

Meta-Activated Nucleophilic Aromatic Substitution Reaction: Poly(biphenylene oxide)s with Trifluoromethyl Pendent Groups via Nitro Displacement

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An aromatic ether linkage is found in many natural and synthetic products including poly(arylene ether)s, one of important high-performance engineering plastics. Among the various reactions that produce an aromatic ether linkage, the nucleophilic aromatic substitution (S_NAr) reaction is a very effective method even though it requires some structural features, a leaving group activated with an electron-withdrawing group.¹ Sulfone, ketone, and imide groups are known as effective activating groups for the S_NAr reaction, and poly(ether sulfone)s, poly(ether ketone)s, and poly(ether imide)s have been successfully commercialized using this reaction.^{2,3} Various heterocyclic rings⁴ and other electron-withdrawing groups⁵ have been used as an activating group to produce high-molecular weight poly(arylene ether)s.

In the S_NAr reaction, the activating group at the ortho or para position to the living group is necessary to stabilize the negative charges developed during the reaction (Meisenheimer complex). Even though there are a few examples of the meta-activated S_NAr reaction,⁶ they are not suitable for the synthesis of linear high-molecular weight polymers through polycondensation.⁷ Generally,

the activating group at the ortho or para position is required to obtain high-molecular weight polymers.

Recently, it is reported that perfluoroalkyl groups including trifluoromethyl groups at the ortho or para position activate fluoro or nitro groups for displacement by phenoxides.⁸ The steric congestion due to bulky trifluoromethyl group at the ortho position of the nitro-leaving group facilitates the formation of a Meisenheimer complex with release of steric strain.⁹ Another advantage of perfluoroalkyl activation in the S_NAr reaction is that it is 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.^{2d–e,10}

In our previous work,¹¹ we have found that trifluoromethyl groups and ether linkages are stable in the nitro displacement reaction even at 190 °C, and the displacement reaction occurs quantitatively without any side reactions which are frequently observed during nucleophilic nitro displacement reaction at high temperature due to the reactive nitrite ion byproduct.¹² In this communication, we report the first successful synthesis of poly-(biphenylene oxide)s with pendent trifluoromethyl groups through the meta-activated nucleophilic nitro displacement reaction.

To investigate the feasibility of the meta-activated nitro displacement as a polymer-forming reaction, model reactions were conducted with 4-nitro-2-trifluoromethylbiphenyl (**1**) and various phenol derivatives as shown in Scheme 1. First, an equimolar amount of **1** and 4-*tert*-butylphenol were reacted in the presence of K_2CO_3 in NMP at 175 °C. Surprisingly, conversion was completed within 12 h without any side reactions and even within 30 min at 190 °C. The yields were quantitative in both cases. To examine the effect of the nucleophilicity of the phenoxide, **1** was reacted with phenol and 4-nitrophenol by taking the same procedure. Again, conversion was completed within 1 h with phenol and 4 h with 4-nitrophenol at 190 °C, respectively.¹³

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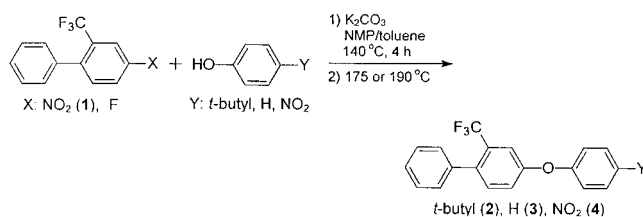
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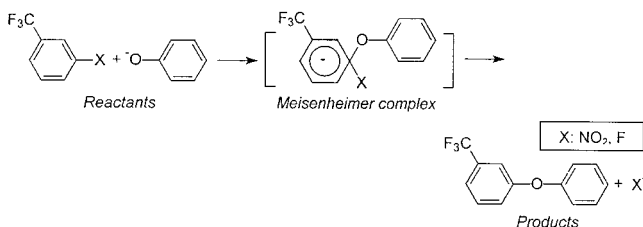
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(13) The detailed synthetic procedure and the spectroscopic data of the synthesized compounds are in the Supporting Information.

Scheme 1



Scheme 2



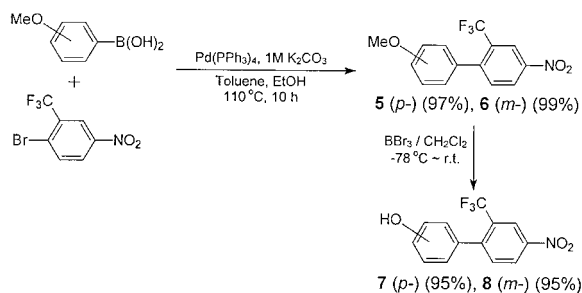
Although the reaction rate depended on the reactivity of the phenoxide ions, the nitro displacement reaction activated by the trifluoromethyl group at the meta position proceeded quantitatively without any side reactions. Also, the reaction of 4-fluoro-2-trifluoromethylbiphenyl, which has fluorine as a leaving group instead of a nitro group, with 4-*tert*-butylphenol was conducted to check the effect of a leaving group. It is known that fluorine and nitro groups have similar reactivity in S_NAr reaction.¹⁶ However, the fluorine-leaving group of 4-fluoro-2-trifluoromethylbiphenyl was not displaced with 4-*tert*-butylphenol in the same reaction condition of **1**. The reaction started to proceed only at 200 °C, but complete conversion was not obtained. Only 21% of the product (**2**) was obtained after 24 h at 200 °C. These results clearly suggest that nitro group is a better leaving group than fluorine in S_NAr reaction, and the nitro displacement reaction activated by the perfluoroalkyl group at meta position can be utilized as a polymer-forming reaction.

To understand the unexpected reaction behavior of a nitro leaving group, quantum mechanical calculation for the energy states in gas phase was conducted with the simplified systems shown in Scheme 2.¹⁴ The nitro displacement showed lower energy difference (ca. 3–4 kcal/mol) between the reactant and the intermediate (Meisenheimer complex) than the corresponding fluorine displacement. And, also the product of the nitro displacement reaction is more stable (ca. 10–13 kcal/mol) than the reactant, while the product and the reactant have similar energy state in the case of the fluorine displacement reaction. The same calculation was also conducted in the case of ortho-activated system. The energy difference between the reactant and the product is larger for the nitro compound (ca. 21 kcal/mol) than the fluorine compound (ca. 10 kcal/mol). The energy difference of the ortho-activated fluorine compound is similar to that of the meta-activated nitro compound. These calculation results suggest that the nitro displacement reaction activated by the trifluoromethyl group at the meta position is a more energetically favorable process than the corresponding fluorine displacement reaction.

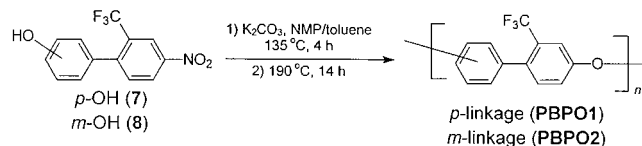
The successful results of the model reactions prompted us to perform the polymerization by using the meta-activated nitro displacement reaction. The monomers, 4'-hydroxy-4-nitro-2-trifluoromethylbiphenyl (**6**) and 3'-isomer (**8**), were prepared as shown in Scheme 3. The structure of the synthesized monomers having both the hydroxy and the nitro-leaving groups was confirmed by spectroscopic data.¹³

(14) The calculation was carried out at Hartree–Fock level using the HF/6-31G(d) and three more models (HF/6-311G(d), HF/6-311G(2d), and HF/6-311G(2df)) as a basis set and initial molecular geometries optimized in vacuo with the GAUSSIAN98 program.

Scheme 3



Scheme 4



The AB type monomers were polymerized with K₂CO₃ as a base in NMP at 190 °C as shown in Scheme 4. The solid contents were maintained over 20 w/v %. The inherent viscosity values of **PBPO1** and **PBPO2** were 0.41 and 0.54 dL/g, respectively. The weight average molecular weights of the polymers determined by GPC with polystyrene standards were over 50 000 in both cases. To our knowledge, this is the first example of successful synthesis of high-molecular weight linear poly(arylene ether)s from the monomers which have an activating group at the meta position. The structures of the polymers were confirmed with FTIR, ¹H NMR, and ¹³C NMR spectroscopy.¹³

The polymers showed good solubility in various organic solvents. They were quite soluble in polar aprotic solvents such as NMP and DMSO and in chlorinated solvents such as 1,2-dichlorobenzene at room temperature. While **PBPO1** was slightly soluble or insoluble in chlorobenzene, 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.

In-plane and out-of plane refractive indices (*n*_{xy} and *n*_z) of the polymers were measured using a prism coupling waveguide technique with a laser beam having 632.8 nm wavelength. The polymers show the refractive indices around 1.61 with very low birefringence (Δ) below 0.002.

Thermal analysis shows that the polymers have high thermal stability as expected for fluoroalkyl-containing poly(arylene ether)s. Dynamic TGA showed 5% weight loss temperatures for **PBPO1** and **PBPO2** at 502 and 469 °C in nitrogen, and at 463 and 420 °C in air, respectively. None of the PBPOs showed crystallization or melt transition in DSC measurement. *T*_g's of **PBPO1** and **PBPO2** measured by DSC were 198 and 154 °C, respectively. Lower thermal stability and large decline of *T*_g of **PBPO2** may be caused by the decreased chain rigidity due to meta-linked structure.

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Supporting Information Available: Details of the experimental procedures, the spectral data for all of the new compounds, FTIR, ¹H NMR, and ¹³C NMR spectra, TGA and DSC thermograms of the synthesized polymers (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.