Isomeric Hexafluoroisopropylidene-Linked Benzophenone Polymers via Nickel Catalysis

Dejan D. Andjelkovic[†] **and Valerie V. Sheares***[,‡]

Department of Chemistry, Iowa State University, Ames, Iowa 50011, and Department of Chemistry, University of North Carolina at Chapel Hill, 15-26 Venable Hall, CB#3290, Chapel Hill, North Carolina 27599-3290

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ABSTRACT: High-performance hexafluoroisopropylidene (HFIP)-linked benzophenone polymers were synthesized by means of Ni(0)-catalyzed polymerization of newly developed bis(aryl triflate) and bis(aryl chloride) monomers. All polymers were amorphous and soluble in most common organic solvents, thus allowing molecular weight determination and spectroscopic analysis. Number-average molecular weights were in the ranges (14−29) × 10^3 g/mol (GPC/RI) and (24−43) × 10^3 g/mol (GPC/MALLS). Polymers exhibited high thermal stabilities with 10% weight loss temperatures ranging from 509 to 573 °C and 497 to 559 °C in nitrogen and air, respectively. Glass transition temperatures ranged from 161 to 190 °C. All polymers were pale yellow to yellow powders with UV absorption in the range 246−304 nm. As with most previously synthesized 2,5-benzophenone polymers, these new materials exhibited poor film-forming properties and produced brittle films when cast from $CHCl_3$. Consequently, a new strategy based on nickel-catalyzed copolymerization was developed to circumvent this problem and to prepare polymers with higher molecular weights, improved film-forming ability, and excellent mechanical properties. The unique structural characteristics of these new HFIP-interrupted poly(paraphenylene)s make them potentially interesting candidates for separations applications as well as for electronics applications, such as nonvolatile organic memory.

Introduction

Ni(0)-catalyzed polycondensation of difunctional monomers has been used extensively over the past two decades as a very attractive approach toward high-performance polymers.[1−8] The process leads to the formation of aromatic carbon−carbon bonds under mild conditions, while also being quite tolerant of numerous aprotic functional groups.[9] Considerable interest in the mechanism of this reaction has resulted in a better understanding of the role of monomer structure, ligands, temperature, and reducing metal on the polymerization.[1,9,10] It has been shown that polymerization of carefully designed difunctional monomers can easily provide an array of polymeric materials for targeted applications from structural to optoelectronic materials.[3−5,11−15]

Our efforts in this area have been focused on the preparation of a number of functionalized poly(benzophenone)s (PBPs)[3,5,10,16] and hexafluoroisopropylidene (HFIP)-containing materials.[11,12,17] PBPs are unique polymers with conjugated and conformationally rigid backbones. They possess superb thermal stability and exceptional strength and stiffness.[4] The tensile modulus of these materials reaches 7−17 GPa (1−2.5 MPSI), which is 2−4 times greater than other high-performance thermoplastics.[13,14]

In spite of the excellent thermal and mechanical properties of the poly(2,5-benzophenone)s, it has been a challenge to synthesize materials having good film-forming properties. This is due to the inherent structural rigidity of the 2,5-benzophenone repeat units that increase the modulus and simultaneously decrease flexibility and film-forming ability.[3,10,13,16] Flexible, creasable films are highly desirable as they are a requirement for potential electronic, coating, and membrane applications.[11,15,18] As such, numerous approaches have been taken to address this issue. Our group has shown that neither a significant increase in the molecular weight (from $\langle M_n \rangle$ of (25−50) × 10^3 g/mol) nor the incorporation of various flexible side groups improves the film-forming properties of the homopolymers.[10] In fact, the only flexible films that have been formed have been made from multiblock copolymers with bisphenol A based polyarylene ether ketone or from cross-linked copolymers that formed thermoset films.[16,19,20]

As previously mentioned, we have also synthesized a new class of HFIP-containing polymers by Ni(0)-catalyzed polymerization of the corresponding bischloride monomers.[11,12] For example, poly[[1,1′-biphenyl]-4,4′-diyl[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]] (**PDTFE**), a highly soluble, aromatic glassy polymer with excellent thermal stability, minimal moisture absorption, low dielectric constant, and very good gas permeability properties, has been produced. In contrast to the polybenzophenones, the HFIP-interrupted polyparaphenylene backbone has increased mobility and solubility, allowing the formation of flexible, creasable films when cast from chloroform solution. These changes are the consequences of the higher degrees of freedom to rotation of sp^3 carbon atoms in HFIP units vs sp^2 carbon atoms in the benzophenone units.

The goal of the present work is the development of a new class of HFIP-containing polymers with the combined structural features of the above-mentioned PBPs and HFIP polymers. This combination of structural features may extend the utility of these materials to applications that were previously inaccessible. Specifically, the design and synthesis of HFIP-linked isomeric benzophenone polymers via Ni(0)-catalyzed coupling polymerization of newly developed bis(aryl chloride) and bis(aryl triflate) monomers are described. On the basis of our model studies, a new method for the optimization of polymer properties using Ni(0)-catalyzed copolymerization of newly developed multifunctional monomers is presented.

[†] Iowa State University.

[‡] University of North Carolina at Chapel Hill.

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Experimental Section

Materials. All materials were purchased from either Aldrich or Fisher and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium and benzophenone prior to use. Bipyridine (Bipy) was purified by recrystallization from ethanol while triphenylphosphine (TPP) was recrystallized from cyclohexane. Both reagents were dried under vacuum for 24 h at room temperature and stored in the glovebox under nitrogen. The catalyst $(Ph_3P)_2NiCl_2$ and powdered (100 mesh) zinc (99.999%) were purchased from Aldrich and stored under nitrogen.

Characterization. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using either a Varian VXR400 (400 MHz) or a VXR300 (300 MHz) spectrometer in deuterated methylene chloride (CD_2Cl_2). FT-IR measurements were conducted on a Schimadzu 8300 instrument in attenuated total reflectance (ATR) mode. Elemental analysis of the synthesized monomers and polymers was performed using a Perkin-Elmer model 2400 series II CHN/S instrument. Molecular weights, relative to narrow polystyrene standards, were measured using a Waters GPC system consisting of a Waters 510 pump, a Waters 717 autosampler, a Wyatt Optilab DSP refractometer, and a Wyatt Dawn EOS light scattering detector. THF was used as the mobile phase at a flow rate of 1 mL/min with a sample injection volume of 200 μL. The system was equipped with four Styragel columns (Polymer labs PLgel 100, 500, 1×10^4, and 1×10^5 Å) and heated at 40 °C. The d*n*/d*c* measurements were performed in THF at a flow rate of 0.2 mL/min using the above-mentioned Wyatt Optilab DSP refractometer connected to the GPC system. Sample solutions were injected manually through the 1 mL loop connected to the switchboard. Glass transition temperatures were determined by differential scanning calorimetry (DSC) at the inflection point of the endotherm using a Perkin-Elmer Pyris 1 instrument under a nitrogen purge at a heating rate of 20 °C/min. Monomer melting points were also measured using DSC. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7 in nitrogen and in air at a heating rate of 20 °C/min. UV−vis spectra were measured on a HP 8542A diode array spectrophotometer using polymer solutions in THF with 0.05 mmol/L concentrations calculated with respect to the repeating units. Dynamic mechanical analysis (DMA) data were obtained using a Perkin-Elmer dynamic mechanical analyzer DMA Pyris-7e in the three-point bending mode. Rectangular specimens of 1 mm thickness and 5 mm depth were used for the analysis. The width to depth ratio was maintained at ∼3.

Monomer Synthesis. 2,2-Bis(*p*-methoxyphenyl)hexafluoropropane (1). Commercially available 60% sodium hydride in oil (7.2 g, 0.18 mol) was added to a 500 mL three-necked round-bottom flask equipped with a condenser. The flask was sealed with a rubber septum and purged with argon. *n*-Pentane (40 mL) was added to the flask via syringe, stirred for 5 min, and then allowed to settle for 1 min. Pentane solution above the solid sodium hydride was removed using a syringe, and the process was repeated twice with pentane and once with dry THF. After all of the oil was removed from the suspension, the flask was charged with 100 mL of dry THF and stirred for 10 min. Commercially available 2,2-bis(hydroxyphenyl)hexafluoropropane (BisAF) (20.0 g, 0.06 mol) was dissolved in 150 mL of THF into a 250 mL round-bottom flask and sealed with a septum. The BisAF solution was added dropwise to the NaH solution via cannula under an argon purge, and the reaction mixture was left to reflux for 12 h. The solution was cooled in an ice bath and slowly charged with a mixture of dimethyl sulfate (17 mL, 0.18 mol) in 200 mL of THF. After addition, the ice bath was removed and the reaction mixture was refluxed for 4 h. The mixture was allowed to cool to room temperature and filtered. The filtrate was concentrated under reduced pressure, dissolved in 500 mL of *n*-pentane, and purified by flash chromatography on basic alumina. Pentane was removed under reduced pressure to give 21.0 g (96%) of colorless dense liquid. Anal. Calcd for $C_{17}H_{14}O_2F_6$: C, 56.04; H, 3.85. Found: C, 56.35; H, 4.14. FT-IR: 3009 (weak), 2964, 1609, 1516, 1250, 1166, 1037, 966, 925, 823, 740 cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.35$ (d, $J_{ortho} = 8.79$ Hz, 2H); 6.90 (dt, $J_{ortho} = 9.18$ Hz, $J_{meta} = 2.10$ Hz, 2H); 3.84 (s, 3H). ^{13}C NMR: $\delta = 64.41$ (septet, $^2J_{C-F} = 100.08$ Hz, $C(CF_3)_2$), 125.34 (quartet, $^1J_{C-F} = 1131.24$ Hz, CF_3), 55.85 (s, $2CH_3$), 114.23, 126.03, 132.14, 160.70. ^{19}F NMR: $\delta = -64.88$ (s, 6F, $2CF_3$).

2,2-Bis((3-benzoyl)-4-hydroxyphenyl)hexafluoropropane (2). 2,2-Bis(*p*-methoxyphenyl)hexafluoropropane (115.23 g, 0.317 mol), 300 mL of nitromethane, and 114 mL (1.266 mol) of benzoyl chloride were mixed in a 1 L round-bottom flask equipped with a $CaCl_2$ drying tube and stirred in an ice bath. The $AlCl_3$ (169.05 g, 1.27 mol) was added in small portions. Upon the addition of $AlCl_3$, the reaction mixture was left to stir overnight at room temperature. HCl that evolved during the reaction was collected in a $NaHCO_3$ trap. The reaction mixture was then poured into 500 mL of 10% HCl in ice water. The precipitate was extracted with CH_2Cl_2, washed twice with saturated $NaHCO_3$ and brine, dried over anhydrous sodium sulfate, and decolorized three times with activated charcoal. The solvent was removed under reduced pressure, and the product recrystallized from *n*-heptane/ethyl acetate (4:1) to yield 120.5 g (70%) of yellow crystals; mp = 149.4 °C (DSC). Anal. Calcd for $C_{29}H_{18}O_4F_6$: C, 63.97; H, 3.31. Found: C, 63.98; H, 3.70. FT-IR: 3063 (broad, weak, OH), 1627 (C═O), 1490, 1334, 1205, 1179, 1135, 1005, 704 cm^{-1}. ^{1}H NMR: $\delta = 7.12$ (d, $J = 9.0$ Hz), 7.47 (t, $J = 7.4$ Hz), 7.54 (d, $J = 8.96$ Hz), 7.57−7.64 (m), 7.70 (d, $J = 1.92$ Hz), 12.05 (s, OH). ^{13}C NMR: $\delta = 63.53$ (septet, $^2J_{C-F} = 103.12$ Hz, $C(CF_3)_2$), 124.30 (quartet, $^1J_{C-F} = 1144$ Hz, CF_3), 115.55, 118.86, 123.01, 128.56, 129.55, 132.87, 135.49, 137.05, 137.45, 163.54, 201.02 (CO). ^{19}F NMR: $\delta = -65.10$ (s, 6F, $2CF_3$).

2,2-Bis(3-(4-fluorobenzoyl)-4-hydroxyphenyl)hexafluoropropane (3). Following the same procedure for the synthesis of **2**, 24.8 g (0.068 mol) of **1** was acylated using 32 mL (0.273 mol) of 4-fluorobenzoyl chloride in the presence of 36.3 g (0.273 mol) of $AlCl_3$. Recrystallization yielded 30.19 g (74.5%) of yellow crystals; mp = 146.6 °C (DSC). Anal. Calcd for $C_{29}H_{16}O_4F_8$: C, 60.0; H, 2.76. Found: C, 60.02; H, 3.43. FT-IR: 3080 (broad, weak, OH), 1627 (C═O), 1601, 1485, 1334, 1227, 1205, 1152, 1006, 850, 793 cm^{-1}. ^{1}H NMR: $\delta = 7.10-7.20$ (m, 6H), 7.51 (dd, $J_{ortho} = 8.96$ Hz, $J_{meta} = 1.76$ Hz, 2H), 7.60−7.63 (m, 4H), 7.64 (d, $J_{meta} = 1.48$ Hz, 2H), 11.89 (s, 2H, OH). ^{13}C NMR: $\delta = 63.88$ (septet, $^2J_{C-F} = 101.6$ Hz, $C(CF_3)_2$), 116.17, (d, $^2J_{C-F(ortho)} = 87.96$ Hz, C_{aryl}), 119.13, 119.30, 123.37, 124.61 (quartet, $^1J_{C-F} = 1141.84$ Hz, CF_3), 132.62 (d, $^3J_{C-F(meta)} = 36.4$ Hz, C_{aryl}), 133.67 (d, $^4J_{C-F(para)} = 12.12$ Hz, C_{aryl}), 135.41, 137.83, 163.77, 165.92 (d, $^1J_{C-F} = 1011.44$ Hz, $C_{aryl}-F$), 199.72 (CO). ^{19}F NMR: $\delta = -65.11$ (s, 6F, $2CF_3$), −106.23 (m, 1F, $C_{ring}F$).

2,2-Bis(3-(4-chlorobenzoyl)-4-hydroxyphenyl)hexafluoropropane (4). Following the same procedure for the synthesis of **2**, 20.7 g (0.057 mol) of **1** was acylated using 28.9 mL (0.228 mol) of 4-chlorobenzoyl chloride in the presence of 45.4 g (0.341 mol) of $AlCl_3$. Recrystallization gave 17.1 g (49%) of yellow crystals; mp = 138.8 °C (DSC). Anal. Calcd for $C_{29}H_{16}O_4F_6Cl_2$: C, 56.78; H, 2.61. Found: C, 56.91; H, 3.11. FT-IR: 3063 (broad, weak, OH), 1631 (C═O), 1592, 1490, 1330, 1254, 1210, 1179, 1121, 921, 779 cm^{-1}. ^{1}H NMR: $\delta = 7.11-7.13$ (d, $J_{ortho} = 9.0$, 2H), 7.46 (dt, $J_{ortho} = 8.48$ Hz, $J_{meta} = 1.92$ Hz, 4H), 7.51 (dd, $J_{ortho} = 9.16$, $J_{meta} = 1.76$ Hz, 2H), 7.56 (dt, $J_{ortho} = 8.6$ Hz, $J_{meta} = 1.92$ Hz, 4H), 7.67 (d, $J_{ortho} = 2.12$, 2H), 11.89 (s, 2H, OH). ^{13}C NMR: $\delta = 63.88$ (septet, $^2J_{C-F} = 101.56$ Hz, $C(CF_3)_2$), 124.60 (quartet, $^1J_{C-F} = 1141.84$ Hz, CF_3), 119.04, 119.38, 123.40, 129.30, 131.39, 135.32, 135.77, 137.97, 139.64, 163.83, 199.95 (CO). ^{19}F NMR: $\delta = -65.06$ (s, 6F, $2CF_3$).

2,2-Bis(3-benzoyl-4-(trifluoromethanesulfonyl)oxyphenyl)hexafluoropropane (5). To an ice cooled biphasic mixture of toluene (20 mL), 30% (w/v) aqueous K_3PO_4 (40.5 mL), and **2** (5.515 g, 10.14 mmol) was added dropwise 4.1 mL of trifluoromethanesulfonic anhydride (24.3 mmol) at a rate to keep the reaction temperature below 10 °C. The reaction was allowed to warm to ambient temperature and stirred for 1 h. The layers were separated, and the toluene layer was washed twice with 50 mL of distilled water, dried over anhydrous sodium sulfate, and concentrated. The resulting dense pale yellow liquid was dissolved in a small amount of ether and precipitated into *n*-pentane. The white precipitate was collected by filtration and was recrystallized twice from ethanol to give 4.46 g (55%) of white crystals; mp = 118 °C (DSC). Anal. Calcd for $C_{31}H_{16}O_8F_{12}S_2$: C, 46.04; H, 1.98; S, 7.92. Found: C, 45.78; H, 2.18; S, 7.95. FT-IR: 3110 (weak), 1670 (C═O), 1430, 1250, 1209, 1135, 1088, 1004, 886 cm^{-1}. ^1H NMR: $\delta = 7.46-7.59$ (m, 3H), 7.62−7.68 (m, 1H), 7.70−7.78 (m, 3H). ^{13}C NMR: $\delta = 64.33$ (septet, $^2J_{C-F} = 104.64$ Hz, $C(CF_3)_2$), 119.08 (quartet, $^1J_{C-F} = 1273.76$ Hz, F_3C-SO_3-), 124.12 (quartet, $^1J_{C-F} = 1143.36$ Hz, F_3C-C), 123.72, 129.44, 130.62, 133.07, 133.38, 133.56, 134.76, 134.94, 136.37, 148.08, 191.73 (CO). ^{19}F NMR: $\delta = -65.00$ (s, 3F, F_3C-C), −74.68 (s, 3F, F_3C-SO_3-).

2,2-Bis(3-(4-fluorobenzoyl)-4-(trifluoromethanesulfonyl)oxyphenyl)hexafluoropropane (6). Following the same procedure for the synthesis of **5**, 15.39 g (26.53 mmol) of **3** was acylated using 11.2 mL (66.3 mmol) of trifluoromethanesulfonic anhydride. Recrystallization from ethanol gave 13.21 g (59%) of white crystals; mp 127.4 °C (DSC). Anal. Calcd for $C_{31}H_{14}O_8F_{14}S_2$: C, 44.07; H, 1.66; S, 7.59. Found: C, 43.71; H, 1.835; S, 7.215. FT-IR: 3110 (weak), 1670 (C═O), 1433, 1252, 1209, 1188, 1135, 1089, 1007, 886, 706 cm^{-1}. ^1H NMR: $\delta = 7.17-7.24$ (m, 4H), 7.53−7.58 (m, 4H), 7.75−7.82 (m, 6H). ^{13}C NMR: $\delta = 64.67$ (septet, $^2J_{C-F} = 104.64$ Hz, $C(CF_3)_2$), 118.98 (quartet, $^1J_{C-F} = 1275.28$ Hz, F_3C-SO_3-), 124.01 (quartet, $^1J_{C-F} = 1137.28$ Hz, F_3C-C), 116.70 (d, $^2J_{C-F(ortho)} = 87.96$ Hz, C_{aryl}), 123.72, 132.78 (d, $^4J_{C-F(para)} = 12.16$ Hz, C_{aryl}), 133.11, 133.18, 133.33, 133.38 (d, $^3J_{C-F(meta)} = 40.0$ Hz, C_{aryl}), 134.75, 147.84, 167.04 (d, $^1J_{C-F} = 1020.52$ Hz, $C_{aryl}-F$), 190.17 (CO). ^{19}F NMR: $\delta = -64.49$ (s, 3F, F_3C-C), −74.09 (s, 3F, F_3C-SO_3-), −103.66 (m, 1F, $F-C_{ring}$).

2,2-Bis(3-(4-chlorobenzoyl)-4-methoxyphenyl)hexafluoropropane (7). A mixture of 5.38 g (8.6 mmol) of **4**, 16.2 mL (172 mmol) of dimethyl sulfate, 23.7 g (172 mmol) of K_2CO_3, 250 mL of acetone, and 5 mL of DMF was heated to reflux for 24 h. The reaction mixture was cooled to room temperature, and the potassium salts were removed by suction filtration. The solvent was removed in a rotary evaporator to give a pale yellow solid. Double recrystallization from ethanol provided 3.88 g (70.6% yield) of colorless crystals; mp 194 °C (DSC). Anal. Calcd for $C_{31}H_{20}O_4F_6Cl_2$: C, 58.04; H, 3.12. Found: C, 57.955; H, 3.505. FT-IR: 3060 (weak), 2964 (weak), 1671 (C═O), 1587, 1503, 1419, 1246, 1183, 1166, 1121, 828 cm^{-1}. ^1H NMR: $\delta = 3.75$ (s, 6H, $2CH_3$), 7.06 (d, 2H, $J = 9.0$ Hz), 7.33 (d, $J = 2.0$ Hz, 2H), 7.40 (dt, 4H, $J_{ortho} = 8.52$ Hz, $J_{meta} = 2.20$ Hz), 7.61 (d, broad, 2H, $J = 8.88$ Hz), 7.69 (dt, 4H, $J_{ortho} = 8.52$ Hz, $J_{meta} = 2.20$ Hz). ^{13}C NMR: $\delta = 56.34$ (s, CH_3), 64.07 (septet, $J = 103.12$ Hz, $C(CF_3)_2$), 124.75 (quartet, $J = 1106.4$ Hz, CF_3), 111.99, 125.56, 128.8, 129.23, 131.52, 131.8, 134.2, 136.31, 140.05, 158.22, 194.16 (CO). ^{19}F NMR: $\delta = -64.86$ (s, 3F, F_3C-C).

General Polymerization Procedure. Poly[(2,2′-dibenzoylbiphenyl-4,4′-diyl)[bis(trifluoromethyl)methylene]] (P1). A previously flame-dried two-necked 50 mL pear-shaped flask equipped with an overhead stirrer was charged with 0.63 g (9.6 mmol, 3.1 equiv) of zinc, 0.4 g (0.62 mmol, 0.2 equiv) of catalyst $(Ph_3P)_2NiCl_2$, 0.162 g (0.62 mmol, 0.2 equiv) of Ph_3P, 0.048 g (0.31 mmol, 0.1 equiv) of Bipy, and 0.23 g (0.62 mmol, 0.2 equiv) of tetrabutylammonium iodide. The reagents were combined in the glovebox under a nitrogen atmosphere. The flask was sealed with the septum, evacuated and refilled with argon three times, and charged with 6 mL of anhydrous THF via syringe. The catalyst mixture was stirred and heated in an oil bath at 25 °C under the argon purge. Once the color of the catalyst mixture changed from deep green to dark red, 2.5 g (3.1 mmol) of monomer **5** dissolved in 3 mL of THF was added via syringe. The reaction continued at 65 °C for 24 h. The reaction mixture was then precipitated into 40% HCl/methanol to remove excess zinc and stirred overnight. The precipitate was collected by suction filtration, washed with saturated sodium bicarbonate and methanol, redissolved in chloroform, and reprecipitated into neutral methanol. The mixture was stirred for an additional 24 h and filtered. The recovered solid was dried in a vacuum oven to give 1.45 g (83% yield) of pale yellow powder. Anal. Calcd for $(C_{29}H_{16}O_2F_6)_n$: C, 68.24; H, 3.14. Found: C, 68.10; H, 3.46. FT-IR: 3060 (weak), 1670 (C═O), 1251, 1213, 1184, 1137, 1014, 698 cm^{-1}. ^1H NMR: $\delta = 7.10-7.45$ (m, 12H), 7.56 (d, $J = 7.48$ Hz, 4H). ^{13}C NMR: $\delta = 64.67$ (septet, $J = 104.6$ Hz, $C(CF_3)_2$), 124.35 (quartet, $J = 1137.3$ Hz, CF_3), 128.68, 130.51, 131.39, 131.84, 132.15, 132.53, 133.64, 137.28, 138.99, 140.52, 196.27 (CO). ^{19}F NMR: $\delta = -64.45$ (s, 6F, F_3C-C).

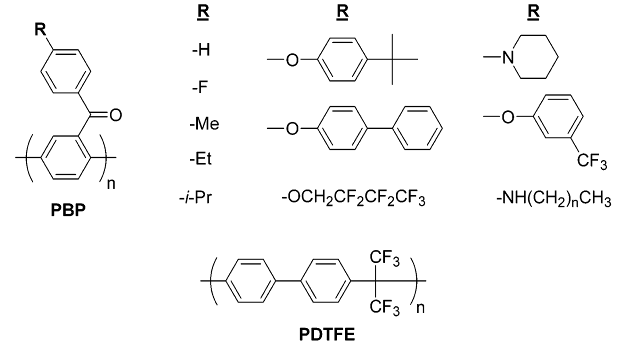


Figure 1. Chemical structures of selected polybenzophenone and HFIP-containing polymers.

Poly[(2,2′-di(4-fluorobenzoyl)biphenyl-4,4′-diyl)[bis(trifluoromethyl)methylene]] (P2). (72% yield). Anal. Calcd for $(C_{29}H_{14}O_2F_8)_n$: C, 63.74; H, 2.56. Found: C, 63.62; H, 2.86. FT-IR: 3074 (weak), 1670 (C═O), 1596, 1503, 1237, 1209, 1184, 1156, 851 cm^{-1}. ^1H NMR: $\delta = 6.93$ (t, $J = 8.52$ Hz, 4H), 7.30−7.50 (m, 6H), 7.58 (m, 4H). ^{13}C NMR: $\delta = 64.73$ (septet, $J = 104.6$ Hz, $C(CF_3)_2$), 115.8 (d, $^2J_{C-F(ortho)} = 87.96$ Hz, C_{aryl}), 124.33 (quartet, $^1J_{C-F} = 1147.88$ Hz, F_3C-C), 131.44, 132.01, 132.37, 132.63, 133.32 (d, $^3J_{C-F(meta)} = 37.92$ Hz, C_{aryl}), 133.56 (d, $^4J_{C-F(para)} = 10.6$ Hz, C_{aryl}), 138.66, 140.65, 164.99, 166.27 (d, $^1J_{C-F} = 1014.2$ Hz, $C_{aryl}-F$), 194.69 (CO). ^{19}F NMR: $\delta = -64.47$ (s, 3F, F_3C-C), −105.52 (m, 1F, $F-C_{ring}$).

Poly[biphenyl-4,4′-diylcarbonyl(6-methoxy-1,3-phenylene)-[bis(trifluoromethyl)methylene](4-methoxy-1,3-phenylene)carbonyl] (P3). 87% yield. Anal. Calcd for $(C_{31}H_{20}O_4F_6)_n$: C, 65.26; H, 3.51. Found: C, 64.59; H, 4.06. FT-IR: 3053 (weak), 2947 (weak), 2840 (weak), 1670 (C═O), 1606, 1251 (ArC−O−C), 1173, 1120, 1028, 1003, 815 cm^{-1}. ^1H NMR: $\delta = 3.75$ (s, 6H, CH_3), 7.06 (d, 2H, $J = 9.08$ Hz), 7.30−7.38 (m, broad low intensity), 7.39 (d, 2H, $J = 1.28$ Hz), 7.42−7.54 (m, broad low intensity), 7.59 (d, 2H, $J = 8.32$), 7.69 (d, 4H, 8.44 Hz), 7.82 (d, 4H, 8.32 Hz). ^{13}C NMR: $\delta = 56.37$ (s, CH_3), 64.10 (septet, $J = 100.08$ Hz, $C(CF_3)_2$), 111.98, 124.79 (quartet, $J = 1137.32$ Hz, CF_3), 125.49, 127.76, 129.17, 130.79, 131.72, 134.05, 137.30, 144.79, 158.23, 194.79 (CO). ^{19}F NMR: $\delta = -64.84$ (s, $(F_3C)_2C$).

Results and Discussion

Monomer Design and Synthesis. The first step toward the synthesis of HFIP-linked benzophenone polymers was the selection of the monomers shown in Figure 2. Structures A and B were designed to resemble 2,2-bis(*p*-chlorophenyl)hexafluoropropane and 2,5-dichlorobenzophenone, whose Ni(0)-mediated polymerizations yield the above-mentioned **PDTFE** and poly(2,5-benzophenone) materials. Type A monomers were structured such that the direction of polymerization coincided with the Bis-AF axis and produced the desired HFIP-linked benzophenone polymers. Because of the ease of synthesis, bistriflates rather than bischlorides were chosen for the type A monomers.

Type B monomers incorporated chlorobenzoyl groups as lateral substituents, allowing the chlorine atoms to serve as reactive sites, while protected hydroxyl groups of the corresponding bisphenol were left available for further chemistry. In this case, the polymerization direction did not coincide with the BisAF axis, but with the lateral substituent axis, leading to a polymer backbone consisting of aromatic rings, carbonyl groups, and HFIP units. Both types of newly developed monomers are symmetrical, rendering triflate and chloro groups

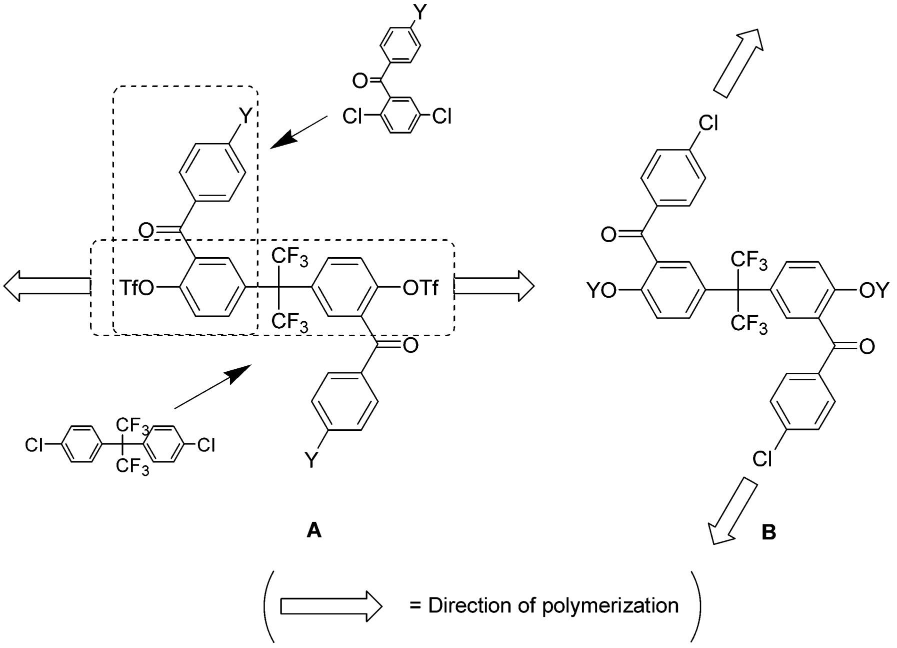
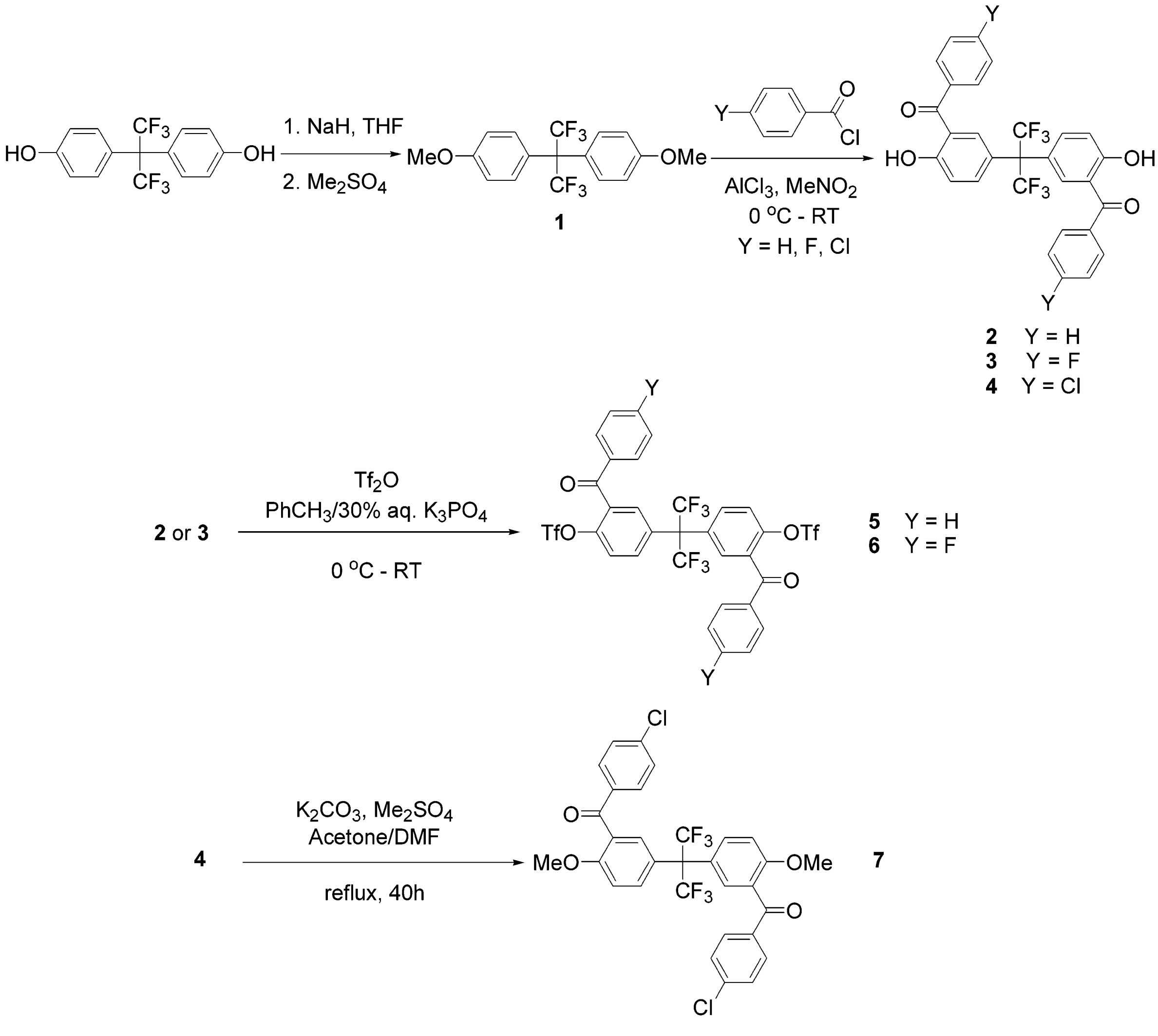


Figure 2. Design of bistriflate (type A) and dichloro (type B) monomers.

Scheme 1. Synthesis of New Bistriflate and Dichloro Monomers 5−7



of equal reactivity and evading problems related to regioselectivity and regularity present in Ni(0)-catalyzed polymerization of unsymmetrical *p*-ditriflates or *p*-dihaloarenes.[1,21]

All monomers were derived from commercially available Bis-AF following the synthesis outlined in Scheme 1. Methylation of Bis-AF yielded 2,2-bis(*p*-methoxyphenyl)hexafluoropropane

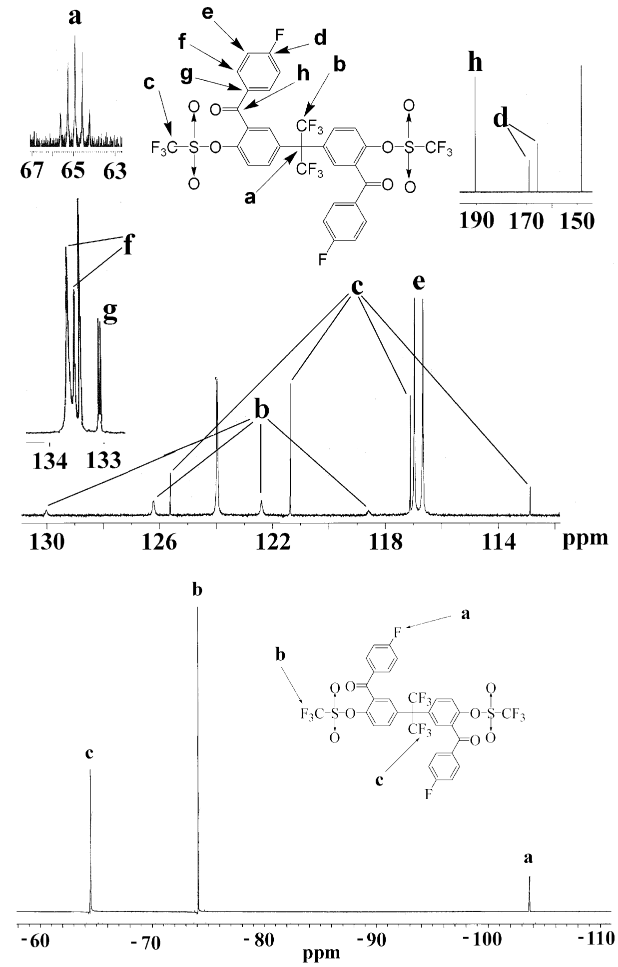


Figure 3. ^{13}C and ^{19}F NMR spectra of monomer **6**.

(**1**), which was subjected to Friedel−Crafts reaction with substituted benzoyl chlorides as acylating agents. Excess $AlCl_3$ catalyzed the demethylation reaction of the acylation products,[20] resulting in symmetrical bisphenols **2**−**4** in 50−75% yield. To the best of our knowledge, this is the first reported synthesis of these bisphenols. The chemical structures of **2**−**4** were verified by NMR, FT-IR, and high-resolution mass spectrometry.

Bisphenols **2** and **3** were converted to bistriflates **5** and **6**, respectively, according to the procedure described by Frantz et al.[22] This method is a straightforward and efficient synthesis of pure aryl triflates under biphasic basic aqueous conditions, avoiding the use of amine bases and time-consuming chromatographic separation. Using this procedure, bistriflate monomers were produced in 55−60% yield. Chemical structures of these new monomers were confirmed by NMR, FT-IR, and high-resolution mass spectrometry. Representative ^{13}C and ^{19}F NMR spectra of **6** are shown in Figure 3. ^{13}C NMR revealed a quintet at 64.6 ppm (a) for the quaternary carbon in HFIP. This peak actually represents a septet due to the coupling with six equivalent fluorine atoms with the outer most peaks hidden in the baseline. ^{13}C also shows two quartets at 119 and 124 ppm (b and c), which correspond to the carbons of the CF_3 groups in trifluoromethanesulfonate (OTf) and HFIP moieties, respectively. The aromatic carbon bound directly to the fluorine atom in the 4-fluorobenzoyl group appeared at 167 ppm (d) as a doublet ($^{1}J_{C-F}$ = 1020.52 Hz) due to the very strong C−F coupling. In addition, the carbonyl carbon is prominent at 190 ppm. The ^{19}F NMR spectrum, as expected, showed three different peaks corresponding to the different types of fluorine atoms present in the monomer.

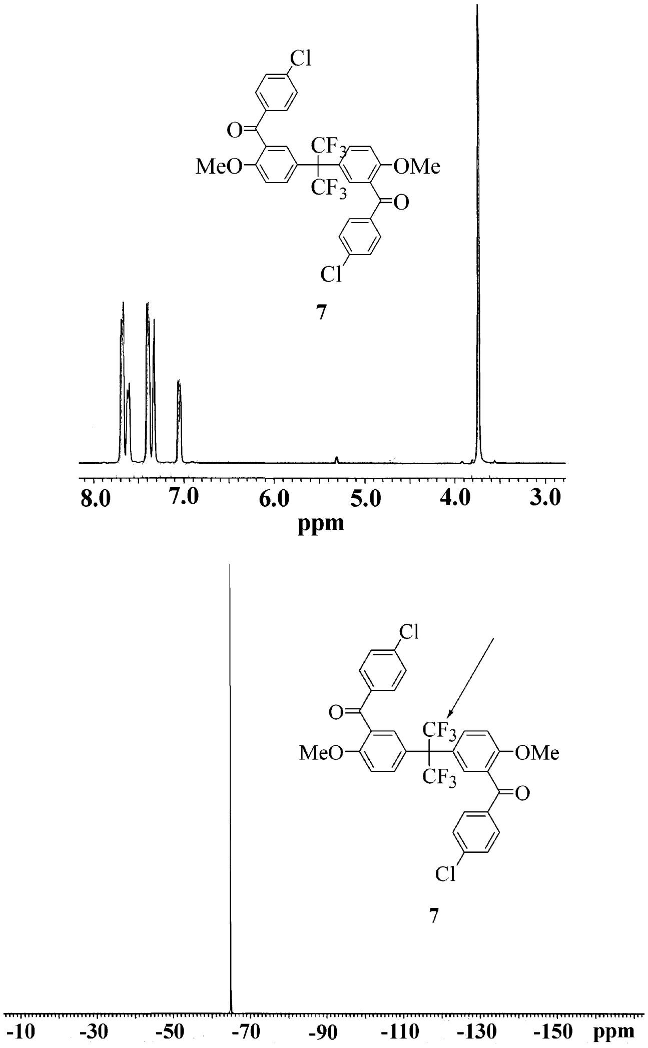
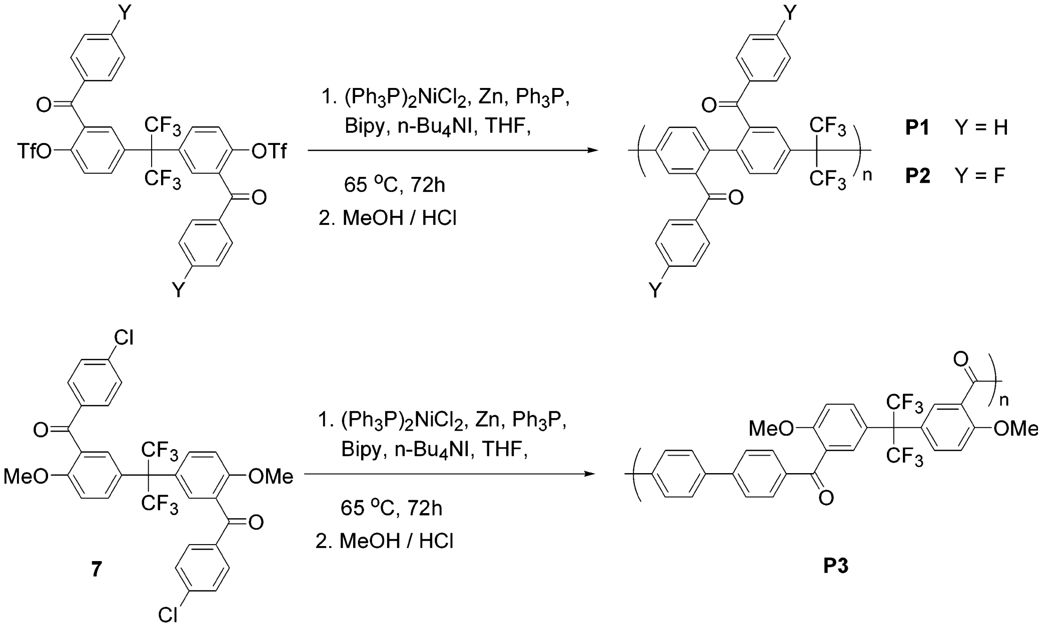


Figure 4. ^{1}H and ^{19}F NMR spectra of monomer **7**.

Type B monomer **7** was prepared by methylation of **4** in 55−70% yield. It has been shown earlier that methoxy groups are compatible with Ni(0)-catalyzed coupling chemistry.[9,23] However, their presence on the benzene ring bearing active (chlorine or triflate) centers has also been shown to promote side reactions, such as phenyl transfer from TPP ligand, which causes premature cease of polymerization and reduction of molecular weights.[9] One of the advantages of monomer **7** is that the methoxy groups are located on the benzene ring which does not bear reactive chlorine atoms (Scheme 1). As a result, the likelihood of side reactions and retardation of reaction rates during polymerization are drastically lowered. Furthermore, if desired, the methoxy groups could be removed during the postpolymerization treatment to yield hydroxyl groups available for further substitution. For example, McOmie et al. described an efficient procedure for demethylation of aryl methyl ethers at or below room temperature using boron tribromide.[24,25] The monomer structure was confirmed by NMR, FT-IR, and high-resolution mass spectrometry. Representative ^{1}H and ^{19}F NMR spectra of **7** are shown in Figure 4. The ^{1}H NMR showed a singlet at 3.75 ppm corresponding to the hydrogen atoms of the methoxy group and several peaks in the 7.0−7.7 ppm region, corresponding to the aromatic hydrogens. Integration of aliphatic to aromatic peaks gave the correct 3:7 ratio. As expected, the ^{19}F NMR spectrum revealed a single peak corresponding to the fluorine atoms in the HFIP unit.

Scheme 2. Synthesis of HFIP-Linked Benzophenone Polymers P1−P3 via Ni(0)-Mediated Homocoupling of Monomers 5−7



Polymer Synthesis and Characterization. The syntheses of HFIP-linked benzophenone polymers **P1−P3** are shown in Scheme 2. All polymerization reactions were conducted in THF using $(Ph_3P)_2NiCl_2$ as a catalyst, Zn as a reducing agent, *n*-Bu_4NI as a bridging agent, and TPP and Bipy as ligands. THF was chosen as the solvent as polymerization of bistriflates, bismesylates, and bischlorides in THF has been shown to minimize reduction and polymer degradation side reactions.[3,10,16,26,27]

Optimization of the reaction conditions (temperature, time, ratio of catalyst components) resulted in the synthesis of moderate to high molecular weight polymers as evidenced by GPC. Number-average molecular weights were in the range $(14-28) \times 10^3$ g/mol by GPC/RI and $(24-43) \times 10^3$ g/mol by GPC/MALLS. The $\langle M_n \rangle$ values determined by GPC/MALLS were higher than those detected by GPC/RI by a factor of 1.5−1.7. These findings were in agreement with our previous observations related to **PDTFE** and were attributed to the differences in the hydrodynamic volumes of polymers **P1−P3** and polystyrene, used as the calibration standard.[11] Similar observations were reported by Carter and co-workers,[15] who also found that GPC/RI underestimated the molecular weight of similar materials by a factor of 1.6−1.8 in comparison with their quasi-elastic light scattering (QELS) data.

Polymers **P1−P3** were confirmed to be the desired HFIP-linked benzophenone materials by ^1H, ^{13}C, ^{19}F NMR, UV−vis, and IR spectroscopies as well as by elemental analysis. In addition, ^{19}F NMR spectral analysis of each polymer showed that all trifluoromethanesulfonate groups at the ends of the polymer chains had been reduced during the acidic workup, rendering the polymer chain ends unreactive. This was confirmed by the complete absence of the resonances at −74 ppm, corresponding to fluorine atoms in these functional groups. Interestingly, this observation was the opposite of that reported by Carter and co-workers, regarding their materials prepared via Ni(0)-mediated Yamamoto-type polycondensation of bisphenol-derived bistriflate monomers.[15] The reason for these differing observations is most likely related to the differences between the two Ni(0)-based polycondensation methods. While Yamamoto's polycondensation method[29,30] requires stoichiometric amounts of Ni(0) catalyst, Bipy, and 1,5-cyclooctadiene (COD) as ligands for the reductive aryl−aryl coupling reaction, the approach that we utilized requires catalytic amounts of Ni(II) salt, bridging agent, and ligands, along with excess reducing agent needed for in situ generation of Ni(0) catalyst.

Table 1. Molecular Weight Data for Polymers P1−P3 and Comparison with the Properties of PBPs and PDTFE[a]

polymer	$\langle M_n \rangle_{GPC/MALLS}$ ($\times 10^{-3}$ g/mol)	$PDI_{GPC/MALLS}$	$DP_{GPC/MALLS}$	d*n*/d*c* (mL/g)
PBP1[28]	24.5	2.4	135	
PBP2[16]	21.1	2.77	106	0.221
PDTFE[11]	19.2/27.5	1.61/1.25	63/91	0.075
P1	28.6/43.0	1.53/1.89	56/84	0.066
P2	14.2/24.4	1.72/1.55	26/45	0.050
P3	17.1/31.4	1.62/1.57	30/55	0.083
P1CRS	43.9/205.0	4.05/6.50	86/402	

[a] Polymerization conditions: $(Ph_3P)_2NiCl_2$ (0.2 equiv), Zn (3.1 equiv), Ph_3P (0.2 equiv), Bipy (0.1 equiv), *n*-Bu_4NI (0.2 equiv), 65 °C, 24 h, equivalents given with respect to the monomer.

Table 2. Thermal and UV−Vis Data for Polymers P1−P3 and Their Comparison with the Properties of PBPs and PDTFE

polymer	$\langle M_n \rangle_{GPC/MALLS}$ ($\times 10^{-3}$ g/mol)	T_g (°C)	$T_{5\%}$ (°C)[a] N_2/air	$T_{10\%}$ (°C)[b] N_2/air	λ_{max} abs (nm)[c]
PBP1[28]	24.5	159	526/530	566/568	
PBP2[16]	21.1	167	576/536	611/566	
PDTFE[11]	19.2/27.5	255	515/515	533/535	266
P1	28.6/43.0	161	548/520	573/553	246
P2	14.2/24.4	163	537/539	557/559	246
P3	17.1/31.4	190	484/469	509/497	304
P1CRS	43.9/205.0	165	527/538	563/558	248

[a] 5% weight loss temperatures determined in nitrogen and air, respectively. [b] 10% weight loss temperatures determined in nitrogen and air, respectively. [c] THF solutions of polymers were used for the analysis.

All polymers were amorphous pale yellow to yellow solids soluble in most common organic solvents such as tetrahydrofuran and chloroform. The materials showed no evidence of crystallinity by wide-angle X-ray diffraction or DSC. An X-ray diffraction pattern of polymer **P1** revealed two peaks at 15° and 24° (see Supporting Information) and closely resembled the X-ray diffraction pattern of the parent **PDTFE** polymer.[11]

Thermal Analysis. The glass transition temperatures (T_g) of the new materials were measured by differential scanning calorimetry (DSC). The results are shown in Table 2. When compared to the parent **PDTFE** (T_g = 255 °C), **P1** and **P2** had significantly lower T_g values of 161 and 163 °C, respectively.

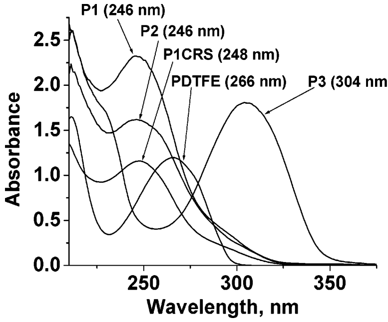


Figure 5. UV−vis spectra of the HFIP-containing polymers measured in THF solution.

This can be attributed to the presence of the bulky benzoyl pendant groups, which effectively separate **P1** and **P2** polymer chains, thus increasing segmental mobility and lowering the activation energy needed for the onset of the long-range cooperative motion of polymer chains.[31] In contrast, the effect of the HFIP unit on PBP materials is quite small, indicating the dominating effect of the benzophenone moiety on conformational rotation in these hybrid structures. Specifically, the T_g values of **P1** and **P2** of 161 and 163 °C, respectively, are similar to their poly(2,5-benzophenone) analogues (**PBP1** = 158 °C, **PBP2** = 167 °C).[16,21] However, the molecular weight of **P2** is significantly lower than the **PBP2** material used for comparison and serves as an indication that the maximum T_g of the polymer has not been achieved. **P3** was compared to a non-HFIP-containing analogue, wholly aromatic polyketone (WAPK) with a T_g of 218 °C, synthesized by Yonezava et al.[32] As expected, **P3** has a much lower T_g due to the presence of the HFIP groups.

Thermal stabilities of the polymers were examined by thermogravimetric analysis (TGA). Polymers **P1** and **P2** showed good thermal stability with 5% weight loss temperatures of 548 and 537 °C in nitrogen and 520 and 539 °C in air, respectively. These values were higher than those for **PDTFE** polymer. Also, these values were higher than those for **P3** (440 °C), whose methoxy groups led to decreased thermal stability. The same trend was observed for 10% weight loss temperatures.

UV−Vis Analysis. The UV−vis spectra of the synthesized polymers were measured in THF solution (Figure 5). Polymers **P1** and **P2** had the same λ_{max} absorbance values of 246 nm, which were blue-shifted when compared to the 266 nm λ_{max} value for **PDTFE** measured in THF. This effect is most likely due to the steric repulsion of the two *ortho* benzoyl groups in the 2,2′-dibenzoylbiphenyl segments of **P1** and **P2**. Namely, bulky groups are known to increase the deviation from coplanarity in biphenyl systems with a consequent loss of conjugation and decrease in λ_{max}.[33] Apparently, this effect is not present in **P3** due to the lack of bulky benzoyl groups on biphenyl segments, which results in a red shift (λ_{max} = 304 nm) when compared to the **PDTFE**. As expected, absorption maxima of the synthesized polymers **P1** and **P2** were much lower than those of analogous **PBP1** and **PBP2** (>350 nm) due to the disrupted conjugation caused by the presence of nonconjugated HFIP unit.

New Cross-Linking Methodology. While new high-performance polymers have been described, the goal of the work was to address the important problems that remain unsolved for 2,5-benzophenone-type polymers. Specifically, the goal was to produce materials with the processable, film-forming properties of our previously synthesized HFIP materials, but with mechanical properties resembling those of the poly(2,5-benzophenone)s. Although the new homopolymers **P1**−**P3** did have good thermal stability and are soluble in common organic solvents, the materials do not have good film-forming properties and gave brittle, noncreasable films when cast from $CHCl_3$. In our previous work, postpolymerization cross-linking chemistry based on nucleophilic aromatic substitution (S_NAr) was used to produce thermoset films with increased chemical resistance, thermal stability, and improved flexibility.[16,20] This method proved to be efficient in the modification of polyparaphenylenes such as poly(4′-fluoro-2,5-diphenyl sulfone)s and poly(4′-fluoro-2,5-benzophenone)s as well as poly(4′-fluorophenyl-bis(4-phenyl)phosphine oxide)s.[8] However, only polymer **P2** meets the structural requirements for this type of modification. Moreover, the resulting materials are thermoset polymers. While useful, the goal here was to gain the desired properties in thermoplastic materials. Therefore, in order to develop a general strategy applicable to any of the polymers made by the nickel coupling chemistry, a different synthetic approach was required. The new method involved Ni(0)-catalyzed copolymerization of the already synthesized monomers **5**−**7** and a newly developed comonomer that is polyfunctional with respect to the polymerization method. This comonomer was used in very small amounts to branch or slightly cross-link the materials.

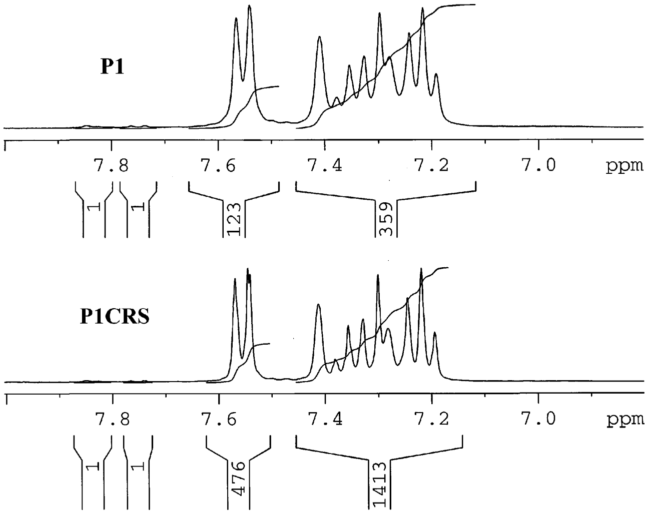
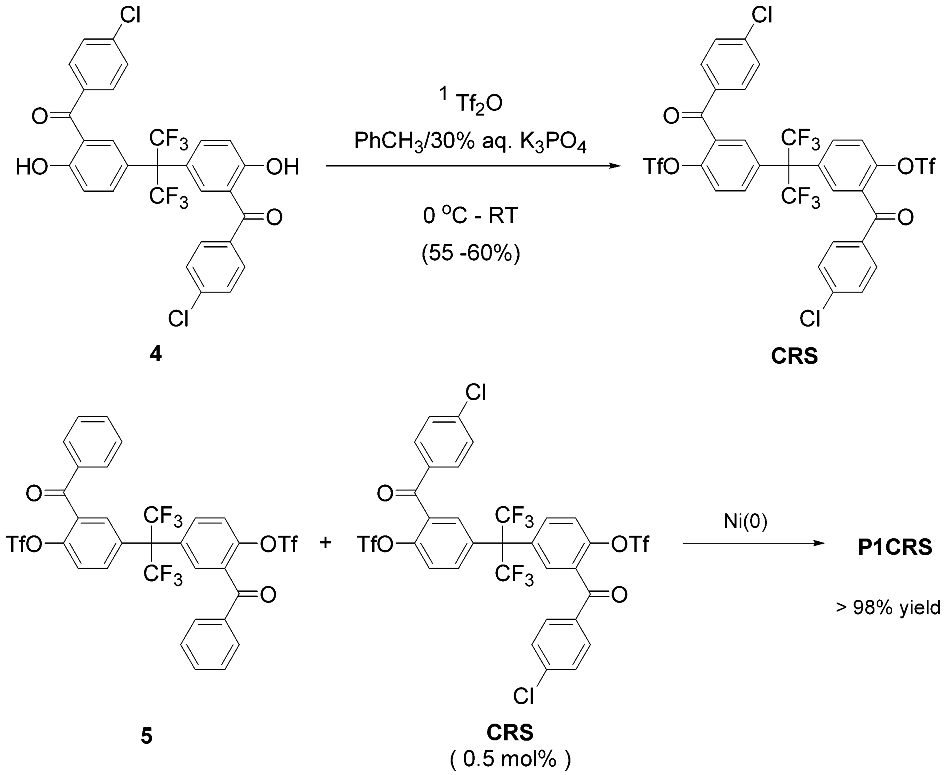


Figure 6. ^1H NMR spectra of polymers **P1** and **P1CRS**.

Again, the first step in this process was the design and synthesis of an effective comonomer. We decided to use the already developed synthetic approach for type A monomers and convert bisphenol **4** into the corresponding bistriflate comonomer 2,2-bis(3-(4-chlorobenzoyl)-4-(trifluoromethanesulfonyl)-oxyphenyl) hexafluoropropane (CRS), as shown in Scheme 3. CRS is a tetrafunctional cross-linker since both chloro and triflate groups are able to effectively undergo Ni(0)-catalyzed coupling. In a model study, the CRS cross-linker was used for Ni(0)-mediated copolymerization with monomer **5**.

The CRS load, as low as 0.5 mol % with respect to monomer **5**, gave almost quantitative yield of soluble, pale yellow copolymer **P1CRS**. The synthesized polymer had a number-average molecular weight of 43 × 10^3 g/mol with a PDI of 4.05 (by GPC/RI) and 20 × 10^4 g/mol and a PDI of 6.50 (by GPC/MALLS) (Table 1). As previously mentioned, in the case of other polymers, GPC/MALLS data gave much higher M_n value than GPC/RI data. The **P1CRS** molecular weight was underestimated by a factor of 4.7. ^1H NMR spectra of **P1** and **P1CRS** revealed two types of peaks in the aromatic region: the low-intensity peaks attributed to the end groups of corresponding polymers and high-intensity peaks attributed to the aromatic hydrogens along the polymer backbone (Figure 6). Their integration provided a good estimate of the average degree

Scheme 3. Synthesis of CRS Comonomer and Copolymerization with Monomer 5 To Produce Copolymer P1CRS



of polymerization (DP) for **P1** (DP = 123) and **P1CRS** (DP = 476). Further comparison of ^{1}H NMR data with the GPC data (Table 1) revealed better correlation with GPC/MALLS data than with GPC/RI data, indicating that the light scattering data were more reliable.

In contrast to the brittle, yellow, opaque films formed when homopolymers of **P1**−**P3** were compression-molded or cast from chloroform, polymer **P1CRS** showed significantly improved properties and led to the formation of more flexible films, which resisted cracking under the same conditions. In addition, **P1CRS** was easily fabricated into rectangular test samples for dynamic mechanical analysis (DMA). DMA of **P1CRS** (Figure 7) was performed in flexure mode with a three-point bending apparatus. The storage modulus of **P1CRS** was very high (~10 GPa at 50 °C). In fact, this value was much higher than the literature values for storage moduli of Nylon-6/6 (2.5 GPa), poly(ether imide) (3.0 GPa), and poly(ether ether ketone) (3.6 GPa) recorded at 50 °C.[34] Furthermore, this value was even higher than the values of **PBP2** (7.5 GPa) and its 4′-biphenyloxy-substituted derivative (6.4 GPa), the highest modulus benzophenone homopolymer prepared earlier in our group.[16]

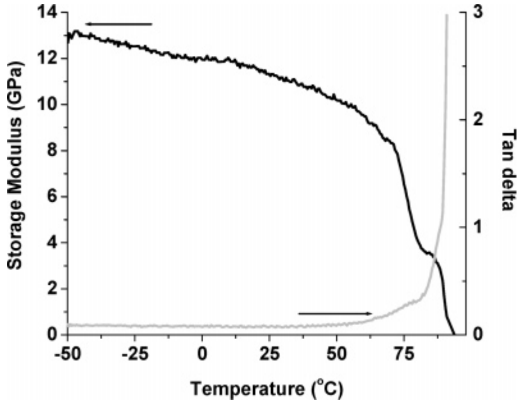


Figure 7. Storage modulus (black) and loss factor (gray) curves obtained form DMA analysis of **P1CRS**.

These initial results confirm that polymer **P1CRS** represents an example of a thermally stable, high modulus, processable high-MW HFIP-linked benzophenone polymer. The unique structural features of these materials also make them potentially interesting in electrical applications where wide-band-gap materials with low current density and good thermoxidative stability are required.[35,36] It has recently been shown that HFIP-containing materials, such as **PDTFE**, demonstrate more stability in terms of a lifetime and thermal stability than poly-(9,9-di-*n*-hexylfluorene) and poly-[(4-*n*-hexyltriphenyl)amine]-based diode-type devices.[15] Moreover, this approach represents a new method of improving the mechanical and film-forming properties of a number of new benzophenone-type materials made via nickel coupling chemistry.

Conclusions

This paper demonstrates the versatility of Ni(0)-mediated polymerization method for the synthesis of variety of isomeric HFIP-containing polymers. Specifically, the results show the efficiency of synthesizing HFIP-linked benzophenone polymers by means of Ni(0)-catalyzed polymerization of newly developed bis(aryl triflate) and bis(aryl chloride) monomers. As with other 2,5-benzophenone containing homopolymers, it was not possible to form flexible tough films. As such, a new strategy was developed incorporating a tetrafunctional monomer. The results confirm that this is a viable route to new 2,5-benzophenone-containing materials that not only are high molecular weight but also are thermally stable and mechanically tough with excellent film-forming properties. On the basis of these initial studies, a range of polymers incorporating 2,5-benzophenone and various functional groups could be synthesized giving materials with a similar combination of desirable properties for electronics, coatings, and separations applications.

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Supporting Information Available: ^{1}H, ^{13}C, ^{19}F NMR, and FT-IR spectra for selected bisphenols, monomers and polymers, a representative X-ray diffraction pattern of polymer **P1**, and GPC, DSC, and TGA graphs for all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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