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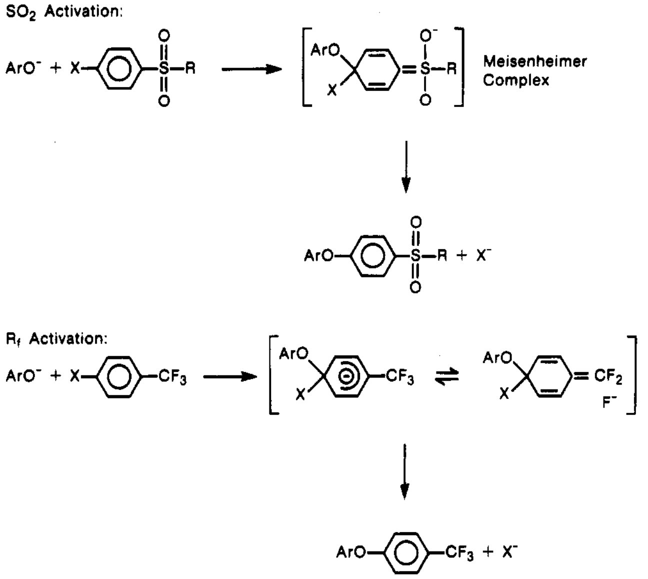
Perfluoroalkylene-Activated Poly(aryl ether) Synthesis

Fluoropolymers are of great interest as insulating materials in the microelectronics industry due to their excellent thermal and chemical stability and low dielectric constant. A major drawback of highly fluorinated materials is their poor solubility characteristics, which often necessitates the use of unusual fluorinated solvents. The solubility characteristics can be improved markedly by incorporation of a sufficient percentage of a nonfluorinated functional group in the polymer, e.g., imide.[1] Most poly(aryl ethers) display excellent solubility characteristics in addition to high thermal and chemical stability. It is likely that an excellent combination of properties could be realized from a polymer structure based on perfluoroalkylene and aryl ether constituents. As a potential route to this polymer structure, we envisaged a poly(aryl ether) synthesis where the perfluoroalkylene group activates the aromatic halo displacement in the generation of the aryl ether linkage. Therefore, we have undertaken a study of perfluoroalkyl-activated aryl ether synthesis and the use of this reaction to prepare novel highly fluorinated poly(perfluoroalkylene aryl ethers).

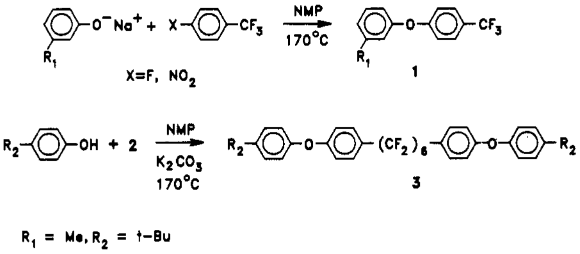
Poly(aryl ethers) are generally synthesized via a step-growth polymerization of activated dichloro, difluoro, or dinitro aromatics with bisphenoxides[2-4] or by a Friedel-Crafts acylation process, applicable for poly(aryl ether ketones).[5,6] The former involves generation of the ether linkages by nucleophilic aromatic substitution as the polymer-forming reaction. Effective activating groups include sulfones and ketones, which are used in the preparation of poly(aryl ether sulfones) and poly(aryl ether ketones), respectively. Heterocyclic rings, e.g., imides,[7] quinoxalines,[8] and benzoxazoles,[9] have also been demonstrated to activate nucleophilic aromatic displacement in the synthesis of high-T_g poly(aryl ethers). The electronic and structural characteristic common to all activating groups is they are electron withdrawing and have a site of unsaturation, which can stabilize the negative charge developed in the displacement through resonance to a heteroatom. This involves the formation of a Meisenheimer complex, which lowers the activation energy of the displacement (Scheme I).[10]

The rationale for perfluoroalkyl-activated ether synthesis is derived from the electron affinity and hyperconjugation displayed by perfluoroalkyl groups, characteristics that we surmised would facilitate nucleophilic displacement at positions ortho or para to the group. The effectiveness of perfluoroalkyls as electron-withdrawing groups can be estimated by Hammett σ values and the chemical shift of aromatic protons ortho to the fluoroalkyl substituent. Comparison of Hammett σ values of the trifluoromethyl group to a ketone group (σ: $CF_3 = 0.54$, $C{=}O = 0.50$) shows them to be similar electronically when resonance effects are discounted. In addition, ^{1}H NMR shows the deshielding of aromatic protons ortho to a trifluoromethyl group ($\delta = 7.6$) versus a ketone group ($\delta = 7.9$) to be similar in para-substituted aryl halides, supporting the equivalency of the trifluoromethyl and ketone group with respect to electron affinity. However, a perfluoroalkyl group is structurally unique relative to other activating groups because it has no site of unsaturation. Therefore, activation by a perfluoroalkyl group would require the participation of hyperconjugation and/or stabilization through the carbon–carbon σ bond to lower the activation energy of the transformation (Scheme I).

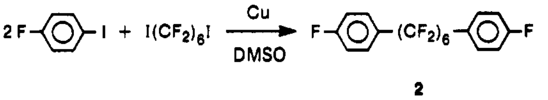
Scheme I



Scheme II



Scheme III



To demonstrate whether a 4-perfluoroalkyl-substituted fluoro- or nitrobenzene would undergo nucleophilic aromatic substitution, model reactions with trifluoromethyl derivatives were studied. Model reactions between sodium *m*-cresolate with both 4-nitro- and 4-fluorobenzotrifluoride were carried out in NMP and followed by HPLC (Scheme II). The reaction with 4-fluorobenzotrifluoride was near completion after 1 h at 160 °C, with the formation of a single product peak by HPLC. After 18 h the reaction was worked up and the expected 3-methyl-4′-trifluoromethyldiphenyl ether was isolated in 96% yield. Reaction with 4-nitrobenzotrifluoride showed similar selectivity; however, complete conversion was not obtained and 10% of the 4-nitrobenzotrifluoride remained after 18 h at 170 °C. From these results it was apparent that perfluoroalkyl-activated fluoro displacement occurred in the high yield and selectivity required for a polymer-forming reaction, while the nitro displacement did not occur in the high conversion required for polymerization under these conditions.

The general structure we sought to employ as the monomer in polymerizations was based on perfluoroalkylene-linked 4-fluorophenyl groups. The copper-catalyzed coupling of α,ω-diiodoperfluoroalkanes and 1-fluoro-4-iodobenzene should provide a one-step synthesis of these monomers.[11] Reaction of 1,6-diiodoperfluorohexane and 1-fluoro-4-iodobenzene was carried out in dimethyl sulfoxide at 120 °C for 48 h to afford 1,6-bis(4-fluorophenyl)perfluorohexane (**2**) (Scheme III). The compound was

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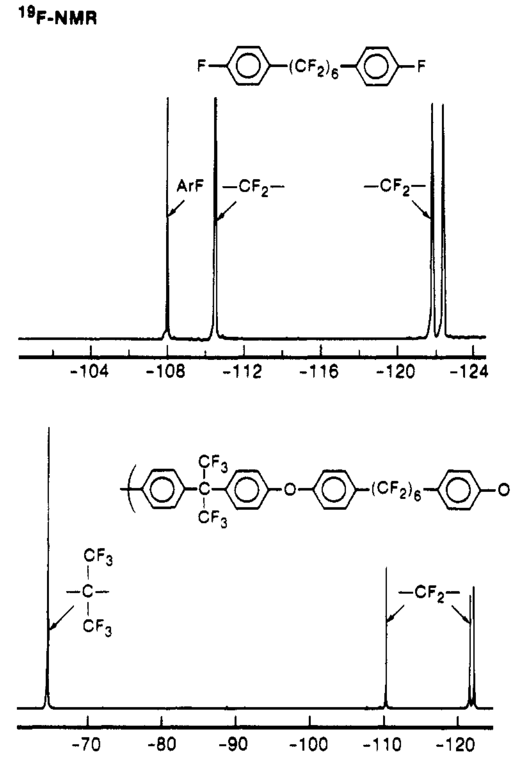

Figure 1. ^{19}F NMR of monomer **2** and polymer **4a**.

purified by vacuum distillation [bp = 95 °C (0.15 mmHg)] to afford a low-melting solid (mp = 40 °C) in 75–85% yield. Both ^{1}H NMR and ^{19}F NMR spectral evidence was consistent with the assigned structure for **2**. The ^{19}F NMR was particularly useful for characterization, as each set of chemically equivalent fluorines had a distinctive chemical shift (Figure 1). When this procedure was used for the synthesis of 1,4-bis(4-fluorophenyl)perfluorobutane, the reaction afforded a multitude of side products.

Compound **2** was subjected to a model reaction to confirm the perfluoroalkylene linkage was effective in activating the displacement. Reaction of **2** with 1.05 equiv of 4-*tert*-butylphenol was carried out in NMP with potassium carbonate (1.5 equiv) as the base (Scheme II). The reaction mixture was dehydrated for 4 h with toluene in an oil bath maintained at 140–150 °C and then heated to 170 °C for 20 h. The product was isolated by partitioning between water and hexane and chromatographed (hexane, silica gel) to afford the expected 1,6-bis[4-(4-*tert*-butylphenoxy)phenyl]perfluorohexane (**3**) in 99% yield. The model compound was a colorless oil and displayed spectral characteristics consistent with the assigned structure.

The polymerization of 1,6-bis(4-fluorophenyl)perfluorohexane (**2**) with several bisphenols was carried out in NMP in the presence of potassium carbonate by analogy to conventional polyether synthesis (Scheme IV).[12] The polymerizations were maintained at a solids content of 25% and were heated at 170 °C for 24 h after dehydration. The solutions became very viscous, indicative of the formation of high molecular weight polymers, and remained clear without any evidence of polymer precipitation. After 24 h an excess of 4-fluorobenzotrifluoride was added to cap unreacted phenoxide end groups. This procedure was used to polymerize **2** with Bisphenol AF, Bisphenol A, and resorcinol to give poly(perfluoroalkylene aryl ethers) **4a–c**, respectively. The ^{19}F NMR spectra of the polymers showed resonances consistent with the assigned structure. Comparison of the ^{19}F NMR of polymer **4a** to the monomer **2** shows the disappearance of the aryl fluoride resonance at δ −108 ($CFCl_3$ standard) in the polymer, as well as the appearance of the fluorine associated with the hexafluoroisopropylidene group at δ −63.8 (Figure 1). The spectrum of **4a** was very clean, with additional resonances at −110.5, −121.8, and −122.4 assigned to the CF_2 groups in the polymer chain. The ^{19}F NMR shows that the polymerization reaction occurred with a high degree of selectivity to give the desired polymer structure.

Scheme IV

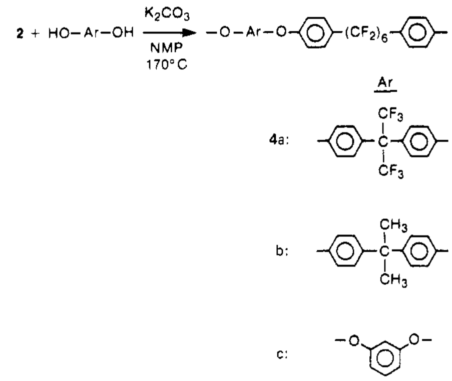

Table I
Polymer Characterization

polymer	PDT,[a] °C	T_g,[b] °C	$[\eta]$,[c] g/dL
4a	480	95	0.80
4b	480	93	1.8
4c	490	49	0.50

[a] N_2, 5 °C/min. [b] 10 °C/min. [c] NMP, 25 °C.

The polymers formed were high molecular weight as determined by the intrinsic viscosity measurements (Table I). The polymers were soluble in a variety of solvents including NMP, chloroform, toluene, and glymes. Clear tough films could be obtained by solution casting. Differential scanning calorimetry on **4a–c** showed distinct glass transition temperatures ranging from 40 to 95 °C (Table I). These are very low T_gs for poly(aryl ethers), which usually are in the 200 °C range, indicating the $(CF_2)_6$ linkage introduces a high degree of flexibility in the polymer backbone. This observation is consistent with previous reports on the effect of perfluoroalkylene linkages on glass transition temperatures, e.g., perfluoroalkylene-based polyimides.[1] The thermal stability of **4a–c** was excellent, with polymer decomposition temperatures between 480 and 490 °C (nitrogen). An isothermal thermal gravimetric analysis of **4a** showed a weight loss of 0.13 wt %/h at 400 °C. The mechanical properties were measured on films of **4** cast from NMP solution and heated to 350 °C to remove solvent. Polymers **4a** and **4b** displayed tough ductile mechanical properties as judged by a yield point and high elongations (35–100%), similar to polysulfone. The moduli were found to be in the 1300–1500-MPa range. The dielectric constant of polymer **4a** was 2.35 at 2 MHz.

In conclusion, fluoroalkyl groups were shown to effectively activate nucleophilic aromatic substitution. This reaction was used to prepare poly(perfluoroalkylene aryl ethers), a new class of poly(aryl ethers) that do not contain polar functionality, e.g., ketones, affording a low dielectric constant. The polymers displayed a low T_g, high thermal stability, and mechanical properties comparable to other glassy poly(aryl ethers). Although the T_gs of these polymers are too low for most dielectric applications, we are investigating their use as components in block copolymers[13] and as impact modifiers for thermosets.[14]

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