

Poly(arylene ether)s via Nitro Displacement Reaction: Synthesis of Poly(biphenylene oxide)s Containing Trifluoromethyl Groups from AB Type Monomers

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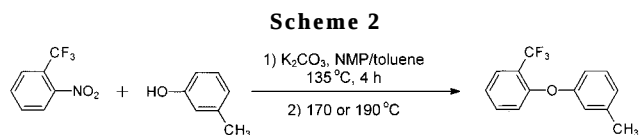
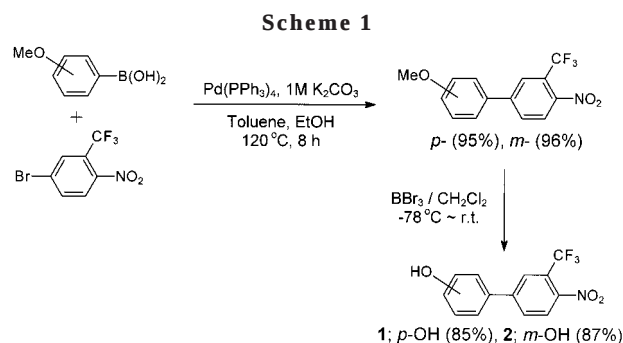
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One of the important classes of the high-performance polymeric materials is poly(arylene ether)s which consist of aromatic rings and ether linkages. These polymers show excellent hydrolytic, thermal, and dimensional stability along with good mechanical properties.¹ A typical example is poly(2,6-dimethylphenylene oxide) (PPO) commercialized by General Electric. It is synthesized by oxidative coupling reaction between carbon and oxygen. A large number of PPO derivatives with various pendent groups instead of methyl groups were prepared, but the structural variation was confined to side groups because of the limitation of the oxidative coupling reaction.² Also, incorporation of electron-withdrawing groups into the polymer main chain has not been accomplished via this route.

Even though poly(biphenylene oxide) (PBPO) can be considered as a class of poly(arylene ether)s and expected to have superior physical properties, high molecular weight PBPOs have not been prepared because of the absence of an appropriate polymerization reaction. It can be prepared from 4-bromo-4-hydroxybiphenyl by Ullmann C–O coupling reaction³ or from 4,4'-dichlorodiphenyl ether or the corresponding dimesylate by nickel coupling reaction, but high molecular weight polymer was not obtained.⁴

Nucleophilic aromatic substitution (S_NAr) reaction is an effective method for the formation of aromatic ether linkages.⁵ Poly(ether sulfone)s, poly(ether ketone)s, and poly(ether imide)s were prepared using the S_NAr reaction and commercialized.⁶

By using S_NAr reaction, appropriate monomers that have electron-withdrawing groups at the ortho position to the leaving group can be polymerized to the corresponding PBPO. In S_NAr reaction, fluorine, chlorine, and nitro groups are typical leaving groups, but a nitro leaving group has not been used frequently in polymerization because of the generation of reactive nitrite ions that cause side reactions at elevated temperature and because of electron-withdrawing characteristics of a nitro group.⁷ However, it is reported that the trifluoromethyl group is an effective activating group for nucleophilic nitro displacement reaction even at relatively high temperature presumably due to inertness of perfluoroalkyl groups to nitrite ions.⁸ Another advantage of perfluoroalkyl activation in S_NAr reaction is that it can be an effective way to incorporate fluorines into the polymer chains, which provides some desirable



properties, such as low dielectric constant, low moisture absorption, and good solubility.⁹

In this study, new PBPOs containing trifluoromethyl groups were prepared from AB type monomers through nucleophilic nitro displacement reaction, and their properties were investigated. In step polymerization, AB type monomers have an inherent stoichiometric balance of the functional groups, and structure regularity of the corresponding polymers is higher than that of the polymers obtained from A–A and B–B type monomers. The monomers, 4'-hydroxy-4-nitro-3-trifluoromethylbiphenyl (**1**) and 3'-isomer (**2**), were prepared as shown in Scheme 1. 5-Bromo-2-nitrobenzotrifluoride was reacted with *p*- and *m*-(methoxyphenyl)boronic acid¹⁰ through Suzuki coupling reaction¹¹ to produce 4'-methoxy-4-nitro-3-trifluoromethylbiphenyl and 3'-isomer, respectively.¹² The methoxy compounds were converted to the corresponding monomers by demethylation with BBr_3 . The total yield of the two steps was over 80%. The monomers were purified by recrystallization from $CHCl_3$ and dried in vacuo for 24 h prior to polymerization. The structure of the synthesized monomers having both the hydroxyl group and the nitro leaving group activated by trifluoromethyl group at the ortho position was confirmed by FTIR, 1H NMR, ^{13}C NMR, and high-resolution mass spectra.¹²

To investigate the feasibility of the polymerization, model reaction was conducted with 2-nitrobenzotrifluoride and *m*-cresol (Scheme 2). An equimolar amount of 2-nitrobenzotrifluoride and *m*-cresol were reacted in the presence of K_2CO_3 in NMP at 170 and 190 °C to obtain 3-methyl-2'-trifluoromethyldiphenyl ether. The model reaction proceeded without any side reactions even at 190 °C. Conversion was complete within 24 and 7 h at 170 and 190 °C, respectively, and the yields were quantitative in both cases. Though it is known that the reactive nitrite ion byproducts cause side reactions at elevated temperature in nitro displacement reaction, the trifluoromethyl group and the ether linkage were stable even at 190 °C.

The successful results of the model reaction prompted us to perform the polymerization at 190 °C. The AB type monomer was polymerized according to the conventional poly(arylene ether) synthesis, with K_2CO_3 as a base in NMP as shown in Scheme 3. The solid content was

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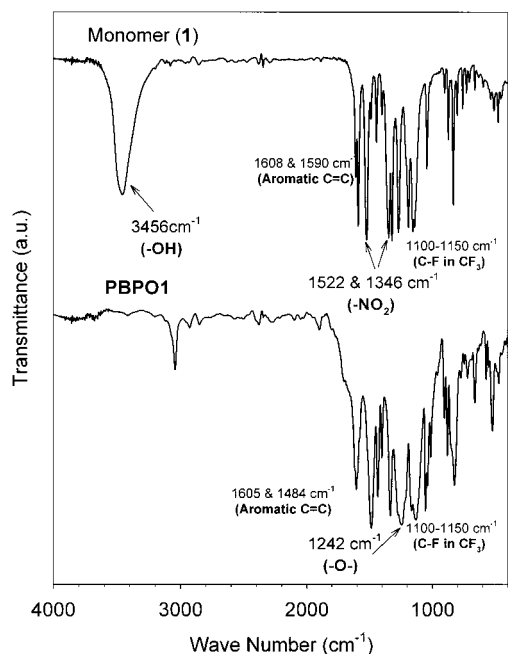
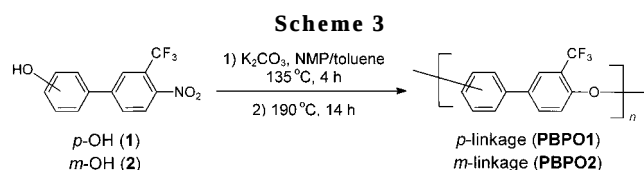


Figure 1. FTIR spectra of monomer **1** (KBr pellet) and polymer PBPO1 (solvent cast thin film).



maintained over 20 w/v %. After 14 h, the pale-yellow polymers were precipitated in water/methanol (v/v = 1/1) mixture and washed with hot water and methanol repeatedly and then dried in vacuo.¹³ The inherent viscosities of PBPO1 and PBPO2 were 0.77 and 0.62 dL/g, respectively. The weight-average molecular weights of the polymers determined by GPC with polystyrene standards were over 80 000 in both cases.

The structures of the polymers were confirmed by FTIR, ¹H NMR, and ¹³C NMR spectroscopy.¹³ FTIR spectra of the monomers showed the broad absorption bands around 3460 cm⁻¹ corresponding to hydroxyl (-OH) stretching and at 1521 and 1347 cm⁻¹ corresponding to nitro (-NO₂) stretching. However, FTIR spectra of the polymers did not show absorption bands corresponding to either group. ¹H NMR spectra of the monomers showed peaks at 9.93 and 9.74 ppm corresponding to the hydroxyl proton of monomers **1** and **2**, respectively, but these peaks disappeared in the spectra of the corresponding polymers. ¹³C NMR spectra showed all expected carbon peaks. The representative FTIR and ¹H NMR spectra of monomer **1** and polymer PBPO1 are shown in Figures 1 and 2, respectively. The high inherent viscosity and absence of detectable hydroxyl and nitro end groups in the ¹H and ¹³C NMR spectra support formation of high molecular weight polymers.

The obtained polymers were quite soluble in polar aprotic solvents, such as NMP and DMSO, and chlorinated solvents, such as chlorobenzene and 1,2-dichlorobenzene, at room temperature. While PBPO1 was slightly soluble in CHCl₃ and THF, PBPO2 dissolved well in these solvents. Transparent, pale-yellow, and flexible films were prepared by solution casting from *N,N*-dimethylacetamide solutions of the polymers.

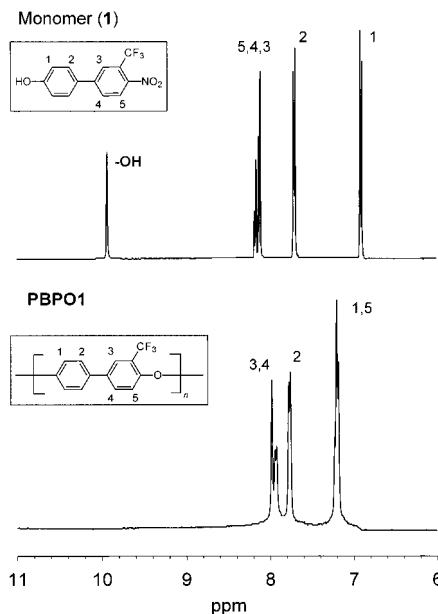


Figure 2. ¹H NMR spectra of monomer **1** (at 25 °C) and polymer PBPO1 (at 100 °C in DMSO-*d*₆).

Table 1. Properties of the Polymers

PBPOs	η_{inh}^a (dL/g)	$M_w^b/10^3$	PDI ^c	T_{d5}^d (°C)			T_g^e (°C)
				in N ₂	in air		
PBPO1	0.77	105.0	2.42	514	466		201
PBPO2	0.62	82.6	2.84	476	421		148

^a Inherent viscosity, measured at a concentration of 0.5 g/dL in DMAc at 30 °C. ^b Determined by GPC using *o*-dichlorobenzene as eluent at 85 °C with polystyrene standards. ^c Polydispersity index = M_w/M_n . ^d 5% weight loss temperature measured by TGA with a heating rate of 10 °C/min. ^e Measured by DSC with a heating rate of 10 °C/min.

Thermal analysis showed that the polymers have high thermal stability as expected for fluoroalkyl-containing poly(arylene ether)s. The physical properties of the polymers are summarized in Table 1. Dynamic TGA showed 5% weight loss temperatures for PBPO1 and PBPO2 at 514 and 476 °C in nitrogen and at 466 and 421 °C in air, respectively. The T_g 's of PBPO1 and PBPO2 measured by DSC were 201 and 148 °C, respectively. The T_g of PBPO1 approaches that of PPO (210 °C) even though it has one pendent group near the ether linkage.

In conclusion, new high molecular weight poly(biphenylene oxide)s were prepared from the AB type monomers through a trifluoromethyl-activated nitro displacement reaction. The resulting polymers were amorphous, dissolved easily in polar aprotic solvents and chlorinated solvents, and showed good thermal properties. By using nucleophilic nitro displacement reaction and properly designed AB type monomers, synthesis of a series of poly(biphenylene oxide)s with other functional groups is in progress.

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- (12) Spectral data of monomers **1** and **2**. 4'-Hydroxy-4-nitro-3-trifluoromethylbiphenyl (**1**): mp 130–131 °C. FTIR (KBr, cm^{-1}): 3456 (O–H); 1608, 1590 (aromatic C=C); 1522, 1346 (NO_2); 1150–1100 (C–F). ^1H NMR ($\text{DMSO}-d_6$, 400.13 MHz, ppm): 9.93 (s, –OH); 8.17 (d, 1H, $J = 8.64$ Hz); 8.11 (dd, 1H, $J = 8.71$ Hz, $J = 1.88$ Hz); 8.10 (s, 1H); 7.71, 7.69, 6.92, 6.90 (dd, 4H). ^{13}C NMR ($\text{DMSO}-d_6$, 100.62 MHz, ppm): 159.01, 145.18, 145.16, 130.65, 128.87, 127.08, 126.39, 124.78 (q, $J = 5.20$ Hz), 122.27 (q, $J = 32.8$ Hz), 122.18 (q, $J = 271.9$ Hz), 116.11. HRMS (m/e): calcd for $\text{C}_{13}\text{H}_8\text{NO}_3\text{F}_3$, 283.045 63; found 283.045 66. 3'-Hydroxy-4-nitro-3-trifluoromethylbiphenyl (**2**): mp 145–146 °C. FTIR (KBr, cm^{-1}): 3458 (O–H); 1607, 1582 (aromatic C=C); 1521, 1347 (NO_2); 1160–1110 (C–F). ^1H NMR ($\text{DMSO}-d_6$, 400.13 MHz, ppm): 9.74 (s, –OH); 8.19 (d, 1H, $J = 8.40$ Hz); 8.13 (dd, 1H, $J = 8.48$ Hz, $J = 1.86$ Hz); 8.11 (s, 1H); 7.32 (t, 1H, $J = 7.85$ Hz); 7.21 (d, 1H, $J = 8.40$ Hz); 7.15 (m, 1H), 6.90 (dd, 1H, $J = 8.41$ Hz, $J = 1.93$ Hz). ^{13}C NMR ($\text{DMSO}-d_6$, 100.62 MHz, ppm): 158.09, 146.11, 145.24, 138.00, 131.94, 130.37, 126.29, 125.84 (q, $J = 5.20$ Hz), 122.14 (q, $J = 32.9$ Hz), 122.10 (q, $J = 271.5$ Hz), 118.13, 116.45, 114.14. HRMS (m/e): calcd for $\text{C}_{13}\text{H}_8\text{NO}_3\text{F}_3$, 283.045 63; found 283.045 68.
- (13) All polymerizations were conducted in deoxygenated dry NMP under dry argon atmosphere. PBPO1: A 25 mL three-necked flask equipped with an argon inlet, mechanical stirrer, Dean–Stark trap, and condenser was charged with 1.822 g (6.434 mmol) of **1**, 1.334 g (9.652 mmol) of K_2CO_3 , 8 mL of NMP, and 5 mL of toluene. The reaction mixture was heated to 135 °C for 4 h at which time the toluene was brought to reflux. The toluene was periodically removed from the Dean–Stark trap, and fresh dry toluene was added to the reaction mixture to ensure phenoxide generation and dehydration of the system. The temperature was raised to 190 °C, and the reaction mixture was allowed to react for 14 h. The polymer was precipitated into a 400 mL of vigorously stirred methanol/water (v/v = 1/1) mixture and then filtered. The precipitated polymer was washed with hot water and methanol repeatedly and dried in vacuo at 100 °C for 24 h (1.495 g, 98.4% yield). Further purification was carried out by dissolving the polymers in *N,N*-dimethylacetamide, filtering the polymer solution, and then precipitating it into methanol. FTIR (thin film, cm^{-1}): 3042 (aromatic C–H); 1605, 1484 (aromatic C=C); 1242 (C–O–C); 1150–1100 (C–F). ^1H NMR ($\text{DMSO}-d_6$, 400.13 MHz, 100 °C, ppm): 7.97 (s, 1H); 7.93 (d, 1H, $J = 8.32$ Hz); 7.21 (d, 1H, 8.81 Hz); 7.77, 7.75, 7.20, 7.18 (dd, 4H). ^{13}C NMR ($\text{DMSO}-d_6$, 100.62 MHz, 100 °C, ppm): 155.68, 152.96, 134.80, 133.79, 131.67, 128.03, 124.53 (q, $J = 4.80$ Hz), 122.80 (q, $J = 271.0$ Hz), 120.25 (q, $J = 30.5$ Hz), 120.01, 118.60. PBPO2: The same procedure was used as for PBPO1 with 1.621 g (5.724 mmol) of **2**, 1.187 g (8.588 mmol) of K_2CO_3 , and 6 mL of NMP (1.343 g, 99.3% yield). FTIR (thin film, cm^{-1}): 3038 (aromatic C–H); 1604, 1486 (aromatic C=C); 1250 (C–O–C); 1160–1110 (C–F). ^1H NMR ($\text{DMSO}-d_6$, 400.13 MHz, 100 °C, ppm): 7.95 (1H); 7.86 (1H); 7.51 (2H); 7.39 (1H); 7.16 (1H); 7.05 (1H). ^{13}C NMR ($\text{DMSO}-d_6$, 100.62 MHz, 100 °C, ppm): 156.05, 154.67, 140.04, 134.28, 131.91, 130.20, 124.83 (q, $J = 4.93$ Hz), 122.23, 120.03 (q, $J = 30.9$ Hz), 122.75 (q, $J = 272.2$ Hz), 119.51, 117.59, 116.78.

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