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

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ABSTRACT: A facile synthesis of poly(ether ketone)s, which involves the nickel-catalyzed coupling of aromatic dichlorides containing ether–ketone structures in the presence of zinc, triphenylphosphine, and bipyridine, has been developed. Polymerizations proceeded smoothly and produced aromatic poly(ether ketone)s with inherent viscosities of up to 0.87 dL/g under mild conditions. The effects of various factors, such as amount of catalyst and ligand, reaction medium, reaction temperature, and time, were studied. Only low molecular weight polymers from the para-substituted monomers were obtained because of the precipitation of the resulting polymers. The thermogravimetry of the aromatic poly(ether ketone)s showed 10% weight loss both in air and nitrogen at 510–570 °C.

Introduction

Since poly(phenylene ether ether ketone) (PEEK) has shown promise as an excellent engineering plastic due to its good mechanical properties and thermooxidative stability, the synthesis of aromatic poly(ether ketone)s has become of interest in recent years.

A number of synthetic routes for producing poly(ether ketone)s have been described in the literature.[1] They can be prepared in two ways, by electrophilic (Friedel–Crafts) or aromatic nucleophilic substitution reactions. PEEK has been prepared by the latter method. In a preceding paper,[2] we showed a new method for the synthesis of aromatic poly(ether ketone)s of high molecular weight using phosphorus pentoxide/methanesulfonic acid (PPMA) as condensing agent and solvent.

Recently, Colon and Kelsey[3] demonstrated that excellent yields of biaryls can be prepared from aryl chlorides in the presence of a catalytic mixture of nickel salt, triphenylphosphine, and reducing metal. It was thought that this route may constitute another promising poly(ether ketone)-forming reaction. Therefore, the nickel-catalyzed coupling was extended to the polymerization with bifunctional monomers.

Yamamoto et al. reported on the synthesis of polymers by the nickel-catalyzed coupling polymerization of aryl dihalides, that is, poly(*p*-phenylene) from the Grignard reagent of *p*-dibromobenzene[4] and poly(2,5-thienylene) from 2,5-dihalothiophenes in the presence of zinc.[5]

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

Experimental Section

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 purified by stirring with acetic acid, filtering, washing thoroughly with ethyl ether, and drying under vacuum. All solvents such as *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), and hexamethylphosphoramide (HMPA) were stirred over powdered calcium hydride overnight, then distilled under reduced pressure, and stored over 4-Å molecular sieves.

The reagent PPMA was prepared according to the reported procedure.[6] Diphenyl ether was used as received. 1,4-Diphenoxybenzene was prepared by the reaction of phenol with dibromobenzene in the presence of copper. Recrystallization from ethanol yielded white plates, mp 78–79 °C (lit.[7] 77 °C).

1,1′-Oxybis[4-(4-chlorobenzoyl)benzene] (1a). A solution of diphenyl ether (0.68 g, 4 mmol) and *p*-chlorobenzoic acid (1.25 g, 8 mmol) was stirred in PPMA (25 mL) at 60 °C for 6 h. The solution was poured into water and neutralized with sodium carbonate. The product was filtered, washed with water, and dried. Recrystallization from tetrahydrofuran gave white needles: yield 0.73 g (40%); mp 257–259 °C; IR (KBr) 1640 (C=O), 1260 cm^{-1} (C—O—C). Anal. Calcd for $C_{26}H_{16}Cl_2O_3$: C, 69.81; H, 3.61. Found: C, 69.63; H, 3.68.

1,1′-Oxybis[4-(3-chlorobenzoyl)benzene] (1b). This compound was prepared from diphenyl ether and *m*-chlorobenzene acid as described above. Recrystallization from acetone yielded white needles: yield (45%); mp 193–194 °C; IR (KBr) 1640 (C=O), 1260 cm^{-1} (C—O—C). Anal. Calcd for $C_{26}H_{16}Cl_2O_3$: C, 69.81; H, 3.61. Found: C, 69.99; H, 3.64.

1,1′-(*p*-Phenylenedioxy)bis[4-(4-chlorobenzoyl)benzene] (1c). This compound was prepared from 1,4-diphenoxybenzene and *p*-chlorobenzoic acid at room temperature for 60 h in PPMA as described above. Recrystallization from tetrahydrofuran gave white plates: yield (71%); mp 264 °C (by DTA); IR (KBr) 1640 (C=O), 1250 cm^{-1} (C—O—C). Anal. Calcd for $C_{32}H_{20}Cl_2O_4$: C, 71.25; H, 3.75. Found: C, 71.23; H, 3.66.

1,1′-(*p*-Phenylenedioxy)bis[4-(3-chlorobenzoyl)benzene] (1d). This compound was prepared from 1,4-dioxybenzene and *m*-chlorobenzoic acid as described above. Recrystallization from ethyl acetate produced white needles: yield (80%); mp 199–200 °C; IR (KBr) 1640 (C=O), 1250 cm^{-1} (C—O—C). Anal. Calcd for $C_{32}H_{20}Cl_2O_4$: C, 71.25; H, 3.74. Found: C, 71.36; H, 3.79.

Polymer Synthesis. A typical example of the polymerization follows.

Polymer 2d from 1d. In a 50-mL two-necked round-bottomed flask were placed $NiCl_2$ (16.2 mg, 0.125 mmol), PPh_3 (65.6 mg, 0.25 mmol), bipyridine (bpy) (19.5 mg, 0.125 mmol), zinc (506 mg, 7.75 mmol), and monomer **1d** (1.35 g, 2.5 mmol). The flask was evacuated and filled with nitrogen three times. Then, dry DMAc (3.0 mL) was added via syringe through the serum cap. The mixture was stirred at 90 °C for 2.5 h. The mixture became red-brown in 20 min. The resulting viscous mixture was diluted with DMAc (25 mL) and poured into a large amount of HCl/methanol. The polymer was collected, washed with methanol, and dried in vacuo at 80 °C for 10 h. The yield was 1.17 g (100%). The inherent viscosity of the polymer in NMP was 0.87 $dL{\cdot}g^{-1}$, measured at a concentration of 0.5 $g{\cdot}dL^{-1}$ at 30 °C. IR (film) 1650 (C=O), 1230 cm^{-1} (C—O—C). Anal. Calcd for $(C_{32}H_{20}O_4)_n$: C, 82.04; H, 4.30. Found: C, 81.79; H, 4.46.

Measurements. The infrared spectra were recorded on a JASCO IRA-1 spectrophotometer, the NMR spectra on a HITACHI R-24B(60 MHz). Viscosity measurements were carried out

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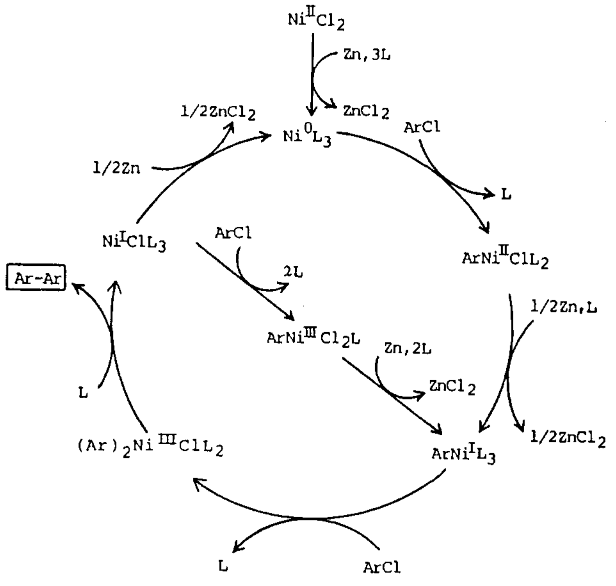
Scheme I

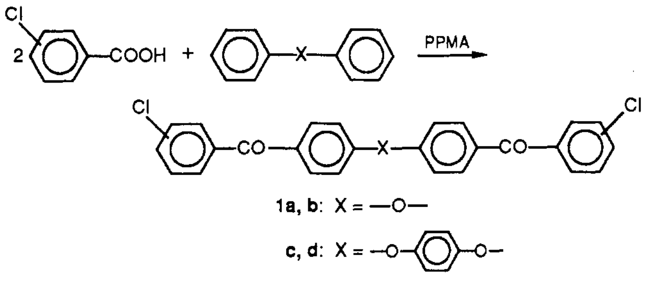


by using an Ubbelohde capillary viscometer at 30 °C. Thermogravimetry (TGA) and differential thermal analysis (DTA) of powder polymer samples were performed with a Seiko SSS 5000 TG/DTA 200 instrument at a heating rate of 10 °C·min^{-1}. Molecular weights were determined by a gel permeation chromatograph (GPC) with polystyrene calibration using a Waters ALC/GPC244 equipped with TSKGH9P, GMH6, Hitachi GL/A-120, A-130 columns at 25 °C in chloroform.

Results and Discussion

Detailed reaction conditions for the nickel-catalyzed coupling of aryl chlorides in the presence of reducing metals have been examined and the probable reaction mechanism has also been proposed as a working model, in which the key step is reduction of an arylnickel species by zinc to an arylnickel complex[3] (Scheme I).

On the basis of these results, we prepared the poly(ether ketone)s. As polymer-forming monomers, four aryl dichlorides containing ether–ketone structures such as 1,1′-oxybis[4-(4-chlorobenzoyl)benzene] (**1a**), 1,1′-oxybis[4-(3-chlorobenzoyl)benzene] (**1b**), 1,1′-(*p*-phenylenedioxy)bis[4-(4-chlorobenzoyl)benzene] (**1c**), and 1,1′-(*p*-phenylenedioxy)bis[4-(3-chlorobenzoyl)benzene] (**1d**) were prepared by the reaction of diaryl ether with chlorobenzoic acid in PPMA. The nickel-catalyzed polymerization was performed with 1 mmol of monomer in DMAc in the presence of zinc, triphenylphosphine, and bipyridine at 80 °C for 20 h to give **2**. The results are listed in Table I.



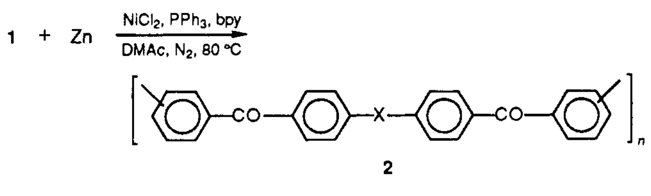


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Table I
Preparation of Aromatic Poly(ether ketone)s 2[a]

	reaction conditions		polymer		
monomer	amt of DMAc, mL	time, h		yield, %	η_{inh},[b] dL·g^{-1}
1a	3	20	**2a**	99	0.09
1b	2	20	**2b**	100	0.50
1c	2	20	**2c**	100	0.11
1d	2	20	**2d**	100	0.36[c]

[a] Monomer (1 mmol), NiCl$_2$ (0.1 mmol), PPh$_3$ (0.3 mmol), Zn (3.1 mmol), bpy (0.1 mmol), 80 °C. [b] Concentration of 0.5 g·dL^{-1} in concentrated sulfuric acid at 30 °C. [c] Concentration of 0.5 g·dL^{-1} in NMP at 30 °C.

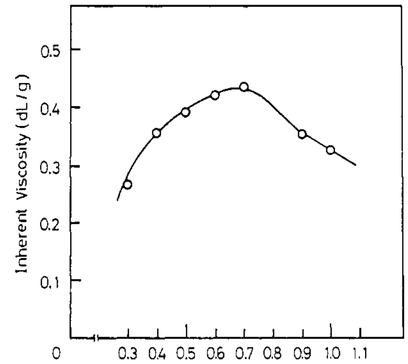


Figure 1. Effect of amount of solvent. Monomer, 0.5 mmol; NiCl$_2$, 0.05 mmol; PPh$_3$, 0.15 mmol; Zn, 1.55 mmol; bpy, 0.05 mmol; 80 °C; 2 h; DMAc.

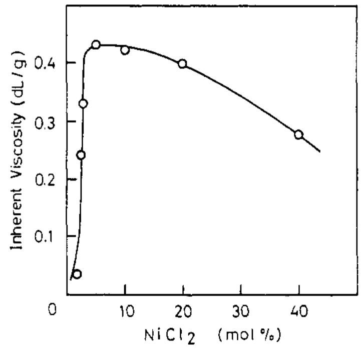
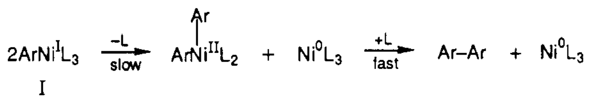


Figure 2. Effect of amount of catalyst. Monomer, 0.5 mmol; PPh$_3$, 0.15 mmol; Zn, 1.55 mmol; bpy, 0.05 mmol; DMAc, 0.6 mL; 80 °C; 2 h.

Scheme II



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

The polymerization of **1a** and **1c** proceeded rapidly with polymer precipitation because of crystalline polymers (Table IV), and that of **1b** proceeded homogeneously and then heterogeneously. On the other hand, monomer **1d** polymerized in a homogeneous state. Although the polymers were isolated in excellent yields, the molecular weights were low to medium.

In order to determine optimal conditions for polymerization, the polymerization of **1d**, which gave soluble polymer in DMAc, was studied in detail. Figure 1 shows the effect of the amount of solvent on the polymerization. The amount of solvent found to be appropriate for the reaction on a 0.5 mmol scale was 0.6–0.7 mL. The effect of amount of catalyst on the polycondensation is shown in Figure 2. The inherent viscosity of the polymer reached its highest value with 5 mol % of the catalyst based on

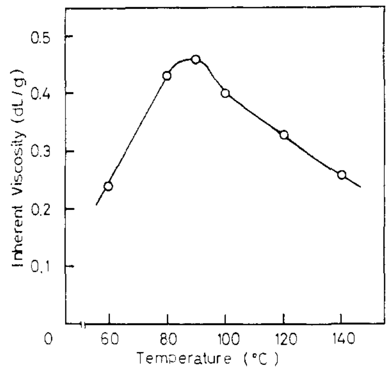


Figure 3. Effect of the reaction temperature on the inherent viscosity of the polymer. Monomer, 0.5 mmol; $NiCl_2$, 0.025 mmol; PPh_3, 0.15 mmol; Zn, 1.55 mmol; bpy, 0.05 mmol; DMAc, 0.6 mL; 2 h.

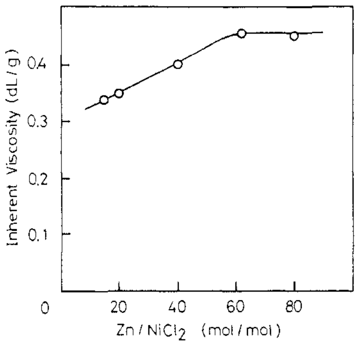


Figure 4. Effect of ratio of zinc to nickel catalyst. Monomer, 0.5 mmol; $NiCl_2$, 0.025 mmol; PPh_3, 0.15 mmol; bpy, 0.05 mmol; DMAc, 0.6 mL; 90 °C; 2 h.

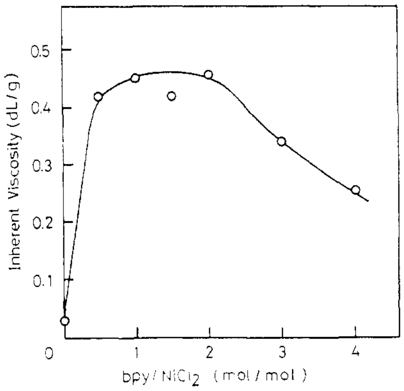


Figure 5. Effect of amount of bipyridine. Monomer, 0.5 mmol; $NiCl_2$, 0.025 mmol; PPh_3, 0.15 mmol; Zn, 1.55 mmol; DMAc, 0.6 mL; 90 °C; 2 h.

the monomer. With consideration of the coupling mechanism in which the metathesis of the arylnickel species I is very slow (Scheme II), 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.

The effect of reaction temperature on the inherent viscosity of the resulting polymer is illustrated in Figure 3. The polycondensation at 90 °C gave polymer with an inherent viscosity at 0.46 $dL{\cdot}g^{-1}$. Raising the temperature to 100–140 °C gave inferior results. As the rate-determining step was reported to be a reduction process involving nickel and zinc metal in the presence of excess aryl chloride, the effect of the ratio of zinc to nickel catalyst on the polymerization was investigated. As shown in Figure 4, a large excess of zinc was required to obtain higher molecular weights of polymer.

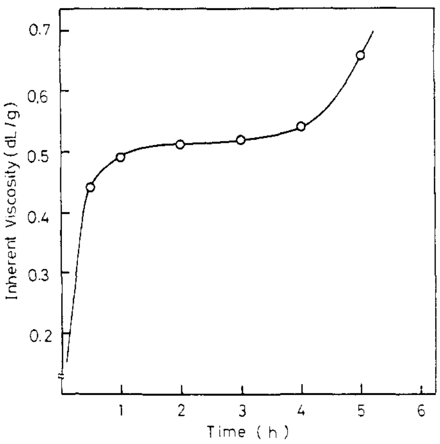


Figure 6. Course of polymerization in terms of the inherent viscosity of the polymer. Monomer, 0.5 mmol; $NiCl_2$, 0.025 mmol; PPh_3, 0.15 mmol; Zn, 1.55 mmol; bpy, 0.025 mmol; DMAc, 0.6 mL; 90 °C.

Table II
Preparation of Poly(ether ketone) 2d in Various Solvents[a]

	polymer	
solvent	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
DMF	100	0.41
DMAc	100	0.45
NMP	100	0.38
HMPA	100	0.25
DMSO	99	0.13

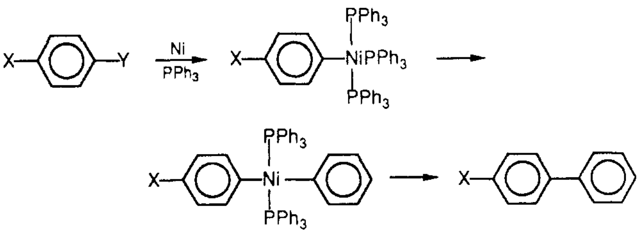
[a] Monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), PPh_3 (0.15 mmol), Zn (1.55 mmol), bpy (0.025 mmol), solvent (0.6 mL), 90 °C, 2 h. [b] Concentration of 0.5 $g{\cdot}dL^{-1}$ in NMP at 30 °C.

Table III
Effect of Ultrasonic Irradiation[a]

	yield, %	η_{inh},[b] $dL{\cdot}g^{-1}$
mech agit	100	0.45
ultrasound	100	0.40

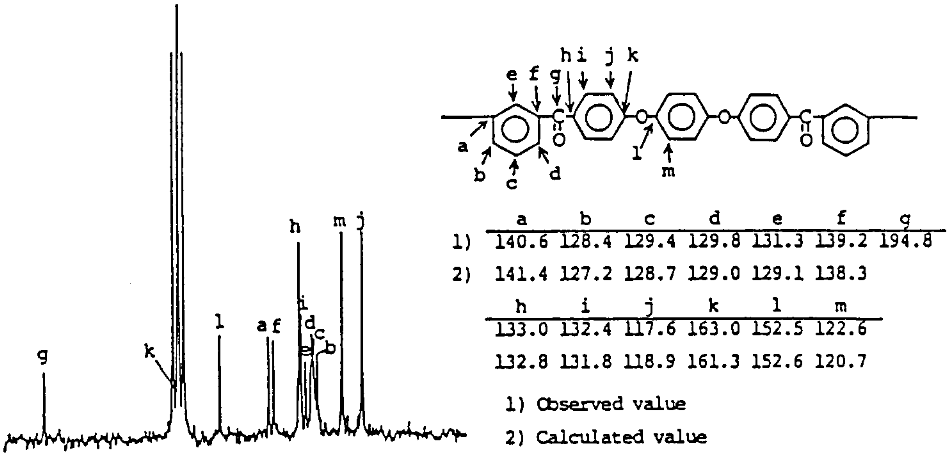
[a] Monomer (0.5 mmol), $NiCl_2$ (0.025 mmol), PPh_3 (0.15 mmol), Zn (1.55 mmol), bpy (0.025 mmol), DMAC (0.6 mL), 90 °C, 2 h. [b] Concentration of 0.5 $g{\cdot}dL^{-1}$ in NMP at 30 °C.

Scheme III



The influence of amount of bipyridine on the polymerization is depicted in Figure 5. A bipyridine/$NiCl_2$ ratio of 1:2 turned out to be effective. Upon addition of a large excess bipyridine to $NiCl_2$ the inherent viscosity of the polymer decreased because of the formation of a stable Ni^0–bipyridine complex, which retarded the oxidative addition of aryl chlorides.

Figure 6 shows the course of the polymerization in terms of inherent viscosity of the resulting polymer. Rapid polymerization occurred in 30 min, followed first by a very slow reaction, and then by an another increase in inherent viscosity. Further polymerization (more than 7 h) gave polymer that contained a few percent of insoluble gel. The concentration of monomer rapidly decreases with the progress of polymerization. After all of the aryl chloride end of polymer is consumed, only arylnickel species I remain at the end of polymerization. The coupling reac-



	a	b	c	d	e	f	g
1)	140.6	128.4	129.4	129.8	131.3	139.2	194.8
2)	141.4	127.2	128.7	129.0	129.1	138.3	

h	i	j	k	l	m
133.0	132.4	117.6	163.0	152.5	122.6
132.8	131.8	118.9	161.3	152.6	120.7

1) Observed value
2) Calculated value

Figure 7. ^{13}C NMR spectrum of polymer **2d** in $CDCl_3$.

Table IV
Preparation of Aromatic Poly(ether ketone)s 2[a]

	reaction conditions		polymer		
monomer (mmol)	amt of DMAc, mL	time, h		yield, %	η_{inh},[b] $dL \cdot g^{-1}$
1a (0.5)	1.5	20	**2a**	100	0.09
1b (0.5)	0.5	2	**2b**	100	0.55
1c (0.5)	2.0	20	**2c**	100	0.11
1d (2.5)	3.0	2.5	**2d**	100	0.87[c]

[a] $NiCl_2$ (0.1 mmol), PPh_3, Zn, bpy, 90 °C. Mole ratio of $NiCl_2$, PPh_3, Zn, and bpy to monomer = 0.05, 0.1, 3.1, and 0.05. [b] Concentration of 0.5 $g \cdot dL^{-1}$ in concentrated sulfuric acid at 30 °C. [c] Concentration of 0.5 $g \cdot dL^{-1}$ in NMP at 30 °C.

Table V
Degree of Polymerization (n) in Polymer 2d

η_{inh}, $dL \cdot g^{-1}$	Cl content,[a] %	n[b]	$10^{-3}M_w$[c]
0.14	0.270	56	26
0.28	0.093	163	76
0.39	0.064	236	111

[a] Chlorine analysis. [b] Calculated from chlorine analyses (Cl at both ends). [c] Polymer **2d**, n was obtained from chlorine analyses.

Table VI
Thermal Properties of Poly(ether ketone)s

			dec temp, °C[a]	
polymer	T_g, °C	T_m, °C	in air	in nitrogen
2a		361	520	530
2b	123		550	560
2c		323	510	520
2d	154		570	570

[a] Temperature at which a 10% weight loss was recorded by TG at a heating rate at 10 $°C \cdot min^{-1}$.

tion of these species is, however, known to be very slow. The polymerization behavior agreed well with that of the nickel-catalyzed coupling of aryl chloride in the presence of excess zinc.[3] Alternatively, this viscosity behavior could be explained in terms of some type of cross-linking. Halide ions, which are effective in the nickel-catalyzed coupling reaction of aryl chlorides, exerted a negligible influence on the polymerization. Table II summarizes the effect of solvent on the inherent viscosity of the polymer. DMF, DMAc, and NMP produced polymers with the highest inherent viscosities.

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. Therefore, the polymerization of **1d** was carried out with sonication but with no discernible effect on the inherent viscosity of the polymer (Table III).

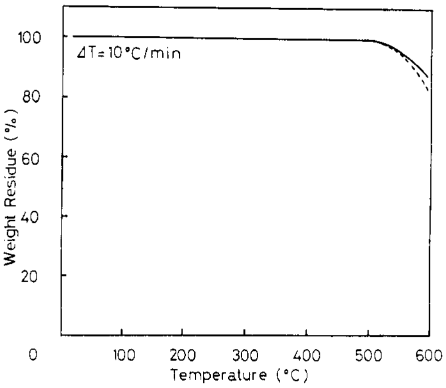


Figure 8. TG curves of polymer **2d**: (- - -) in air, (—) in nitrogen.

It is very important to suppress side reactions in order to improve the molecular weight of polymer. The main side reactions in the nickel-catalyzed coupling of aryl chlorides are 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 (Scheme III). The former side reaction was minimized by using thoroughly dried solvents in which the water content was less than 20 ppm. The latter reaction was also suppressed by using bipyridine and excess amounts of triphenylphosphine to $NiCl_2$, which are very effective for the suppression of this reaction.

The results from the various studies are summarized in Table IV. Poly(ether ketone)s with inherent viscosities up to 0.87 $dL \cdot g^{-1}$ could be obtained.

Polymer Characterization

The polymer were confirmed to be the corresponding poly(ether ketone)s by means of infrared spectroscopy and elemental analysis. The IR spectra exhibited characteristic absorptions at 1650 and 1230 cm^{-1} due to the C=O and C—O—C stretching. Elemental analyses also supported the formation of the expected polymers.

The most conclusive spectral evidence for the proposed poly(ether ketone) structures was provided by ^{13}C NMR. The typical ^{13}C NMR spectrum of polymer **2d** is shown in Figure 7 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 ketone) **2d**.

The poly(ether ketone)s were white solids. The polymers **2a** and **2c** were soluble only in concentrated sulfuric acid and methanesulfonic acid. In contrast, polymers **2b** and **2d** were soluble both in strong acids and in polar aprotic solvents. In particular, polymer **2d** was soluble in haloalkane. A film, cast from the solution of polymer **2d** in dichloromethane shows a high degree of toughness.

The degree of polymerization (n) was calculated from the chlorine analyses (Table V), assuming that both polymer ends have chlorine atoms. This estimation evidently gave higher values for n since it did not consider the side reactions, such as reduction of the aryl chloride ends of the polymers during the polymer-isolation step.[8]

Therefore, the molecular weight of polymer **2d** having an inherent viscosity of 0.87 dL·g^{-1} was determined by means of GPC. The chromatogram indicated that the M_n and M_w values were 28 000 and 140 000, respectively, for standard polystyrene, and the ratio of M_w/M_n was 5.0. Generally, the value of M_w/M_n increases with the extents of reaction and approaches 2 in the limit of large extents of reaction. At this time we cannot explain this large value of 5.

The thermal stability of the polymer was examined by thermogravimetry (TG). A typical trace for polymer **2d** is shown in Figure 8. The polymer showed a 10% weight loss at 570 °C both in air and in nitrogen. Differential scanning calorimetry on powder showed weak but reproducible endotherms at 154 °C, which reflected the glass transition temperature. These data are presented in Table VI.

In summary, our studies indicate that poly(ether ketone)s with high molecular weights can readily be prepared by nickel-catalyzed coupling polymerization of aromatic dichlorides containing ether–ketone structures. This method is advantageous for the formation of poly(ether ketone)s because of the rapidity and simplicity of the reaction and mild conditions compared to conventional methods. The disadvantage of this method is that crystalline poly(ether ketone)s with high molecular weights cannot be prepared because of the limited solubility of the polymers.

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References and Notes

(1) (a) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1096. (b) Colquhoun, H. M.; Lewis, D. F. *Polymer* **1988**, *29*, 1902. (c) Litter, M. I.; Marvel, C. S. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 2205.
(2) Ueda, M.; Sato, M. *Macromolecules* **1987**, *20*, 2675.
(3) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.
(4) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091.
(5) Yamamoto, T.; Osakada, K.; Wakabayashi, T.; Yamamoto, A. *Makromol. Chem. Rapid Commun.* **1985**, *6*, 671.
(6) Eaton, P. E.; Carlson, G. R. *J. Org. Chem.* **1973**, *38*, 4071.
(7) Ullmann, F.; Sponagel, P. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 2211.
(8) Colon, I. *J. Org. Chem.* **1982**, *47*, 2622.

Registry No. **1a**, 63175-37-1; **1a** (homopolymer), 124418-68-4; **1a** (SRU), 124418-76-4; **1b**, 124418-66-2; **1b** (homopolymer), 124418-69-5; **1b** (SRU), 124418-77-5; **1c**, 29924-09-2; **1c** (homopolymer), 124418-70-8; **1c** (SRU), 88099-20-9; **1d**, 124418-67-3; **1d** (homopolymer), 124418-71-9; **1d** (SRU), 124418-75-3; DMF, 68-12-2; DMAc, 127-19-5; NMP, 872-50-4; HMPA, 680-31-9; DMSO, 67-68-5; NiCl$_2$, 7718-54-9; PPh$_3$, 603-35-0; ZN, 7440-66-6; diphenyl ether, 101-84-8; *p*-chlorobenzoic acid, 74-11-3; *m*-chlorobenzoic acid, 535-80-8; 1,4-diphenoxybenzene, 3061-36-7; bipyridine, 37275-48-2.

Oxidative Polymerization of Diphenyl Disulfides with Quinones: Formation of Ultrapure Poly(*p*-phenylene sulfide)s

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ABSTRACT: Poly(*p*-phenylene sulfide)s are prepared through the oxidative polymerization of diphenyl disulfides or thiophenol with quinones at room temperature. The formed polymer is isolated as a white and pure powder having a 1,4-conjugated structure. The oxidative polymerization preferentially proceeds through a novel cationic mechanism. Diphenyl disulfide forms a charge-transfer complex with quinones and is oxidized to a sulfonium cation. The cation electrophilically substitutes on the phenyl ring to yield poly(*p*-phenylene sulfide). Influences of the quinones on this polymerization are discussed in connection with their redox potentials.

Introduction

Poly(*p*-phenylene sulfide) (PPS) is available as an engineering plastic having excellent performances,[1–6] such as high order of moldability, thermal stability, and good electrical characteristics. It is well-known that PPS is commercially produced by polycondensation of *p*-dichlorobenzene with sodium sulfide in *N*-methylpyrrolidone at ca. 200 °C under high pressure.[7–9] Lenz and co-workers have reported[10–16] the preparation of PPS by the poly-

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