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Facile Synthesis of Poly(phenylene ether) and “in-Situ” Functionalization of Polymer Backbones

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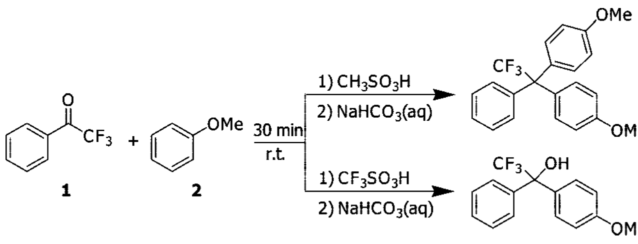
The hydroxyalkylation reaction is one of the most versatile carbon−carbon forming reactions at the carbonyl carbon of activated aldehydes or ketones with various types of aromatic compounds, providing a convenient method for the synthesis of *sec*- and *tert*-aromatic alcohols. However, more often the alcohol initially formed reacts with another aromatic compound to give a diarylation product.[1] A number of diarylated syntheses catalyzed by superacid have been reported in the literature. The protonation of the 1,2-dicarbonyl group,[2] aldehydes,[3] nitriles,[4] and other systems[5] resulted in the formation of highly reactive dication intermediates which are sufficiently condensed with aromatic compounds.[6] By applying this concept, Zolotukhin et al. recently reported that a linear poly(phenylene ether) with a high molecular weight was prepared by the polycondensation of 2,2,2-trifluoroacetophenone (**1**) with 4,4′-diphenoxybenzophenone in trifluoromethanesulfonic acid (TFSA) at room temperature.[7] This result prompted us to design a new AB_2 monomer based on the 2,2,2-trifluoroacetophenone structure for the synthesis of a 100% hyperbranched polymer. Surprisingly, we found that the polymerization of 2,2,2-trifluoro-1-[4-(4-phenoxyphenoxy)phenyl]ethanone (**5**) as an AB_2 monomer in TFSA produced a linear polymer instead of the hyperbranched polymer. Furthermore, a versatile functionalization of a repeating unit in the linear polymer was easily accomplished by selecting a solvent for polymer precipitation.

Herein, we report the first synthesis of a linear poly(phenylene ether) by a hydroxyalkylation reaction in TFSA; the structure of its repeating unit can be easily modified by quencher variation.

During the course of the investigation of the synthesis of a hyperbranched polymer with 100% degree of branching,[8] we studied the reaction of an equimolar amount of **1** with anisole (**2**) in different acidity of catalyst, methanesulfonic acid (MSA) and TFSA at room temperature. It was found that only the diarylation product, 4,4′-(2,2,2-trifluoro-1-phenylethane-1,1-diyl)bis(methoxybenzene), was selectively obtained in MSA, whereas a hydroxyalkylation product, 2,2,2-trifluoro-1-(4-methoxyphenyl)-1-phenylethanol, was formed quantitatively in TFSA (Scheme 1). When 2 equiv of **2** to **1** was used, only diarylation products were isolated in the cases of both MSA and TFSA. These products were isolated by pouring the reaction solution into water.

These results suggest that the condensation reaction of **1** with **2** in MSA proceeds via intermediate **3**, whose reactivity is much higher than that of starting compound **1** (Scheme 2). Therefore, when **3** was formed in a mixture, it will be readily attacked by **2** to provide the diarylated product. On the other hand, in the TFSA medium the rate constant of the second substitution is considerably slower than that of the first one.

Scheme 1. Model Reaction in MSA and TFSA



According to the observation of Olah,[6] a superacid is highly ionizing and low-nucleophilicity media. Unexpectedly, the electrophile primarily formed was activated by further superelectrophilic solvation, which is an interaction between the electrophile and Lewis/Brønsted superacid. Such interaction of these cations can only exist in a superacid medium, resulting in extremely reactive dication species in the condensed state. Olah[9] and Shudo[3] suggested that the similar dication intermediate was predominant in the Friedel−Crafts reaction of the carbonyl compound with benzene in a superacid, although Fomine et al.[10] proposed another mechanism resulting only the monocation intermediate without the formation of dication. Diprotonated carbonyl compound **4** in superacid condenses with **2** to give intermediate **3**, whose reactivity is lower than that of the dication. When 1 equiv of **2** was used, the total amount of **2** was consumed in the first substitution. Therefore, we assumed that the above reaction in TFSA would generate a different substitution product when the nucleophilic solvent for precipitation changes (Scheme 3).

First, we initially confirmed our hypothesis by changing the work-up nucleophilic solvent in the model reaction between **1** and **2** from water to methanol and anisole (Scheme 4). The corresponding methoxy and anisolyl substituent products were isolated in quantitative yields.

Moreover, when phenol, which has two possible nucleophilic sites, was used as a nucleophilic solvent, only an aromatic nucleophilic product, 4-[2,2,2-trifluoro-1-(4-methoxyphenyl)-1-phenylethyl]phenol, was obtained in excellent yield. These results support our hypothesis; that is, in a superacid medium the first substitution proceeds faster than that of the second one, and the total amount of compound **2**

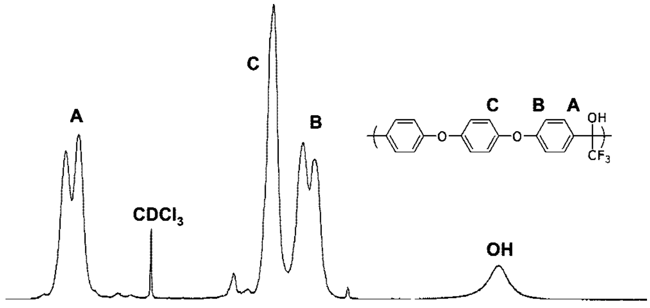


Figure 1. ^1H NMR spectrum of polymer **6a** in $CDCl_3$.

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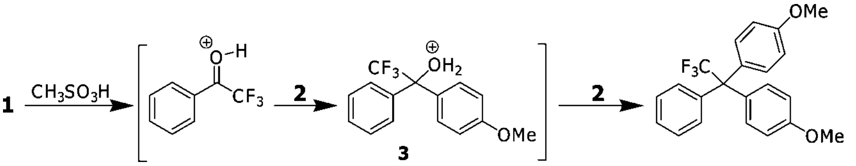
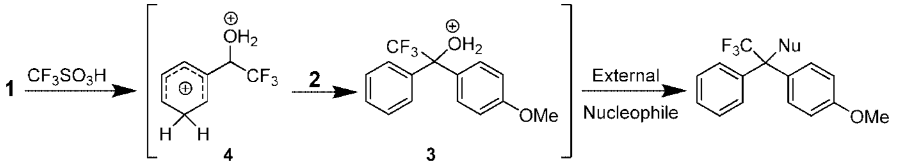
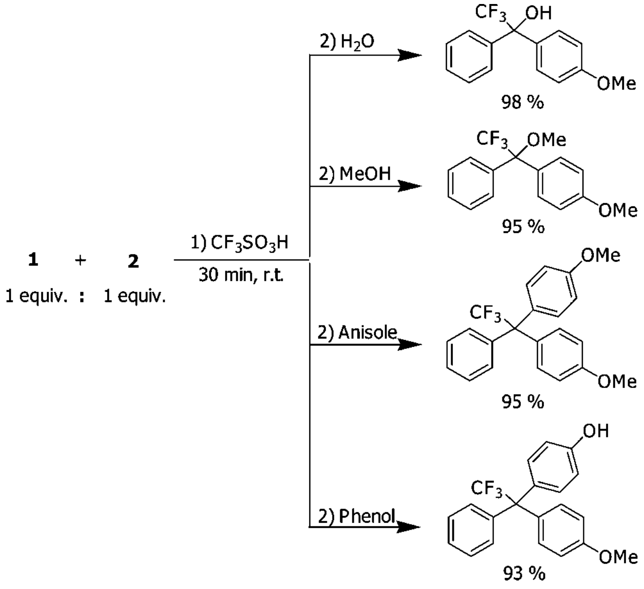
Scheme 2. Plausible Reaction Mechanism in MSA



Scheme 3. Plausible Reaction Mechanism in TFSA



Scheme 4. Model Reaction with Variation of Nucleophilic Solvent



was completely used in the first one. The formation of products was confirmed by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis (Supporting Information). According to the results from the model reaction, self-polycondensation of a monomer having a combined structure of **1** and **2** in TFSA is expected to give a linear polymer whose structure can be easily altered by changing the work-up nucleophilic solvent. A new monomer, **5**, containing 2,2,2-trifluoroacetophenone and anisole units, was designed and synthesized. Monomer **5** was successfully prepared in one step by the Friedel−Crafts reaction of 1,4-diphenoxybenzene and trifluoroacetic anhydride in the presence of *N*,*N*-dimethylaminopyridine (DMAP) and $AlCl_3$ as a catalyst (Scheme 5). The structure of monomer **5** was determined by FT-IR and NMR spectroscopy and elemental analysis (Supporting Information).

Self-polycondensation of **5** was carried out in TFSA at room temperature (Scheme 6). The polymerization proceeded in a homogeneous state and was completed in 1 h. The purple solution was poured into water to yield a white fibrous polymer, hydroxy-substituted poly(phenylene ether) (**6a**). The molecular weight and polydispersity index of **6a** are 18 100 g/mol and 1.7, respectively.

The structure of **6a** was confirmed by FT-IR and NMR spectroscopy. The FT-IR spectrum showed characteristic absorptions at 3455 and 1234 cm^{-1} due to the stretching of the OH and C−O bonds, respectively. No absorption due to the C=O group of **5** was observed at 1712 cm^{-1}. Figure 1 shows the ^{1}H NMR spectrum of **6a** with the assignment of the observed resonance. The singlet signal and two doublet signals at 6.85, 6.82, and 7.27 ppm assignable to the aromatic protons C, B, and A, respectively, were observed, and the broad singlet signal of the hydroxy proton clearly appeared at 2.65 ppm.

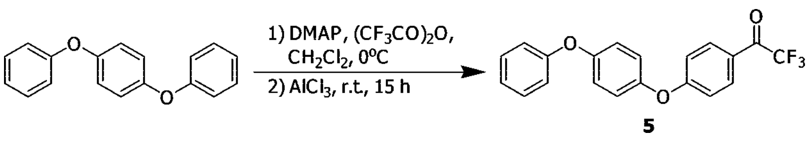
The ^{13}C NMR spectrum also supported the formation of a polymer to which six peaks were assigned to be aromatic carbons in the range of 115−157 ppm. A signal corresponding to the aliphatic quaternary carbon at 77.88 ppm, quartet, was observed, and a carbonyl peak of a ketone group at 190 ppm could not be detected (see Supporting Information).

Then, poly(phenylene ether)s **6** with other functional groups in a repeating unit were prepared by pouring the solution mixture into other work-up nucleophilic solvents such as methanol, anisole, and phenol (Scheme 6). Polymers **6b**, **6c**, and **6d** with the methoxy, anisolyl, and *p*-hydroxyphenyl groups, respectively, were successfully prepared in quantitative yields (see Supporting Information).

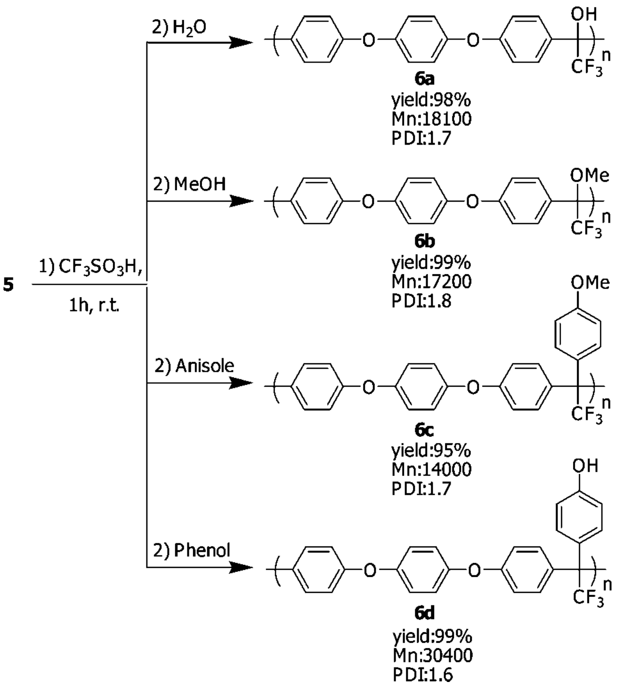
The thermal properties of polymer **6a** were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The polymers exhibited a 5% weight loss temperature at 380 °C in nitrogen. The glass transition temperature (T_g) determined by DSC measurement was 150 °C.

In summary, we have found that linear polymers **6** are easily prepared by self-polycondensation of **5** in TFSA at room temperature, and poly(phenylene ether)s **6** with various functional groups in all their repeating units are formed by pouring the polymer solutions into nucleophilic solvents. To the best of our knowledge, this is the first report on the direct structure transformation from polymerization solutions in the synthesis

Scheme 5. Monomer Synthesis



Scheme 6. Synthesis of Polymers 6a−d



of condensation polymers. Further research toward its application is currently ongoing.

Supporting Information Available: Full experimental details and the copies of NMR spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

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