Synthesis of Poly(phenylene oxide) Containing Trifluoromethyl Groups via Selective and Sequential Nucleophilic Aromatic Substitution Reaction

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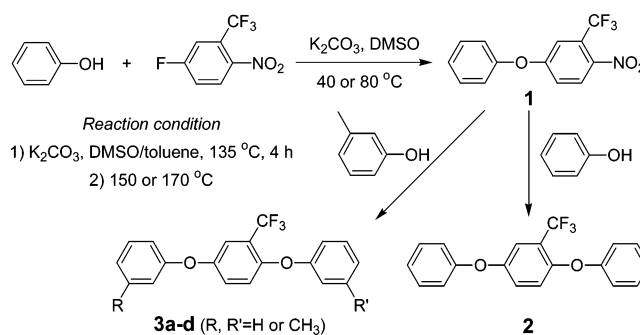
The nucleophilic aromatic substitution reaction (S$_N$Ar) has been known as a very effective one for the formation of aromatic ether groups and utilized in the synthesis of many organic and polymeric compounds.[1] The S$_N$Ar reaction generally requires a leaving group activated with an electron-withdrawing group at the ortho or para position. Typical leaving groups are fluorine, chlorine, and nitro groups. The fluorine leaving group shows good reactivity due to its small size and high electronegativity. A properly activated nitro group is also displaced readily, but it produces a reactive nitrite ion as a byproduct which causes side reactions at elevated temperature.[2] However, trifluoromethyl groups act as an effective activating group for the nucleophilic nitro displacement reaction at relatively high temperature (190 °C) due to the inertness of perfluoroalkyl groups to the nitrite ions.[3] Interestingly, the meta-activated nitro leaving group with CF$_3$ group undergoes the S$_N$Ar reaction.[4] The above structural requirements for the S$_N$Ar reaction put a limitation of this reaction in the synthesis of the compounds with two ether linkages on the same aromatic ring. For example, poly(phenylene oxide) (PPO) consisting of benzene rings and para-linked ether groups[5] requires a monomer with two electron-withdrawing groups[6a] or a reactive initiator with an AB type monomer.[6b] Oxidative coupling[7] or the Ullman coupling reaction[8] is another feasible way to obtain para-linked PPO, but the structural variation through oxidative coupling reaction is limited. 2,6-Disubstituted phenol must be used to obtain a linear polymer, and the incorporation of electron-withdrawing substituents into the polymer main chain is difficult due to the high oxidation potential of the corresponding phenolic monomers, even though the regioselective oxidative polymerization of phenoxyphenol and 2,6-difluorophenol with the peroxo dicopper complex has been reported recently.[9]

In this communication, we report the selective and sequential nucleophilic aromatic substitution reaction and its utilization in the synthesis of poly(phenylene oxide) containing pendent trifluoromethyl groups from AA and BC type monomers. The BC type monomer has the fluorine leaving group activated by the nitro group at the para position and the nitro leaving group activated by the trifluoromethyl group at the ortho position. Another advantage of the CF$_3$ activating group is that the incorporation of fluorines into the polymer chain provides some desirable properties such as low dielectric constant, low moisture absorption, and good solubility.[10]

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Scheme 1. Selective and Sequential Displacement of the Fluorine and the Nitro Group of 5-Fluoro-2-nitrobenzotrifluoride
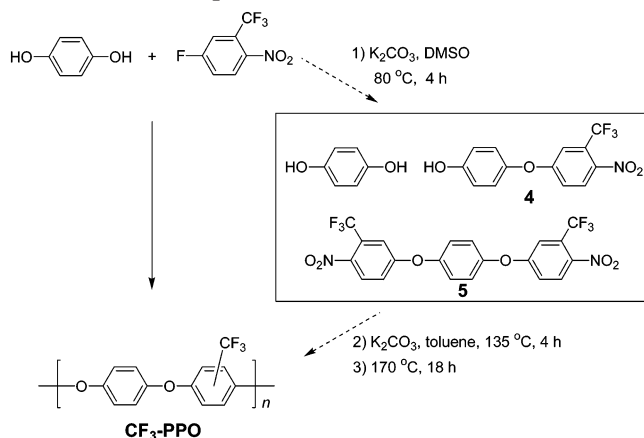

To investigate the feasibility of selective and sequential displacement of the fluorine and the nitro leaving group of 5-fluoro-2-nitrobenzotrifluoride, model reactions were carried out at various reaction conditions as shown in Scheme 1. The reaction with phenol in the presence of K$_2$CO$_3$ in dimethyl sulfoxide (DMSO) quantitatively produced 4-nitro-3-trifluoromethyldiphenyl ether (**1**) without any side reactions. The reaction was complete within 12 h at 40 °C and 4 h at 80 °C. The model reaction indicates that the nitro group is not displaced with phenol below 100 °C, which is essential for polycondensation because the fluorine group cannot be displaced after the displacement of the nitro group. The nitro group acts not only as a leaving group but also as an activating group. The nitro displacement reaction of **1** with phenol was conducted in the presence of K$_2$CO$_3$ in DMSO/toluene at 150 or 170 °C. Despite the electron-donating phenoxy group at the para position to the nitro leaving group, conversion was complete within 4 h at 150 °C and 1 h at 170 °C. Steric congestion between the bulky trifluoromethyl group and the nitro leaving group facilitates the formation of a stable Meisenheimer complex with release of steric strain.[11] The above model reaction results reveal that the selective and sequential displacement of the fluorine and the nitro group of 5-fluoro-2-nitrobenzotrifluoride is feasible at proper reaction conditions.
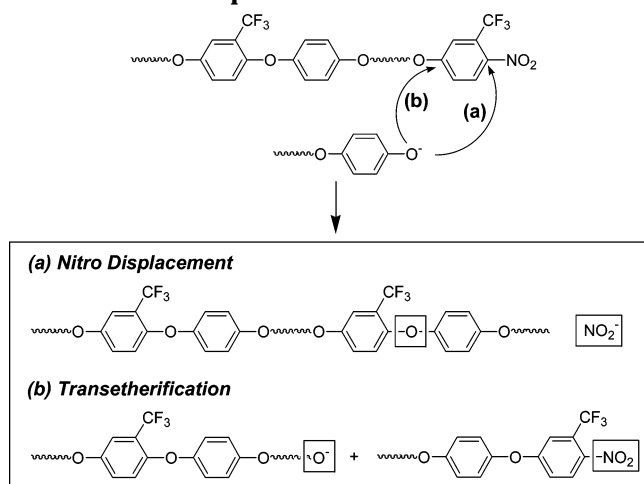
However, during the displacement of the nitro group of **1**, transetherification is expected to occur. The model reaction of **1** with *m*-cresol at 150 and 170 °C produced a mixture of four compounds (**3a−d**: R = R′ = H; R = R′ = CH$_3$; R = H, R′ = CH$_3$; R = CH$_3$, R′ = H) despite complete conversion. It seems that the electron-withdrawing nitro group is strong enough to make the ether linkage susceptible for the nucleophile. The results of model reactions were confirmed by spectroscopic data.[12]

On the basis of the results of the model reactions, synthesis of a new poly(phenylene oxide) containing pendent trifluoromethyl groups (CF$_3$-PPO) was attempted by nucleophilic aromatic substitution of 5-fluoro-2-nitrobenzotrifluoride with hydroquinone, as shown in Scheme 2. The polymerization was carried out via the one-pot method, but in a sequential manner—the selective fluorine displacement followed by the nitro displacement. Fluorine displacement of 5-fluoro-2-nitrobenzotrifluoride with hydroquinone in the presence of K$_2$CO$_3$ in DMSO at 80 °C for 4 h gave three kinds of intermediates[13] that were subjected to the nitro displacement reaction at 170 °C for 18 h to give the off-

Scheme 2. Synthesis of High Molecular Weight Poly(phenylene oxide) (CF$_3$-PPO) via Selective and Sequential S$_N$Ar Reaction

Scheme 3. Transetherification during the Nitro Displacement Reaction

white polymer. The weight-average molecular weight of the polymer determined by GPC with polystyrene standards was 32.1K, and the polydispersity index was 2.01. To our knowledge, this is the first example of successful synthesis of high molecular weight poly-(phenylene oxide) via the selective and sequential nucleophilic aromatic substitution reaction.

It seems that the cleavage of aryl ether bonds by the phenoxide ions (transetherification) occurs mainly at the polymer chain ends, where the ether linkages are activated by the strong electron-withdrawing nitro group at the para position. Therefore, the transetherification and the nitro displacement are competitive at the polymer chain end, as shown in Scheme 3. Nitro displacement at the chain end leads to the growth of polymer chain, while transetherification at the same position leads to the ether exchange, which generates another reactive oligomeric phenoxide. However, the equimolar ratio of two kinds of functional groups is maintained, and formation of high molecular weight polymer is feasible.

The structure of the synthesized polymer was confirmed by spectroscopic data.[12] The FTIR spectrum of CF$_3$-PPO showed characteristic absorption bands of aromatic ether at 1200 cm^{-1} and C−F stretching at 1134 cm^{-1}. However, it did not show any absorption band corresponding to nitro stretching. The ^{1}H NMR spectrum of CF$_3$-PPO was consistent with its structure.

While the ^{1}H NMR spectrum of CF$_3$-PPO did not show any peaks corresponding to the proton of nitro-substituted benzene ring, it showed the peaks around 6.9 ppm corresponding to the proton of terminal hydroquinone, indicating the existence of hydroxyl end group in both chain ends. The ^{13}C NMR spectrum of CF$_3$-PPO showed all expected 13 carbon peaks. It has the structure with randomly arranged trifluoromethyl groups because of the formation of three kinds of intermediates during the fluorine displacement reaction and transetherification in the nitro displacement reaction. As a result, three regioisomeric units, head-to-head, tail-to-tail, and head-to-tail placements, exist in the polymer backbone, and these local environments were reflected in the ^{13}C NMR resonance of the hydroquinone moiety.[13]

CF$_3$-PPO, having inherent viscosity of 0.32 dL/g, showed good solubility in common organic solvents, such as acetone, toluene, THF, chlorobenzene, and CHCl$_3$ as well as polar aprotic solvents (NMP, DMAc, and DMSO). The thermal stability of the polymer is similar to those of fluoroalkyl-containing poly(arylene ether)s. The glass transition temperature (T_g) of CF$_3$-PPO measured by DSC was 108 °C, which was slightly higher than the literature value (ca. 95 °C) of poly(1,4-phenylene oxide). The 5% weight loss temperature of CF$_3$-PPO measured by TGA was 529 °C in nitrogen and 499 °C in air.

In summary, a new poly(phenylene oxide) containing pendent trifluoromethyl groups (CF$_3$-PPO) was synthesized by the S$_N$Ar reaction of 5-fluoro-2-nitrobenzotrifluoride with hydroquinone. The polymerization was carried out in a sequential and selective manner based on the preferential fluorine displacement reaction followed by the nitro displacement reaction.

Supporting Information Available: Details of the experimental procedures, the spectral data for all of the new compounds, FTIR spectra, NMR spectra, TGA, and DSC thermograms of the synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. (b) Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: Amsterdam, 1968. (c) Bartoli, G.; Todesco, P. E. *Acc. Chem. Res.* **1977**, *10*, 125. (d) Terrier, F. In *Nucleophilic Aromatic Displacement: The Influence of the Nitro Group*; VCH Publishers: New York, 1991. (e) Cotter, R. J. *Engineering Plastics: A Handbook of Polyarylethers*; Gordon and Breach Publishers: Amsterdam, 1995; p 1. (f) Labadie, J. W.; Hedrick, J. L.; Ueda, M. In *Step-Growth Polymers for High-Performance Materials, New Synthetic Methods*; Hedrick, J. L., Labadie, J. W., Eds.; ACS Symposium Series 624; American Chemical Society: Washington, DC, 1996; p 210. (g) Theil, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 2345.

(2) (a) Williams, F. J.; Donahue, P. E. *J. Org. Chem.* **1977**, *42*, 3414. (b) Markezich, R. L.; Zamek, O. S. *J. Org. Chem.* **1977**, *42*, 3431. (c) Markezich, R. L.; Zamek, O. S.; Donahue, P. E.; Williams, F. J. *J. Org. Chem.* **1977**, *42*, 3435. (d) Takekoshi, T.; Wirth, J. G.; Heath, D. R.; Kochanowski, J. E.; Manello, J. S.; Webber, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3069. (e) Takekoshi, T. *Polym. J.* **1987**, *19*, 191. (f) In, I. S.; Eom, H. J.; Kim, S. Y. *Polymer (Korea)* **1998**, *22*, 544.

(3) Chung, I. S.; Kim, S. Y. *Macromolecules* **2000**, *33*, 9474.

(4) Chung, I. S.; Kim, S. Y. *J. Am. Chem. Soc.* **2001**, *123*, 11071.

(5) Meta-linked poly(phenylene oxide) with cyano or benzoyl groups was prepared by the S_NAr reaction. See: (a) Kricheldorf, H. R.; Meier, J.; Schwarz, G. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 529. (b) Kricheldorf, H. R.; Delius, U. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 41.

(6) (a) Konno, K.; Deguchi, N.; Yonetake, K.; Ueda, M.; Cassidy, P. E.; Fitch, J. W. *J. Polym. Sci., Polym. Chem. Ed.* **1997**, *35*, 605. (b) Yokozawa, T.; Suzuki, Y.; Hiraoka, S. *J. Am. Chem. Soc.* **2001**, *123*, 9902.

(7) (a) Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustance, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 6335. (b) Hay, A. S. *J. Polym. Sci., Polym. Chem. Ed.* **1998**, *36*, 505.

(8) (a) van Dort, H. M.; Hoefs, C. A. M.; Magre, E. P.; Schopf, A. J.; Yntema, K. *Eur. Polym. J.* **1968**, *4*, 275. (b) Stammatoff, G. S. U.S. Patent 3228910, 1966. (c) Jurek, M. J.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (1), 180.

(9) (a) Higashimura, H.; Fujisawa, K.; Moro-oka, Y.; Kubota, M.; Shiga, A.; Terahara, A.; Uyama, H.; Kobayashi, S. *J. Am. Chem. Soc.* **1998**, *120*, 8529. (b) Ikeda, R.; Tanaka, H.; Uyama, H.; Kobayashi, S. *Macromolecules* **2000**, *33*, 6648. (c) Oyaizu, K.; Kumaki, Y.; Saito, K.; Tsuchida, E. *Macromolecules* **2000**, *33*, 5766.

(10) (a) Tullos, G. L.; Cassidy, P. E. *Macromolecules* **1991**, *24*, 6059. (b) Bruma, M.; Fitch, J. W.; Cassidy, P. E. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1996**, *C36*, 119. (c) Hougham, G. In *Fluoropolymers*; Hougham, G. et al., Eds.; Plenum Press: New York, 1999; p 233. (d) Chung, I. S.; Kim, S. Y. *Macromolecules* **2000**, *33*, 3190. (e) Chung, I. S.; Park, C. E.; Ree, M.; Kim, S. Y. *Chem. Mater.* **2001**, *13*, 2801.

(11) (a) Carter, K. R.; Kim, S. Y.; Labadie, J. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (1), 415. (b) Park, S. K.; Kim, S. Y. *Macromolecules* **1998**, *31*, 3385.

(12) The detailed synthetic procedure and the spectroscopic data of the synthesized compounds are in the Supporting Information.

(13) While the ratio of the intermediate **4** and **5** (Scheme 2) is 93:7, the ratio of three regioisomeric units (H-H, T-T, and H-T placements) in the synthesized polymer is about 25:25:50 due to the transetherification during the polymerization.