Hyperbranched Polyfluorinated Benzyl Ether Polymers: Mechanism, Kinetics, and Optimization

Matthew J. Quast, Anja Mueller

Science of Advanced Materials, Central Michigan University, Mount Pleasant, Michigan 48858
Correspondence to: A. Mueller (E-mail: muell1a@cmich.edu)

Received 1 November 2013; accepted 12 December 2013; published online 9 January 2014
DOI: 10.1002/pola.27078

ABSTRACT: Highly fluorinated, hyperbranched polymers were synthesized from the polycondensation of AB_2 monomers, 3,5-bis[(pentafluorobenzyl)oxy]benzyl alcohol and 3,5-bis[(pentafluorobenzyl)-oxy]phenol with potassium carbonate base, and 18-crown-6 phase transfer agent in a variety of polar aprotic solvents. The regioselectivity of the polymerization was optimized and was found to be temperature dependent. The new polymerization technique produced higher molecular weight polymer using safer conditions than earlier methods. The resulting optimization was used to control substitution of oxygen-bearing nucleophiles along nonactivated fluoroaryl systems in high yield. Water was found to induce side reactions that generate a highly conjugated fluoroaryl phenol with lowered reactivity. The removal of a methylene spacer in the polymer backbone of the hyperbranched polymer produced a polymer with greater thermal stability. The reaction conditions for polymerization were found to be general for nucleophile-bearing perfluorinated systems. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 985–994

KEYWORDS: fluoropolymers; hyperbranched; kinetics (polym.); polyethers; thermal properties

INTRODUCTION Perfluorinated polymers are an outstanding building block for thin film and membrane technologies that require materials with low surface energy, low wettability, and high thermal stability. The chemical inertness and oxidative/hydrolytic stability of C—F bonds provides an excellent barrier against chemical and environmental wear.[1–4] As a result, fluorinated polymers are used in self-assembling materials such as superhydrophobic coatings, antifouling surfaces, electrolyte membranes, and organic semiconductors.[5–12] While fluorinating agents may be used for the introduction of fluorine, this often results in a random distribution of fluorinated units along the polymer mainchain.[13,14] Traditional fluorinated polymers such as poly(tetrafluoroethylene) (PTFE) have stiff main chains and are difficult to tailor, which limits their utility toward nanometer-scale-ordered structures and specialized applications.

Hyperbranched polymers have lower glass transition temperatures and enhanced flexibility in comparison to linear polymers, which makes them more favorable building blocks toward nanometer-scale-ordered structures. It is well known that branching in hyperbranched polymers produces a material with lowered solution viscosities and enhanced solubility, which help permit simple casting of membranes and thin films.[7,15] Additionally, fluorination effectively lowers surface energy, making the material even more suitable for manufacturing thin films or membranes.

Hyperbranched, perfluorinated polymers (HBFP) are highly attractive because of their desirable properties. The hyperbranched material described here contains two perfluoroaryl groups suitable for reaction with various nucleophiles to generate a range of functionalized materials, including polymer additives or material modifiers. Functional density is increased from branching, which enhances postpolymerization modification capabilities. Industrially, the current method of preparation for hyperbranched perfluorinated polymer is not safe for large scale-up; here is presented an alternative system for preparing HBFPs that yields improved polymer properties from safer conditions.[16]

Attack by oxygen-, nitrogen-, or sulfur-containing nucleophiles along perfluorinated aromatics normally occurs at the *para*-position with respect to the point of attachment.[17,18] Additional substitution at the *ortho*-position of fluoroaryl rings is also documented.[19] Computational models have been designed for determining the principal site of nucleophilic substitution. The position of attack directly reflects the stability of the Meisenheimer complex associated with nucleophilic aromatic substitution (S_NAr) processes (Fig. 1).[20] The energy of this intermediate can be lowered via activating

Additional Supporting Information may be found in the online version of this article.

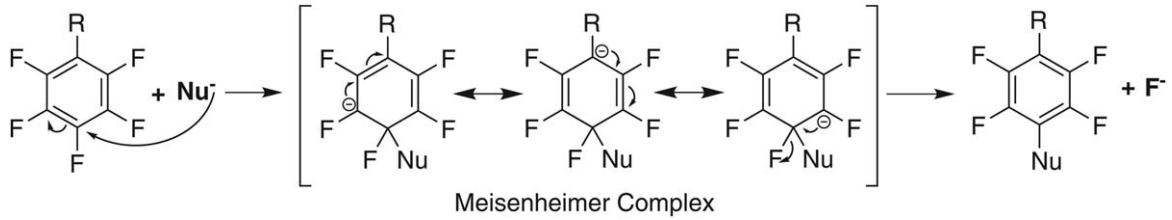

FIGURE 1 Meisenheimer complex associated with nucleophilic aromatic substitution in perfluorinated aromatics.

groups in perfluorinated aromatics, as seen in systems bearing an electron withdrawing groups such as benzophenones, acetophenones, and oxadiazoles.[17,21–23]

The extent of nucleophilic aromatic substitution for nonactivated perfluorinated aromatics using oxygen-containing nucleophiles has been investigated in this research. This was done to establish conditions to maximize *para*-selectivity during S_NAr polymerization to generate HBFPs. In addition, promotion of the polymerization by various bases in the presence of phase transfer agent has been explored. A new phase transfer agent/base system for polymerization has been established. Herein is described the synthesis conditions required for quantitative conversion of oxygen-bearing perfluorinated AB_2 monomers to the corresponding hyperbranched polymers (Fig. 2). Reaction of a model compound was used to assess which species lead to crosslinking reactions. The extent of substitution at various positions in the perfluoroaryl group was assessed. The versatility of the new method has been demonstrated for the polymerization of AB_2 monomers-bearing phenol-based nucleophiles.

EXPERIMENTAL

Materials

3,5-Dihydroxybenzyl alcohol (99%), 2,3,4,5,6-pentafluorobenzyl bromide (99%), 18-crown-6 (99%), resorcinol (99%), and phloroglucinol (99%) were purchased from Sigma Aldrich. All reagents were stored in a desiccator and were used as received. Potassium carbonate (reagent grade-Sigma Aldrich) was used for preparation of 1 and 4. Analytical grade potassium carbonate powder (Sigma-Aldrich, +99.99%) was used for all other syntheses. Dry solvents: acetone (HPLC grade, Fisher Sci.), acetonitrile (HPLC grade,

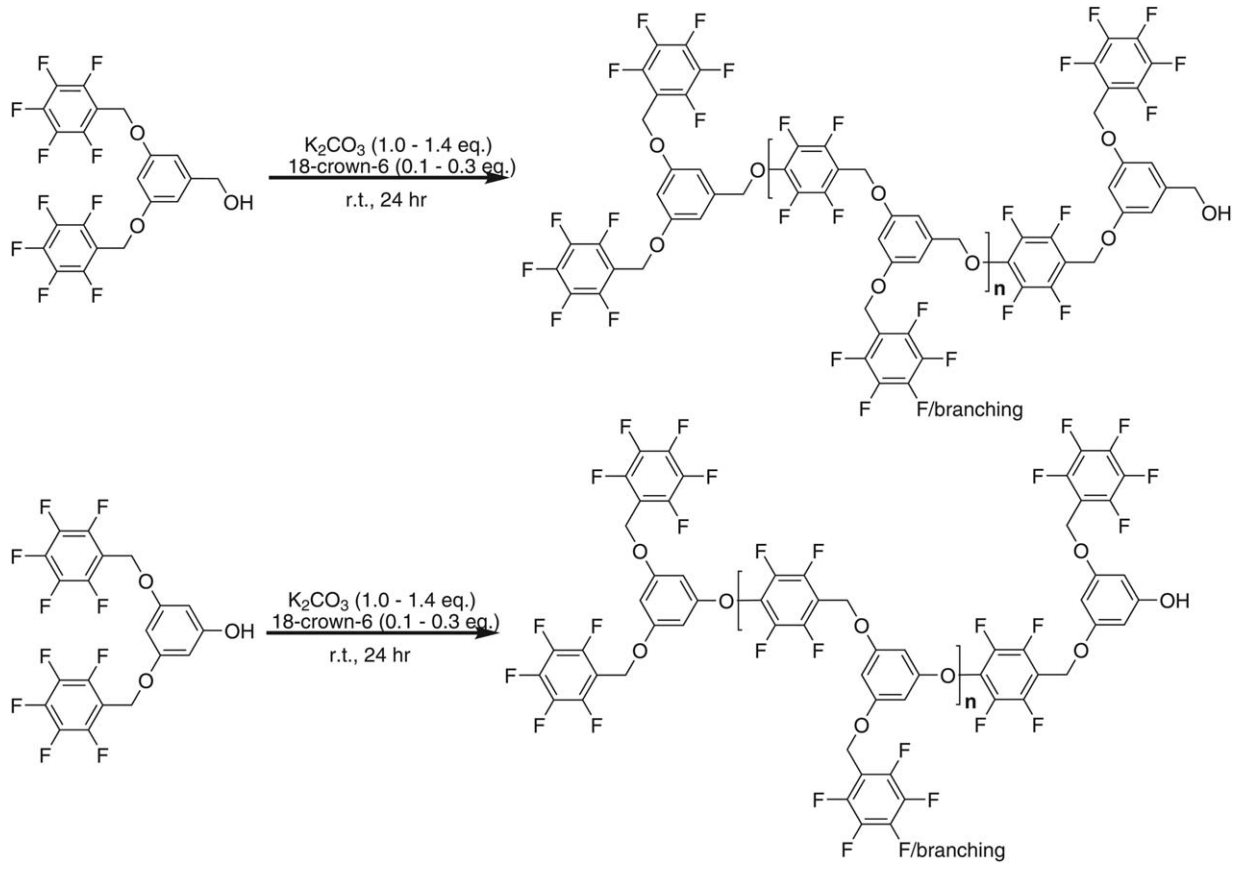

FIGURE 2 Synthesis of hyperbranched, perfluorinated polymer-bearing benzyl alcohol (5) and phenol (7) nucleophile.

Fisher Sci.), and toluene (EMD) were stored over molecular sieves. Chloroform-*d* (99.8+ atom% D-ACROS) and deuterated dimethyl sulfoxide (99.5+ atom% D-ACROS) were used as received.

Characterization

All spectra were recorded at 298 K. FTIR spectra were recorded using a Thermoscientific Nicolet iS50 ATR and analyzed using TA Instruments Universal Analysis 2000 software.

^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded using a Varian Mercury 300 MHz or Varian Inova Unity 500 MHz spectrometer. $CDCl_3$ was used as solvent and TMS as reference [$\delta(1H) = 0.00$ ppm; $\delta(13C) = 77.0$ ppm]. ^{19}F NMR spectra were referenced to external C_6F_6 standard [$\delta(19F) = -162.9$ ppm].

Thermal decomposition was examined using a TA Instruments TGA Q500 with a 10 °C/min heating ramp under nitrogen. DSC measurements were recorded using a TA Instruments DSC Q1000 with 10 °C/min heating rate in nitrogen. Glass transition temperature was determined from cyclic heating ramps after an isothermal step well above the glass transition temperature of the material.

Mass spectra were recorded using a Waters Micromass MS Technologies LCT Premier XE unit. GCMS spectra were recorded using a Waters Micromass GCT Premier instrument. MALDI-TOF spectra were recorded using a Bruker Daltonics autoflex unit and using Compass FlexControl software.

Molar mass distribution and PDI was determined by gel permeation chromatography (GPC) equipped with a Viscotek VE1122 solvent delivery system, PAS102 and PAS103 columns (Polyanalytik), and Perkin Elmer series 200 differential refractive index detector. All samples were injected at a concentration of 3 mg/mL in 100 μL volumes and THF was used as the mobile phase. Mass distribution was analyzed using OmniSEC 4.6 software (Malvern Instrument). To ensure accuracy of molar mass distributions among samples the GPC instrument assembly was calibrated with external polystyrene standards (Shodex, Showa Denko K.K.). Percent monomer conversion was determined by ^{1}H NMR by using the ratio between peak areas for the benzyl alcohol proton to that for the internal aromatic protons.

Synthesis

3,5-Bis[(pentafluorobenzyl)oxy]benzene (1)

A mixture of resorcinol (2.20 g, 20.0 mmol), 18-crown-6 (0.529 g, 0.20 mmol, 0.1 equiv), and 2,3,4,5,6-pentafluorobenzyl bromide (6.34 mL, 42.0 mmol, 2.1 equiv) was dissolved in anhydrous acetone (100 mL). To the solution was added finely ground K_2CO_3 (5.80 g, 42.0 mmol, 2.1 equiv), and the mixture was stirred at room temperature under nitrogen for 4 days. The solvent was removed under reduced pressure and the solid taken up in CH_2Cl_2 and partitioned between water (50 mL, two times) and 1 M aqueous potassium chloride solution (50 mL, two times). The organic layer was dried over anhydrous $MgSO_4$. The solution was filtered and the solvent removed under reduced pressure. After evaporation, the white solid was recrystallized from 90% hexanes/dichloromethane: yield 3.57 g (76%).

T_m 82–85 °C, decomposition onset 179.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.11 (s, 4H), 6.59 (t, $J = 2.3$ Hz, 1H), 6.62–6.66 (dd, $J = 2.4$ and 8.2 Hz, 2H), 7.25 (t, $J = 8.2$ Hz, 1H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 57.7, 102.6, 108.3, 110.2, 130.6, 136.1, 139.5, 140.3, 143.7, 144.3, 147.6, 159.4; ^{19}F NMR (300 MHz, $CDCl_3$) δ −143.0 (m, 4F, *ortho-F*), −153.3 (m, 2F, *para-F*), −162.3 (m, 4F, *meta-F*); IR (ATR, cm^{-1}) 2957, 2890, 1659, 1590, 1521, 1503, 1380, 1179, 1155, 1058, 937 cm^{-1}; GCMS calculated for $C_{20}H_8F_{10}O_2$ 470.0365, found 470.0417.

3,5-Bis[(4-(benzyloxy)−2,3,5,6-tetrafluorophenyl)oxy] benzene (2)

To a mixture of 3,5-bis[(pentafluorobenzyl)-oxy]benzene (0.2 g, 0.43 mmol, 1.0 equiv), 18-crown-6 (0.034 g, 0.13 mmol, 0.3 equiv) and benzyl alcohol (0.138 g, 0.132 mL, 1.3 mmol, 3 equiv) in acetonitrile (15 mL) was added K_2CO_3 (0.176 g, 1.3 mmol, 3 equiv) and the mixture was vigorously stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the white residue was taken up in chloroform (50 mL) and partitioned between water (50 mL) and 1 M potassium chloride (50 mL, two times). The organic layer was dried over magnesium sulfate, the solvent removed under reduced pressure and a white solid was recrystallized from 90% methanol/acetone: yield 0.146 g (53%).

T_m 93–95 °C; decomposition onset 269.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.04 (s, 4H), 5.26 (s, 4H), 6.56–6.64 (m, 3H), 7.22 (t, 1H), 7.32–7.46 (m, 4H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 57.6, 76.3, 102.2, 107.9, 108.5, 128.3, 128.6, 128.9, 130.2, 135.4, 137.6, 140.2, 142.2, 139.8, 146.8, 159.3; ^{19}F NMR (300 MHz, $CDCl_3$) δ −144.20 (m, 4F, *ortho*-F), −156.03 (m, 4F, *meta*-F); IR (ATR, cm^{-1}) 3040, 2957, 2899, 1655, 1594, 1488, 1377, 1250, 1127, 1039, 932; HRMS (ESI): calcd. for ($M+H^+$): 647.1463 found 647.3107.

(2-((3-(2,4-Bis(benzyloxy)−3,5,6-trifluorobenzyl-oxy) phenoxy)methyl)−4,6-difluorobenzene-1,-3,5-triyl)tris(oxy) tris(methylene)tribenzene (3)

To a mixture of 3,5-bis[(pentafluorobenzyl)oxy]-benzene (0.25 g, 0.53 mmol, 1.0 equiv), 18-crown-6 (0.14 g, 0.53 mmol, 1.0 equiv) and benzyl alcohol (0.38 g, 0.364 mL, 3.5 mmol, 6.6 equiv) in acetonitrile (15 mL) was added K_2CO_3 (0.483 g, 3.5 mmol, 6.6 equiv), and the mixture was vigorously stirred at reflux for 24 h. The solvent was removed under reduced pressure and the orange residue was taken up in chloroform (50 mL), extracted with 1 M potassium chloride (50 mL, two times), and dried over magnesium sulfate. The residue was purified by flash chromatography eluting with 80% hexane/ethyl acetate, increasing polarity to ethyl acetate, to yield a colorless oil: yield 0.11 g (25.2%).

T_g −12.93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.95 (s, 2H), 4.97 (s, 2H), 5.05 (s, 2H), 5.08 (s, 4H), 5.26 (s, 4H), 5.29 (s, 2H), 6.57–6.69 (m, 3H), 7.18–7.52 (ArH, 25H); ^{19}F NMR −144.2 (m, *ortho*-F), −148.0 (dd, $J = 3.79$ and 10.32, *ortho*-F),

−156.0 (m, *meta*-F), −156.0 (dd, $J = 8.71$ and 22.2 Hz, *meta*-F); IR (ATR, cm^{-1}) 3065, 3033, 2953, 2891, 1640, 1592, 1492, 1481, 1454, 1375, 1281, 1258, 1175, 1146, 1052, 989; MALDI-TOF MS calcd for $C_{48}H_{36}F_6O_6K^+$ 861.2053 found 861.3570 (tetrabenzylalcohol addition); cald for $C_{55}H_{43}F_5O_7K^+$ 949.2566 found 949.452 (pentabenzyl alcohol addition).

3,5-Bis[(pentafluorobenzyl)oxy]benzyl Alcohol (4)

The synthesis and work up of **(4)** was adapted from previous methods.[16] A dry round bottomed flask equipped with a gas inlet adapter was charged with a magnetic stirrer, 2,3,4,5,6-pentafluorobenzyl bromide (39.67 g, 0.152 mol, 2.1 equiv), 3,5-dihydroxybenzyl alcohol (10.14 g, 0.0724 mol, 1 equiv), finely ground K_2CO_3 (21.01 g, 0.152 mol, 2 equiv) and 18-crown-6 (1.92 g, 7.2 mmol, 0.1 equiv) and allowed to react under vigorous stirring in acetone (400 mL) at room temperature under nitrogen. After 4 days, the solvent was removed under reduced pressure. The residue was partitioned between CH_2Cl_2 (300 mL) and water (200 mL, two times), the aqueous layer was back extracted with CH_2Cl_2 (100 mL), and all CH_2Cl_2 layers were combined. The CH_2Cl_2 extracts were extracted with 4 M KCl solution (150 mL, two times) to help extract 18-crown-6. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The product, **4,** was recrystallized from 70% hexane/CH_2Cl_2: yield 29.1 g (80%).

T_g 4 °C; T_m 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.67 (d, $J = 3.72$ Hz, 2H), 5.10 (t, $J = 1.5$ Hz, 4H), 6.50 (t, $J = 2.30$ Hz, 1H), 6.66 (d, $J = 2.32$ Hz, 2H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 57.69, 65.17, 70.43, 101.5, 106.4, 110.1, 136.1, 139.5, 140.3, 143.7, 144.2, 147.6, 159.5; ^{19}F NMR δ −143.0 (dd, $J = 8.19$ and 22.0 Hz, *ortho*−4F), −153.3 (t, $J = 20.7$ Hz, *para*−2F), −162.3 (dt, $J = 10.5$ and 20.8, *meta*-4F); IR (ATR, cm^{-1}) 3363, 2891, 1659, 1597, 1524, 1507, 1456, 1434, 1383, 1314, 1290, 1164, 1059, 977, 941, 835, 774, and 689 cm^{-1}; HRMS (ESI): calcd for ($M+H^+$): 501.0543; found 501.1920.

Synthesis Optimization of Hyperbranched Polyfluorinated Poly(benzyl ether)s (5)

The general method for the polymerization optimization of **1** was to a solution of **1** (0.05–1.25 M) under nitrogen, add K_2CO_3 (1.0–1.4 equiv) and 18-crown-6 (0.10–0.30 equiv) in the chosen solvent (dry) and vigorously stir for 24 h at room temperature (see Table 1). The reaction mixture was quenched with excess dichloromethane and dried over anhydrous $MgSO_4$ followed by filtration. The solvent removed under reduced pressure and product was fully characterized without further purification.

From a mixture of monomer (4) (0.25 g, 0.50 mmol, 1.0 equiv), 18-crown-6 (0.040 g, 0.15 mmol, 0.30 equiv), K_2CO_3 (0.083 g, 0.60 mmol, 1.2 equiv) in acetonitrile (0.50 mL, 1.25 M) stirred for 24 h and by precipitation into 70:30 MeOH/$CHCl_3$, yield 80%, $M_w = 99{,}800$; $M_w/M_n = 1.86$, from GPC calibrated with PS standards; T_g 57.6 °C; $T_d = 315.5$ °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.08–5.10 (m, 4H), 5.21 (s, 2H), 6.55 (s, 1H), 6.72 (s, 2H); ^{19} F NMR δ −142.76 (m, *ortho*-F), −144.40 (m, *ortho*-F), −152.92 (m, *para*-F), −156.53 (m, *meta*-F), −161.94 (m, *meta*-F); IR (ATR, cm^{-1}) 2955, 1657, 1596, 1523, 1493, 1455, 1430, 1374, 1291, 1137, 1051, 937.

TABLE 1 Initial Conditions Used in Stoichiometry Optimization of 5

Entries	Conc. (M)	K_2CO_3 (equiv)[a]	18-crown-6 (equiv)[a]	Conv. (%)
A1	0.8	1.0	0.3	89
A2	0.8	1.2	0.3	98
A3	0.8	1.4	0.3	98
B1	0.8	1.2	0.2	94
B2	0.8	1.2	0.1	89

[a] Equivalents to monomer.

3,5-Bis[(pentafluorobenzyl)-oxy]phenol (6)

To a dry three-necked 100-mL round bottomed flask equipped with a gas inlet adapter and pressure equalizing addition funnel was charged a magnetic stirrer, phloroglucinol (1.5 g, 11.9 mmol, 1.0 equiv) potassium carbonate (1.81 g, 13.09 mmol, 1.1 equiv), 18-crown-6 (0.314 g, ca. 0.1 equiv) and acetone (75 mL). The mixture was stirred for 45 min at room temperature before the drop-wise addition of 2,3,4,5,6-pentafluorobenzyl bromide (3.105 g, 11.9 mmol, 1.0 equiv), and the mixture was stirred for 3 days. The reaction mixture was filtered, solvent was removed under reduced pressure, and the beige/orange solid was taken up in ethyl acetate (75 mL) and partitioned between 1 M HCl (50 mL), water (50 mL, two times) and saturated potassium chloride. The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure. The solid was purified by flash column chromatography with eluting with 80% hexanes/ethyl acetate increasing polarity to ethyl acetate to yield a white solid: yield 0.48 g (16.6%).

T_g 1.1 °C; $T_d = 181.7$ °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.04 (t, $J = 1.47$ Hz, 4H), 6.12 (d, $J = 2.13$ Hz), 6.17 (t, $J = 2.13$ Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 57.42, 94.61, 96.01, 109.8, 135.8, 139.2, 140.1, 143.5, 144.0, 147.3, 157.5, 159.9; ^{19}F NMR δ −142.29 (dd, $J = 9.56$ and 15.36 Hz, *ortho*-F), −152.51 (t, $J = 20.68$ Hz, *para*-F), −162.01 (dt, $J = 7.81$ and 13.59 Hz), *meta*-F; IR (ATR, cm^{-1}) 3384, 2962, 1658, 1597, 1522, 1502, 1466, 1380, 1309, 1146, 1053, 974, 938; GCMS: calcd for $C_{20}H_8F_{10}O_3$ (M^+) 486.0314; Found 486.0320.

Polyfluorinated Poly-(benzyl-oxyphenol) Polymers (7)

To a dry flask under nitrogen was added 3,5-bis[(pentafluorobenzyl)oxy]phenol (0.1 g, 0.21 mmol, 1.0 equiv), potassium carbonate (0.0341 g, 60.25 mmol, 1.2 equiv), 18-crown-6 (0.0163 g, 0.06 mmol, 0.3 equiv), dry toluene (0.25 mL, 0.8 M), and a magnetic stirrer. The mixture quickly turned purple and was vigorously stirred for 24 h. After 2 h, a small aliquot was taken for MALDI-TOF analysis. After 24 h, the mixture was taken up in dichloromethane (50 mL) and partitioned between 1 M HCl (40 mL), water (40 mL), saturated

potassium chloride (30 mL), and the organic layer dried over magnesium sulfate. The solvent was removed under reduced pressure to afford an off-white yellowish solid. The product was characterized without any further purification; yield 84 mg (86%).

$M_w = 54{,}423$, $M_w/M_n = 2.54$; T_g 80.9 °C; $T_d = 341.0$ °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.04 (t, $J = 1.47$ Hz, 4H), 6.12 (d, $J = 2.13$ Hz), 6.17 (t, $J = 2.13$ Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 57.42, 94.61, 96.01, 109.8, 135.8, 139.2, 140.1, 143.5, 144.0, 147.3, 157.5, 159.9; ^{19}F NMR δ −142.29 (dd, $J = 9.56$ and 15.36 Hz, *ortho*-F), −152.51 (t, $J = 20.68$ Hz, *para*-F), −162.01 (dt, $J = 7.81$ and 13.59 Hz, *meta*-F); IR (ATR, cm^{-1}) 3384, 2962, 1658, 1597, 1522, 1502, 1466, 1380, 1309, 1146, 1053, 974, 938.

RESULTS AND DISCUSSION

Previous work demonstrated the synthesis for hyperbranched perfluorinated polymers from sodium/toluene suspensions or sodium potassium alloy, which prevent any safe scale up of the polymerization.[16] Therefore, potassium carbonate was investigated here as an alternative base. Initial polymerization experiments using potassium carbonate were successful, although a phase transfer agent was required to achieve high conversions. Rarely, red gelatinous side products were observed—which was a common side product of earlier polymerizations using sodium metal. A model compound was used to identify the red side products, which are characteristic of pregelation processes in hyperbranched perfluorinated systems. Furthermore, the new polymerization system was versatile toward polymerization of other perfluorinated polymers.

Model Experiments

A model compound (**1**) was exposed to a variety of bases in presence of 18-crown-6 phase transfer agent. This allowed for the source of discoloration and sequential gelation during polymerization of perfluorinated AB_2 monomers to be identified for the first time. It was expected that the source of discoloration could be attributed to extended conjugation resulting from interlinking reactions between pentafluorophenyl rings. The model (**1**) was chosen because the absence of a benzyl alcohol group allows for study of the nucleophilic aromatic substitution reaction on the pentafluorophenyl ring exclusively. Furthermore, steric hindrance and activation energy of the perfluorinated rings of both the model (**1**) and the monomers (**4**) and (**6**) were considered similar (Fig. 3).

Side Product Identification

Reaction of the model with potassium carbonate/18-crown-6 in acetonitrile with water (10 equiv) induced reddening in 24 h at reflux, or over several days at room temperature. Negatively charged mass spectral analysis revealed the formation hydoxy-substituted model as well as ether-linked oligomers of the model (Fig. 4, also GPC data, not shown). Signals for the dimer and trimer of the model in the HRMS spectrum show that the negative ion being generated corresponds to oligomers with no terminal hydroxyl groups

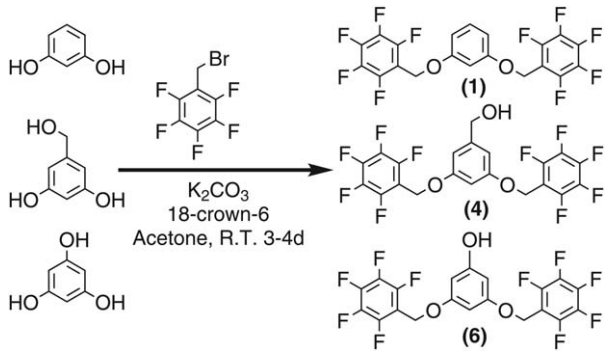

FIGURE 3 Synthetic pathway for penta-fluorinated model (1), benzyl alcohol-bearing monomer (4), and phenol-bearing monomer (6).

(dimer, $C_{40}H_{15}F_{18}O_5^-$, calcd $m/z = 917.0638$, found $m/z = 916.9954$). This suggested that the anion was being generated from proton abstraction along the hydrocarbon backbone. While unexpected, this proton abstraction may be possible at the benzyl ether position. Deprotonation at the benzyl ether position would produce a carbanion, which is stabilized by extended conjugation with both aromatic rings (Fig. 4). Furthermore, a carbanion generated at the benzyl ether position would be stabilized inductively with the neighboring oxygen and neighboring electron-deficient perfluorinated ring. When the benzyl ether is deprotonated, conjugation between aromatic rings combined with the electron withdrawing characteristics of perfluorinated segments results in a low-energy, highly stable ionic species that is red in color. These results suggest that a reactive hydroxide species that was capable of crosslinking perfluorinated rings was produced by hydroxide substitution along the perfluorinated ring. Hydroxide was generated from the *in situ* association of water with the potassium carbonate/crown ether system. Additional base (present as K_2CO_3) then deprotonated the newly formed arylfluoro-phenol, creating a nucleophile attacking a *para*-fluorine on another model compound.

In a second experiment, the model was reacted with potassium hydroxide in presence of 18-crown-6 in acetonitrile at room temperature to examine the susceptibility and regioselectivity of perfluorinated aromatics to hydroxide substitution. In this case, the hydroxide was directly introduced into the system rather than generated *in situ* from the association of K_2CO_3 with water. Discoloration ensued almost immediately after the addition of potassium hydroxide to the model. Negatively charged mass spectral analysis revealed that hydroxide was incorporated along the perfluorinated ring. Because this experiment did not rely on *in situ* hydroxide generation, and no (non-nucleophilic) K_2CO_3 base was present, substitution processes were enhanced, while interlinking processes leading to oligomerization were suppressed. This allowed for more detailed characterization of the regioselectivity for hydroxide substitution.

The ^{19}F NMR revealed that the hydroxide was incorporated at the *para* position of the perfluorinated ring and upon

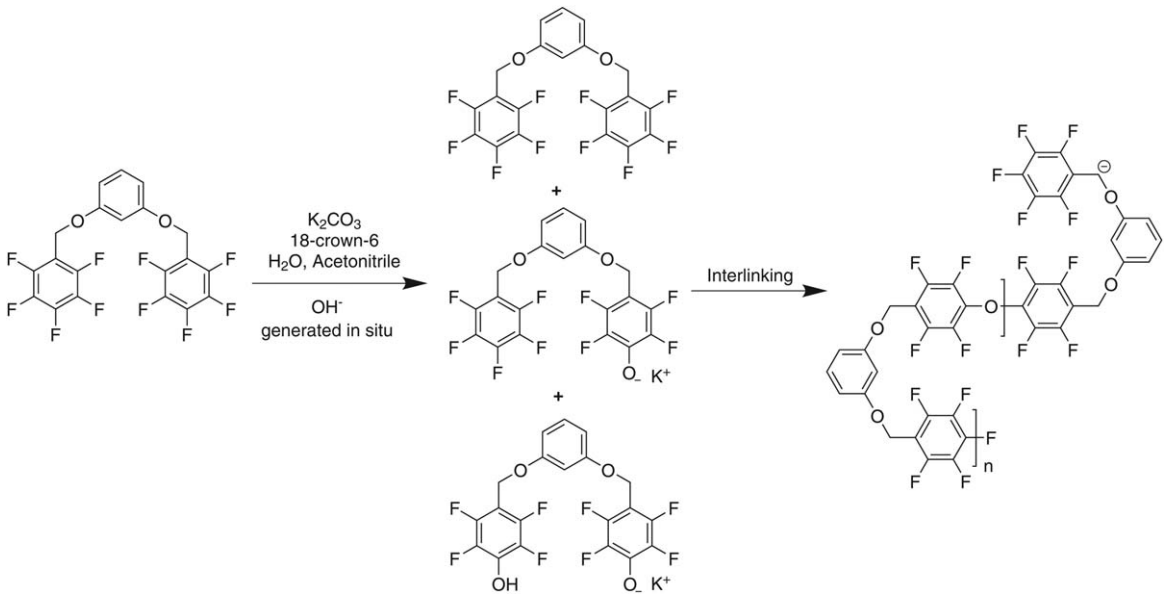

FIGURE 4 Interlinking processes from hydroxide substitution in nonactivated perfluorinated aromatics (anion depicted at benzyl ether position, stabilized by extended conjugation, confirmed by ESI).

treatment of the hydroxide-substituted model with acetic acid the two new fluorine signals immediately shifted downfield (Fig. 5). Further treatment with potassium carbonate illustrated the proton absorption at the phenol was reversible. The downfield shift suggests that the hydroxide substituted perfluorinated ring existed as an anion stabilized by extended conjugation. This stabilizing effect slows kinetics of the interlinking processes due to lowered nucleophilicity associated with extended conjugation. The effect of pH was also demonstrated by UV–vis spectroscopy where, immediately after acidification with acetic acid, the absorption bands at 404 and 486 nm disappeared (Fig. 6), suggesting that the conjugation length decreased upon proton uptake. These data show that the colored side product is a result of the combination of *para*-hydroxy-substituted fluoraryl rings and fluoroaryl ether-linked oligomers. Under appropriate conditions, the hydroxyl can be deprotonated and react with another pentafluorophenyl group (Fig. 4). During a polymerization, this would lead to crosslinking and thus gelation. Deprotonation of the benzyl ether proton results in a stabilized anion with extended conjugation that is red in color. These results suggest that a polymerization should be performed in absence of water and would be best in a solvent that is immiscible with water or less susceptible to water uptake.

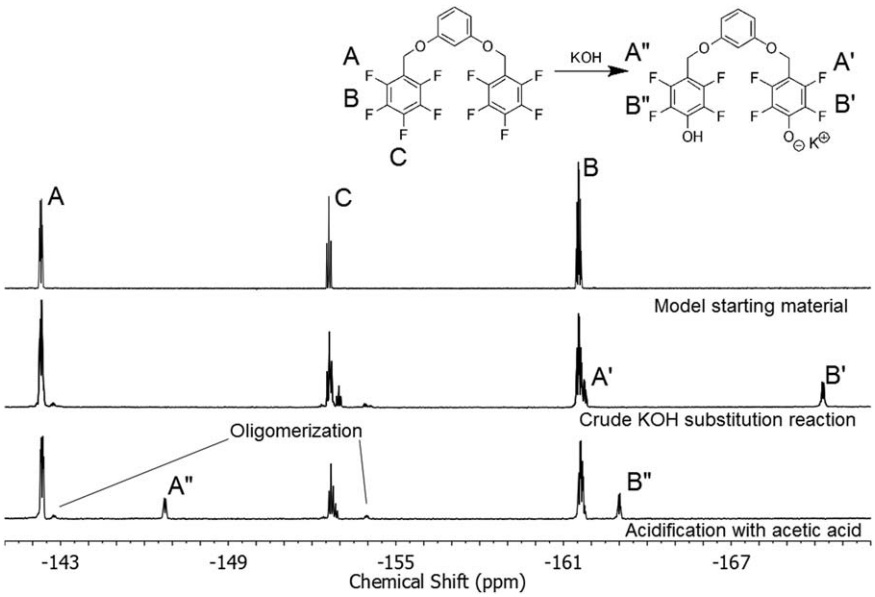

FIGURE 5 ^{19}F NMR of hydroxide-substituted model compound.

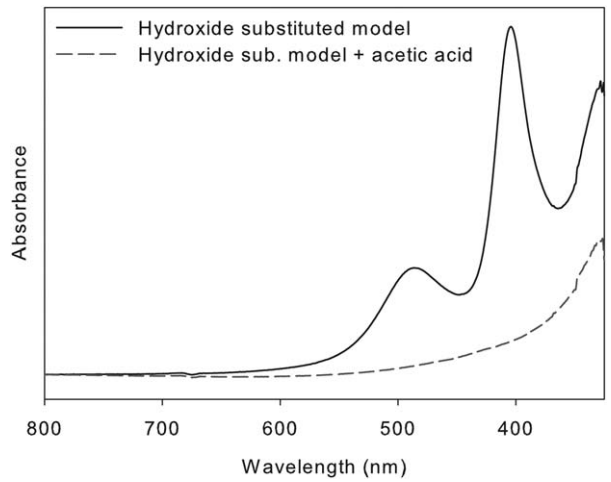

FIGURE 6 Effect of adjusting the pH with acetic acid on hydroxide substituted model (reversible).

Benzyl Alcohol Substitution Along the Model (2) and (3)

To assess the reactivity along the perfluorinated ring during a polymerization at room temperature or reflux, the model was exposed to excess benzyl alcohol in presence of base/phase transfer catalyst mixture. Benzyl alcohol was chosen since this nucleophile has similar electronic and steric features as the monomer (Fig. 7). Characterization by ^{19}F NMR illustrated that only the *para*-fluorine carbon centers were susceptible to nucleophilic aromatic addition reactions at room temperature, which resulted in the dibenzyl alcohol substituted model (Fig. 7, Supporting Information Figs. SI1 and SI2). In comparison, when the model was exposed to excess benzyl alcohol in presence of base/phase transfer catalyst mixture at reflux, extensive substitution occurred along the perfluorinated ring (Fig. 7, Supporting Information Figs. SI3 and SI4). Analysis by MALDI-MS in positive ion reflectron mode showed that primarily a tetrasubstituted model formed. Only a minor amount of model substituted with 5 equiv was seen at reflux. No product substituted with 6 equiv was seen in the mass spectrum, which is likely a result of steric hindrance around the fluoroaryl ring. Substitution beyond the *para*-position was found to occur at *ortho*-positions. Alkyl groups are *para*- and *ortho*- directing while oxygen groups are *ortho*- and *meta*- directing in perfluorinated aromatics.[24] This combined activation results in benzyl ether substitutions occurring at the *ortho*- position of the perfluorinated ring, which was expected from activation predictions.[20]

These results suggested that all polymerizations should be performed at room temperature and in a dry atmosphere to avoid crosslinking and enhance *para*-fluorine selectivity in the polycondensation of perfluorinated AB_2 monomers.

Optimization of Polymer Yield and Molecular Weight

The synthesis of monomer (**4**) was modified from previous work[16] by the addition of a saturated potassium chloride wash during the workup. This step was used in each experiment to help draw 18-crown-6 into the aqueous layer and to ensure polymers were potassiated for mass spectral analysis.

The polymerization optimization used the above results to achieve high purity. The reagent stoichiometry and concentration of the polymerization are herein optimized for maximum monomer conversion, maximum molecular weight, and minimal polydispersity. It is known that the reactivity of the *para*-fluorine toward nucleophilic aromatic substitution of strong and weak nucleophiles is dependent on temperature.[20] The group of Zhao et al. reported that the pentafluorophenyl group exhibited temperature-based stepwise reactivity toward nucleophilic aromatic substitution; however, this was more reactive than the monomer (**4**).[23] When monomer (**4**) was exposed to similar conditions in DMF using potassium fluoride as the base no polymerization occurred and slight discoloration ensued. This was attributed to the poor basicity of the fluoride ion. The addition of phase transfer agent (18-crown-6, in excess) induced polymerization, but only 60% conversion was seen after one week. The poor conversion and slow kinetics associated with potassium fluoride-catalyzed polymerization of our monomer is also due to the decreased acidity of the benzyl alcohol relative to the phenol used by Zhao et al. In another report, Xu prepared oligomers of pentafluorobenzyloxy fluorophenones from potassium carbonate and 18-crown-6 in toluene at

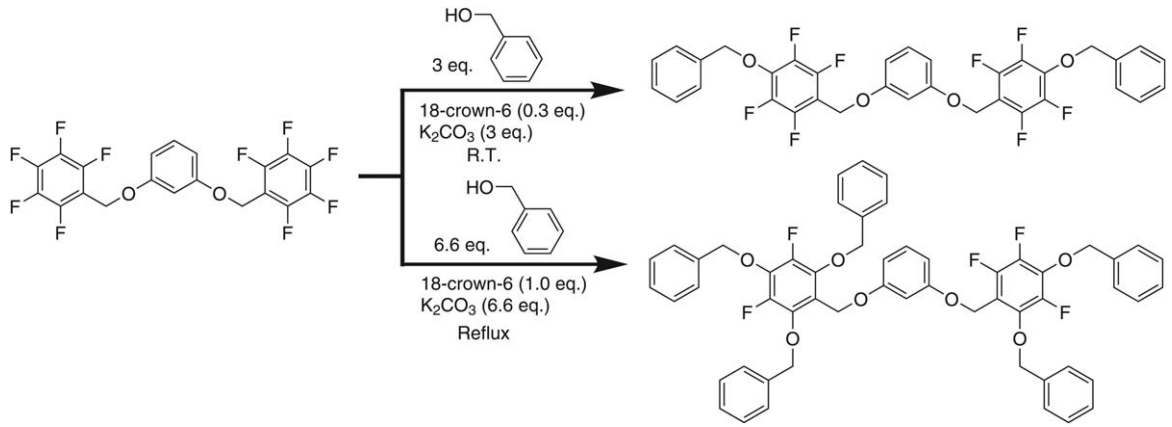

FIGURE 7 Addition of benzyl alcohol (excess) to the model at room temperature and reflux in acetonitrile.

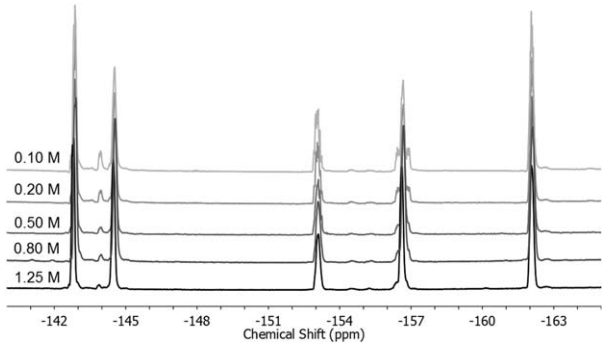

FIGURE 8 Effect of varying the concentration in a polymerization mixture using 1.2 equiv K_2CO_3 and 0.3 equiv 18-crown-6.

room temperature in good yield.[22] Herein, we investigate methods similar to work by Xu toward the preparation of hyperbranched perfluorinated systems.

Initially, the addition of potassium carbonate (1 equiv, in absence of phase transfer agent) to (**4**) in acetonitrile resulted in polymerization with little byproduct formation. Additional potassium carbonate up to 10 equiv, or reducing the particle size of potassium carbonate yielded larger molecular weight, however, even at long reaction time (>3 days), only oligomers were obtained.

That demonstrates that a phase transfer agent is required. The addition of 18-crown-6 to the reaction mixture was found to significantly improve polymerization rates, as seen for similar substitutions.[24,25] The base/phase transfer agent system was optimized for maximum conversion of **4** and purity using a multiparameter approach by varying potassium carbonate stoichiometry, minimalizing 18-crown-6 stoichiometry, varying monomer concentration, and varying solvents at near ideal conditions (Table 1).

The percent conversion during a polymerization was monitored via ^{1}H NMR using unreacted benzyl alcohol groups as a reference and was measured over a variety of conditions. Initial results suggested that 0.8-M monomer concentration yielded large molecular weight and nearly quantitative monomer conversion. The effect of the potassium carbonate equivalence (entry A) was measured in presence of excess phase transfer catalyst (0.3. equiv) (Table 1). The difference in conversion percent between 1.4 and 1.2 equiv of potassium carbonate was negligible, and polymerizations using 1.4 equiv of potassium carbonate were more likely to redden; therefore, 1.2 equiv of potassium carbonate was used for the remainder of the study. Reducing the amount of phase transfer agent (entry B, Table 1) reduced the percent conversion of monomer in polymerization. Quantitative monomer conversion was achieved from 0.3 equiv of 18-crown-6 phase transfer agent. These results suggest that the amount of phase transfer agent determines the quantity of active nucleophiles in the system.

Interestingly, varying the concentration of the monomer during a polymerization alters the structure of the polymer (Fig. 8). This change may be attributed to cyclization. Cyclization occurs when a highly branched polymer closes on itself by a unimolecular reaction. As the concentration of a polymerization mixture increases, the probability of intramolecular cyclization decreases and the probability of bimolecular reactions increases. The effect of monomer concentration on molecular weight is shown in Table 2. The preliminary model studies demonstrated that the nucleophilic aromatic substitution along (**1**) was *para*-specific at room temperature and only at reflux was further substitution possible. This suggests the three new signals in the ^{19}F NMR can be attributed to cyclization during a polymerization, which has been previously demonstrated in HBFPs.[26] This assignment was confirmed by MALDI-TOF (Supporting Information Figs. SI5 and 6). The data confirms that, as concentration is reduced, the probability of intramolecular cyclization increases. Likewise, at 0.05-M monomer concentration, only the cyclic polymer was seen and, at 0.8-M monomer concentration, almost no cyclic polymer was seen relative to the acyclic structure.

Polymerization Kinetics

Interpreting kinetics of phase transfer-assisted nucleophilic aromatic substitutions is difficult due to the complex influence of cations and anions on the activity of charged and neutral species involved in a polymerization.[27] The addition of cation complexing agents are known to activate substitution processes by reducing ion association of the crown ether complex with the alkoxide ion, generating a "free" alkoxide ion with greater reactivity.[28] For simplicity, the kinetics of nucleophilic substitution in polymerizations were studied in acetonitrile, acetone, and toluene from a dilute (0.1 M) monomer mixture by monitoring monomer conversion over time. Kinetic plots of $\ln([M]_0/[M])$ versus time revealed pseudo first-order kinetics, which are characteristic of phase transfer catalyzed nucleophilic aromatic substitution (Fig. 9).[29] Polymerization rate increased with increasing solvent

TABLE 2 Effect of Concentration on Molecular Weight of **(5)** in Acetonitrile

Entries	Conc. (M)	K_2CO_3 (equiv)[a]	18-crown-6 (equiv)[a]	Conversion (%)	M_n (kDa)	M_w/M_n
C1	0.50	1.2	0.3	98.7 ± 1.9	39.2 ± 1.7	2.45 ± 0.13
C2	0.80	1.2	0.3	98.8 ± 1.0	52.7 ± 3.7	2.64 ± 0.45
C3	1.25	1.2	0.3	97.2 ± 0.5	55.2 ± 3.9	1.89 ± 0.02
C4	1.75	1.2	0.3	95.3 ± 1.6	46.8 ± 1.6	1.75 ± 0.10

[a] Equivalents to monomer.

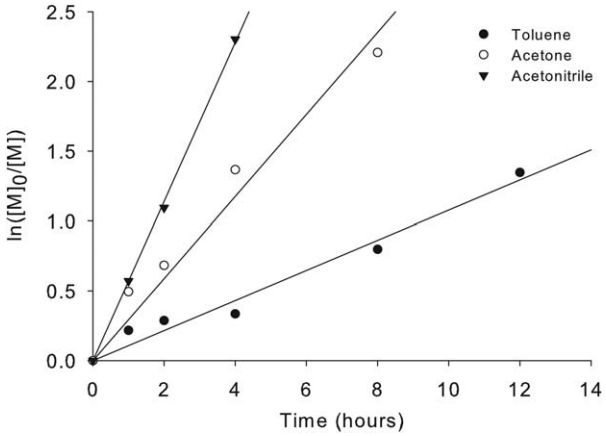

FIGURE 9 Monomer conversion versus time for 0.1 M polymerizations in acetonitrile, acetone, and toluene.

polarity (see dielectric constants). The rate determining step in S_NAr reactions is the formation of the carbon-nucleophile bond of a tetrahedral geometry corresponding to a negatively charged Meisenheimer intermediate (Fig. 1).[27] In more polar solvent, the solvation shell around of the nucleophile is reduced, which effectively increases energy and reactivity of the alkoxide ion, ultimately increasing the rate.[30] The negative charge in this intermediate is delocalized in the electron deficient perfluorinated ring. Kinetic data demonstrated that the nucleophilic aromatic substitution along the fluoroaryl rings occurred most readily in polar aprotic solvents. The rate increased with increasing polarity. For similar systems, solvent should be chosen based on the solubility of the product and kinetics can be enhanced by increasing polarity.

Versatile Polymerization

To demonstrate the versatility of the potassium carbonate/18-crown-6 system in the nucleophilic aromatic substitution of perfluorinated aromatics a second, phenol-bearing AB_2 monomer system was polymerized (Fig. 2). Phloroglucinol was used as precursor to prepare the phenol-bearing monomer in a single step. Low yields for the phloroglucinol monomer synthesis may be attributed to the equivalent electronic environment at each phenol center, which prohibits any regioselective control of the pentafluorobenzyl bromide substitution process. The substitution extent was therefore manipulated by adjusting the stoichiometry of phloroglucinol to pentafluorobenzyl bromide (1 equiv of phenol to 3 equiv of pentafluorobenzyl bromide). The disubstituted phloroglucinol was obtained in relatively good yields (16.6%) compared with similar phloroglucinol etherifications that additionally required tedious protection/deprotection steps (19%).[31]

The phenol-bearing AB_2 system, missing a methylene spacer when compared with the benzyl ether polymer, was expected to be less susceptible to cyclization. By exposing the phenol-based AB_2 monomer to the optimum potassium carbonate/18-crown-6 stoichiometry in a concentrated solution (0.8 M) of toluene and dilute solution of acetonitrile (0.1 M), the cyclization probability during a polymerization was assessed. MALDI-MS revealed that at high concentration a mixture of cyclic and acyclic polymer was present (Fig. 10). At low concentration, only the cyclic structure was observed (Supporting Information Fig. SI7). These results showed instead that removal of one carbon along the benzyl alcohol had insignificant effect on cyclization probability. The cyclized polymer revealed a similar signal (Supporting Information SI8) in the ^{19}F NMR as that for (**5**) (Fig. 8).

Thermal Properties of Hyperbranched Polymers

It was anticipated that removing the benzyl alcohol from the monomer in place for a phenol would increase the stability of the polymer. Thermogravimetric analysis revealed that before polymerization the decomposition onset of the benzyl alcohol-bearing monomer ($T_d = 218.5$ °C) was higher than that of the phenol-bearing monomer ($T_d = 213.6$ °C). After polymerization, the thermal decomposition of both materials increased to 315.5 and 341.0 °C, respectively. The phloroglucinol polymer possessed a considerably higher decomposition onset, which was likely a result of increased stability of the phenyl ether linkage when compared with the benzyl ether. The glass transition temperature of the phloroglucinol polymer was significantly higher as well when compared with the benzyl ether polymer (Fig. 11) due to the reduced

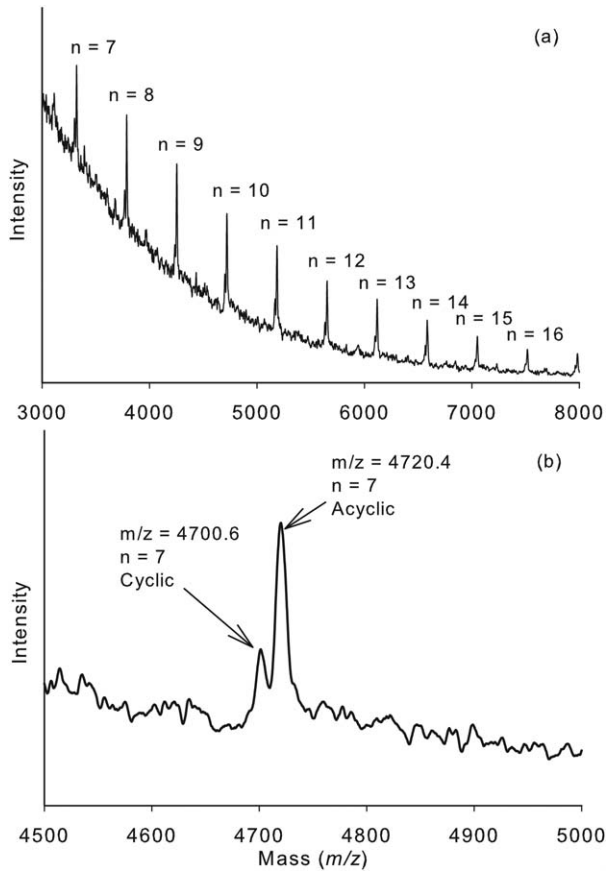

FIGURE 10 MALDI-MS spectrum of polymer (7) from a 0.8 M monomer polymerization after 2 h illustrating primarily acyclic polymer. (a) Full spectrum; (b) enhanced scale.

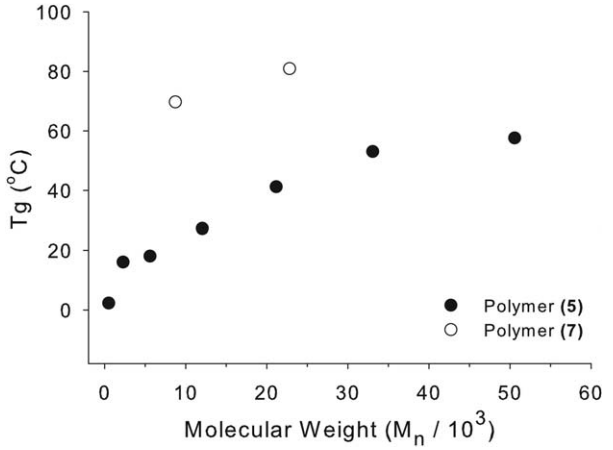

FIGURE 11 Effect of number average molecular weight on glass transition temperature (● benzyl ether HBFP – 5) (○ phenyl ether HBFP – 7).

flexibility of the phenol linkages and smaller free volume associated with a more linear structure. In both polymers, the effect of molecular weight on glass transition temperature leveled off near 20k M_n. This was attributed to the reduced concentration of chain ends associated with higher molecular weights.

CONCLUSIONS

In summary, a facile, alternative synthesis for hyperbranched perfluorinated polymers with greater purity, greater molecular weight, and lower polydispersity index was developed. The extent of substitution along nonactivated perfluorinated aromatics can be controlled with temperature to achieve hierarchical reactivity using 18-crown-6 phase transfer agent and potassium carbonate base system. Cyclization probability and molecular weight of benzyl ether and phenyl ether perfluorinated AB_2 polymers were governed by concentration. Perfluorinated aromatics are susceptible to substitution by hydroxide, which in basic polar aprotic media can further react to yield crosslinked tetrafluorinated aryl ethers. This method is a general method that can be used for nucleophile-bearing perfluorinated systems.

ACKNOWLEDGMENTS

Support from the Science of Advanced Materials graduate program at the University of Central Michigan is gratefully acknowledged.

REFERENCES AND NOTES

1 R. D Chambers, In Fluorine in Organic Chemistry; Wiley: New York, **1973**; Chapter 1, pp 3–5.

2 B. E. Smart, Characteristics of C-F Systems, In Organofluorine Chemistry: Principles and Commercial Applications; B. E. Banks, B. E. Smart, J. C. Tatlow, Eds.; Plenum Press: New York and London, **1994**; Chapter 3, pp. 57–88.

3 R. F. Brady, *Chem. Br.* **1990**, *26*, 427.

4 S. V. Gangal, Perfluorinated polymers, tetrafluoroethylene-perfluorovinyl ether copolymers, in styrene polymers to toys, In Encyclopedia of Polymer Science and Engineering, 2nd Ed.; H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, Eds.; Wiley Interscience: New York, **1989**; Vol. 16, pp 677–679.

5 B. J. Basu, V. D. Kumar, *ISRN Nanotechnology*, **2011**, *2011*, 803910.

6 P. Graham, M. Stone, A. Thorpe, T. G. Nevell, J. Tsibouklis, *J. Fluorine Chem.* **2000**, *104*, 29–36.

7 D. Gan, W. Cao, Z. Wang, *J. Fluorine Chem.* **2002**, *116*, 59–63.

8 J. Shen, T. Hogen-Esch, *J. Am. Chem. Soc.* **2008**, *130*, 10866–10867.

9 D. W. Shin, S. Y. Lee, C. H. Lee, K. Lee, C. H. Park, J. E. McGrath, M. Zhand, R. B Moore, M. D. Lingwood, L. A. Madsen, Y. T. Kim, I. Hwang, Y. M. Lee, *Macromolecules* **2013**, *46*, 7797–7804.

10 Y. Xiu, D. W. Hess, C. P. Wong, In A Novel Method to Prepare Superhydrophobic, Self-Cleaning and Transparent Coatings for Biomedical Applications, Electronic Components and Technology Conference, Reno, NV, May 29–June 1, **2007**.

11 H. Jeong, B. Lim, D. Khim, M. Han, J. Lee, J. Kim, J. Yun, K. Cho, J. Park, D. Kim, *Adv. Mat.* **2013**, *25*, 6416–6422.

12 C. S. Gudipati, C. M. Greenlief, J. A. Johnson, P. Prayongpan, K. L. Wooley, *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 6193–6208.

13 M. E. Arnold, K. Nagai, R. J. Spontak, B. D. Freeman, D. Leroux, D. E. Betts, J. M. DeSimone, F. A. DiGiano, C. K. Stebbins, R. W. Linton, *Macromolecules* **2002**, *35*, 3697–3707.

14 M. A. Hillmyer, T. P. Lodge, *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1–8.

15 M. Seiler, *Fluid Phase Equilib.* **2006**, *241*, 155–174.

16 A. Mueller, T. Kowalewski, K. L. Wooley, *Macromolecules* **1998**, *31*, 776–786.

17 S. Buscemi, A. Pace, R. Calabrese, N. Vivona, P. Metrangolo, *Tetrahedron* **2001**, *57*, 5865–5871.

18 J. Ogikubo, J. L. Worlinsky, Y. Fu, C. Bruckner, *Tetrahedron Lett.* **2013**, *54*, 1707–1710.

19 I. R. Hardcastle, A. M. Barber, J. H. Marriott, M. Jarman, *Tetrahedron Lett.* **2001**, *42*, 1363–1365.

20 J. Baker, M. Muir, *Can. J. Chem.* **2010**, *88*, 588–597.

21 P. D. Buttero, R. Gironda, M. Moret, A. Papagni, M. Parravicini, S. Rizzato, L. Miozzo, *Eur. J. Org. Chem.* **2011**, 2265–2271.

22 L. Xu, R. W. Giese, *J. Fluorine Chem.* **1994**, *67*, 47–51.

23 Z. Zhao, X. Ma, A. Zhang, N. Song, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2423–2433.

24 B. Davis, *Anal. Chem.* **1977**, *49*, 832–834.

25 S. Montanari, C. Paradisi, G. Scorrano, *J. Org. Chem.* **1991**, *56*, 4274–4279.

26 J. K. Gooden, M. L. Gross, A. Mueller, A. D. Stefanescu, K. L. Wooley, *J. Am. Chem. Soc.* **1998**, *120*, 10180–10186.

27 C. A. Bunton, L. Robinson, *J. Am. Chem. Soc. Perk. Trans.* II **1968**, *90*, 5972–5979.

28 C. Paradisi, G. Scorrano, Nucleophilicity, Advances in Chemistry Series 215; American Chemical Society: Washington DC, **1987**; pp 339–354.

29 C. Mariani, G. Modena, G. P. Pizzo, G. Scorrano, *J. Am. Chem. Soc. Perk. Trans. II* **1979**, 1187–1193.

30 C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, 3rd ed.; Wiley-VCH: Weinheim, **2003**.

31 P. M. Tadross, C. D. Gilmore, P. Bugga, S. C. Virgil, B. M. Stoltz, *Org. Lett.* **2010**, *12*, 1224–1227.