), bpy (0.025 mmol), DMAc (0.5 ml), 95°C, 2 h.

[b] Measured at a concentration of 0.5 d gl^{-1} in NMP at 30°C.



	a	b	c	d	e	f	g	h
1)	142.8	130.0	127.8	140.7	136.0	128.3	119.7	159.1
2)	145.1	127.9	127.4	139.8	135.5	127.5	118.5	160.5

1) Obseved value
2) Calculated value

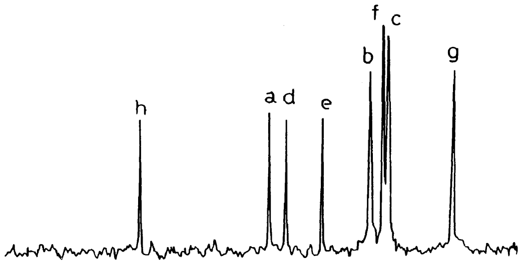


Figure 1. ^{13}C NMR spectra of polymer **4c** in $(CD_3)_2SO$.

Based on these results, various poly(ether sulfone)s **4a**—**4c** were prepared from monomers **3a**—**3c** under the optimal reaction conditions. The results are summarized in Table VIII.

Polymer Characterization

The polymers **4** were confirmed to be the corresponding poly(ether sulfone)s by means of infrared spectroscopy and elemental analysis. The IR spectra exhibited characteristic absorptions at 1320—1325 and 1235—1245 cm^{-1} due to the SO_2 and C–O–C stretching, respectively. Elemental analyses also supported

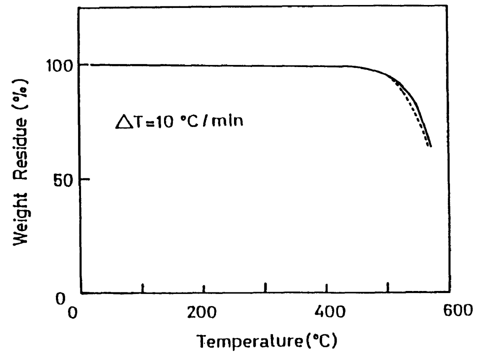


Figure 2. TG curves of polymer **4c** in air (------) and in nitrogen (——).

Table IX. Thermal properties of poly(ether sulfones)s **4**

Polymer	T_g	Decomposition temp/°C	
Type	°C	In air	In nitrogen
4a	190	540	565
4b	142	560	570
4c	269	525	530

the formation of the expected polymers.

The most conclusive spectra evidence for the proposed poly(ether sulfone) structures was provided by ^{13}C NMR. Typical ^{13}C NMR spectrum of polymer **4c** is shown in Figure 1 together with assignments of the observed resonances. The calculated chemical shifts are all within 2 ppm of observed values. No duplication of peaks was found, clearly indicating formation of expected poly(ether sulfone) **4c**.

The poly(ether sulfone)s were white solids. Polymer **4c** was soluble only in strong acids and dipolar aprotic solvents. In contrast, Polymers **4a** and **4b** were soluble even in THF and chloroform at room temperature.

The thermal stability of the polymer was examined by thermogravimetry (TG). A typical trace for polymer **4c** is shown in Figure 2. The polymer showed a 10% weight loss at 530°C in nitrogen and at 525°C in air, respectively. Differential scanning calorimetry on powder showed weak but reproducible endotherms at 269°C, which reflected the glass transition temperature. These data are presented in Table IX. The thermal stability of poly(ether-sulfone)s **4** in nitrogen is much higher than that (around 500°C) of a typical poly(ether–sulfone) probably because of the intoduction of biphenyl unit in the polymer-backbone.

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