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Polydimethylsiloxane- (PDMS-) Grafted Fluorocopolymers by a "Grafting through" Strategy Based on Atom Transfer Radical (Co)polymerization

Chong Cheng,[†] Kenya T. Powell,[†] Ezat Khoshdel,[‡] and Karen L. Wooley*,[†]

Center for Materials Innovation, Department of Chemistry and Department of Radiology, Washington University in Saint Louis, Saint Louis, Missouri 63130-4899, and Unilever Research, Port Sunlight, Quarry Road East, Bebington, CH63 3JW, U.K.

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ABSTRACT: Three types of PDMS-grafted fluorocopolymers with various branching features were synthesized based on atom transfer radical polymerization (ATRP) techniques via a "grafting through" approach using methacryloxypropyl-terminated PDMS (PDMSMA) as macromonomer. Copolymers **1**, with a linear fluorinated backbone and linear PDMS grafts, were prepared by copolymerizations of 2,3,4,5,6-pentafluorostyrene (PFS) with PDMSMA. Copolymers **2**, with a hyperbranched fluorinated backbone and linear PDMS-based grafts, were prepared by self-condensing vinyl copolymerization (SCVCP) of an inimer, *p*-chloromethylstyrene (CMS), with PFS and PDMSMA. Copolymers **3**, with a hyperbranched fluorinated core and linear PDMS grafts, were prepared by ATRP of PDMSMA, initiated by benzylic chloride-functionalized hyperbranched fluorocopolymer (obtained by SCVCP of PFS and CMS). A series of characterization methods, including ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies, gel permeation chromatography, elemental analysis, thermogravimetric analysis, and solubility tests, were used to investigate the reaction kinetics, and the compositions, molecular weights, and properties of these copolymers.

Introduction

Over the past few decades, complex polymers, those composed of multiple types of architectural and/or compositional building blocks, have aroused significant and broad interest, due to their special structures and properties.[1−7] Complex polymers not only possess some of the advantageous properties of each of their polymeric components but also can have new and useful properties that emerge from the unique combinations of subunits. Therefore, a broad variety of complex polymers have been developed, and some of them have had important industrial applications.

The synthesis of polymers with hybridized macromolecular architectures and compositions has attracted significant attention from synthetic polymer chemists,[8−12] and atom transfer radical polymerization (ATRP) has been used broadly as a powerful living radical polymerization technique for the preparation of such intricate polymers.[13,14] Many examples exist in the literature, in which multicomponent polymers with grafted structures have been synthesized by ATRP via a "grafting through" approach.[15−29] On the basis of the synthetic methodology of self-condensing vinyl (co)polymerization (SCVP),[30−33] complex polymers with hyperbranched architectures containing different polymer blocks have also been obtained using the ATRP technique.[34]

Fluoropolymers and polysiloxanes are important types of polymers with useful properties. In general, fluoropolymers have low surface energy, low coefficient of friction, excellent dielectric properties and weatherability, and considerable solubilities in supercritical carbon dioxide.[35−38] Polysiloxanes are thermally stable and elastomeric, with low surface energy and high gas permeability.[39−41] With exceptionally good chemical, thermal, and thermooxidative resistance, fluorosilicones (i.e., fluorinated polysiloxanes) have been used as commercial high-temperature lubricants and elastomers.[42−44] Moreover, a variety of complex polymers consisting of fluoropolymer and polysiloxane building blocks have also been prepared for the development of new types of polymer materials with excellent properties.[45−49] For instance, Baradie and Shoichet synthesized graft copolymers with a fluorinated backbone and polydimethylsiloxane (PDMS) grafts by conventional radical copolymerization via a "grafting through" approach and used the thermoplastic graft copolymers for the preparation of hydrophobic and thermally stable coatings.[45]

Our group has long-term interests in fluoropolymers and macromolecular architectures constructed with fluoropolymer building blocks.[50−61] Three types of hyperbranched fluoropolymers (HBFP) with different structural features have been synthesized in our laboratory by either polycondensation of fluorinated AB$_x$ monomers or self-condensing vinyl (co)polymerization using fluorinated inimers and/or monomers.[51−54] Complex cross-linked networks have also been further prepared from hyperbranched fluoropolymers and linear diamine-terminated poly(ethylene glycol) (PEG) or PDMS.[56−58] These networks exhibited enhanced anti-biofouling abilities,[59] unusual sequestration and release behaviors for a variety of small molecule guests,[60] and special mechanical performance.[61]

In this paper, we report our recent synthesis and characterization of three types of PDMS-grafted fluorocopolymers (Figure 1). All these copolymers were prepared based on the ATRP technique via a "grafting through" approach using methacryloxypropyl-terminated PDMS (PDMSMA) as the macromonomer.[62−64] The copolymers **1**, with a linear fluorinated backbone and linear PDMS grafts, were prepared by atom transfer radical copolymerization (ATRCP) of 2,3,4,5,6-pentafluorostyrene (PFS) with PDMSMA. In contrast to polymers reported with similar grafting features,[45−48] **1** possesses poly(PFS)-based backbones having

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* Corresponding author. E-mail: klwooley@artsci.wustl.edu. Telephone: (314) 935-7136. Fax: (314) 935-9844.

[†] Center for Materials Innovation, Department of Chemistry and Department of Radiology, Washington University in Saint Louis.

[‡] Unilever Research.

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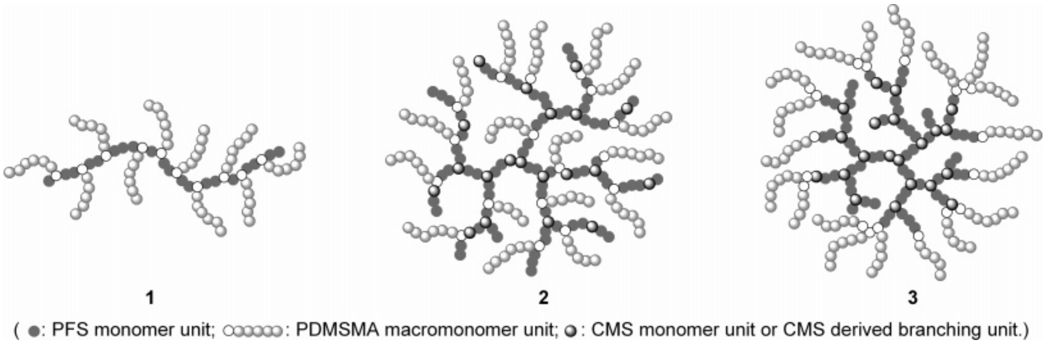


Figure 1. Schematic representations of PDMS-grafted fluorocopolymers: **1** with a linear fluorinated backbone, **2** with a hyperbranched fluorinated backbone, and **3** with a hyperbranched fluorinated core.

reactive pentafluorophenyl functionalities that allow for further derivatization, chain growth, and cross-linking.[51,56,57] The copolymers **2**, with a hyperbranched fluorinated backbone and linear PDMS grafts, were prepared by atom transfer radical self-condensing vinyl copolymerization (ATR−SCVCP) of an inimer, *p*-chloromethylstyrene (CMS), with PFS and PDMSMA. The copolymers **3**, having HBFP-based cores and linear PDMS chains, were prepared by ATRP of PDMSMA initiated by HBFP containing benzylic chloride functionalities.[53] To the best of our knowledge, **2** and **3** are the first examples of PDMS-grafted copolymers with hyperbranched fluorinated backbones or cores.

Experimental Section

Methods. Infrared spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR system as neat samples on NaCl plates. ^{1}H NMR spectra were recorded at 300 or 500 MHz on solutions in $CDCl_3$ on a Varian Unity-plus 300 or Varian Inova 500 spectrometer, respectively, with the solvent proton signal as standard. ^{13}C NMR spectra were recorded at 125.7 MHz on solutions in $CDCl_3$ on a Varian Inova 500 spectrometer with the solvent carbon signal as standard. Quantitative ^{13}C NMR analyses were performed with collection of spectra using a pre-delay of 15 s. ^{19}F NMR spectra were recorded at 282.2 MHz on solutions in $CDCl_3$ on a Unity-plus 300 spectrometer, using $CFCl_3$ as an external standard.

Gel permeation chromatography (GPC) was conducted on a Waters 1515 HPLC (Waters Chromatography, Inc.) equipped with a Waters 2414 differential refractometer, a PD2026 dual-angle (15 and 90°) light scattering detector (Precision detectors, Inc.), and a three-column series PLgel 5 μm Mixed C, 500 Å, and 10^4 Å, 300 × 7.5 mm columns (Polymer Laboratories Inc.). The system was equilibrated at 35 °C in anhydrous THF, which served as the polymer solvent and eluent with a flow rate of 1.0 mL/min. Polymer solutions were prepared at a known concentration (*ca.* 3 mg/mL) and an injection volume of 200 μL was used. Data collection and analysis were performed, respectively, with Precision Acquire software and Discovery 32 software (Precision Detectors, Inc.). Interdetector delay volume and the light scattering detector calibration constant were determined by calibration using a nearly monodispersed polystyrene standard (Pressure Chemical Co., $M_p = 90$ kDa, $M_w/M_n < 1.04$). The differential refractometer was calibrated with standard polystyrene reference material (SRM 706 NIST), of known specific refractive index increment d*n*/d*c* (0.184 mL/g). The d*n*/d*c* values of the analyzed polymers were then determined from the differential refractometer response.

Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851^e instrument (Mettler-Toledo, Inc.) measuring the total mass loss on approximately 10 mg samples from 25 to 550 °C at a heating rate of 10 °C/min in a nitrogen flow of 50 mL/min.

Solubility tests were performed by dissolving 7−15 mg polymer samples in solvents (1.0 mL per 10 mg sample) at room temperature overnight.

Elemental analyses were conducted by Galbraith Laboratories (Knoxville, TN) as a typical commercial service.

Materials. All chemicals were purchased from Aldrich unless otherwise noted. CuCl (99.995+%), $CuCl_2$ (99.999%), (1-bromoethyl)benzene (PhE-Br; 98%), 2,2′-bipyridine (Bipy; 99+%), 1,4-dimethoxybenzene (DMB), and fluorobenzene (PhF) were used as received. *p*-Chloromethylstyrene (CMS) and 2,3,4,5,6-pentafluorostyrene (PFS) were distilled over CaH_2 and stored under argon at 4 °C.

Two methacryloxypropyl-terminated PDMS macromonomers (PDMSMA-870, $M_n = 0.87$ kDa; PDMSMA-4400, $M_n = 4.40$ kDa) were purchased from Gelest, Inc. and used as received. Their M_n values were determined by ^{1}H NMR analysis based upon the resonance of a methacrylic vinylic proton at 5.58 ppm. For PDMSMA-870, TGA in N_2: 25−155 °C, 1% mass loss; 155−250 °C, 14% mass loss; 250−370, 77% mass loss; 370−425 °C, 5% mass loss. For PDMSMA-4400, TGA in N_2: 25−385 °C, 1% mass loss; 385−415 °C, 4% mass loss; 415−550 °C, 86% mass loss.

Two samples of HBFPs with benzylic chloride functionalities (HBFP-8600, $M_n^{GPC} = 8.60$ kDa, $PDI^{GPC} = 2.23$; HBFP-258000, $M_n^{GPC} = 258$ kDa, $PDI^{GPC} = 2.70$) were prepared by ATR−SCVCP of PFS with CMS, as described in a recent publication.[53] For HBFP-8600 and HBFP-258000, the molar fractions of PFS units were 44% and 62%, respectively, according to elemental analysis data for their percentages of F. For HBFP-8600, TGA in N_2: 25−250 °C, 1% mass loss; 250−350 °C, 9% mass loss; 350−440, 39% mass loss; 440−550 °C, 6% mass loss. For HBFP-258000, TGA in N_2: 25−270 °C, 1% mass loss; 270−350 °C, 11% mass loss; 350−440 °C, 41% mass loss; 440−550 °C, 12% mass loss.

General Procedure for the Preparation of Poly(PFS-*co*-PDMSMA), 1. To a round-bottom flask with a magnetic stir bar was added PFS, PDMSMA, PhE-Br, Bipy, DMB, and PhF. The flask was sealed with a rubber septum, and the mixture was frozen with a liquid nitrogen bath. After the flask was pumped and refilled with nitrogen, it was opened, and CuCl was added. After the flask was sealed again, the reaction mixture was degassed by at least three freeze−pump−thaw cycles and then heated at 81 °C with an oil bath. Aliquots (∼0.2 mL) of the reaction mixture were withdrawn from the flask with a degassed dry syringe at time intervals during polymerization. A portion of each aliquot was analyzed directly by ^{1}H NMR spectroscopy to determine the extents of conversions of PFS and PDMSMA, based on comparisons of the reference DMB methoxy proton intensity at 3.80 ppm with the intensities of the signals for a β-vinylic proton of PFS resonating at 5.75 ppm and for a methacrylic vinyl proton of PDMSMA resonating at 5.58 ppm. A portion of each aliquot was passed through neutral alumina, concentrated in vacuo, and analyzed by GPC to monitor the formation of copolymer. After the polymerization time of 30 h (for trials using PDMSMA-870) or 45 h (for trials using PDMSMA-4400) was reached, the remainder of the reaction mixture was allowed to cool to room temperature, diluted with THF, passed through a neutral alumina column, concentrated in vacuo, and precipitated 2−3 times in 1:9, THF:methanol (for trials using PDMSMA-870) or 1:2, THF:methanol (for trials using PDMSMA-4400). The polymer recovered by filtration was dried in vacuo for 1−2 days: IR (NaCl) 3150−2800, 1732, 1652, 1520, 1504, 1456, 1417, 1367, 1303, 1258, 1046, 792, 702, 666 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ −0.40−0.60 (m, SiCH_3 and SiCH_2 from PDMSMA), 0.60−3.15 (m, all protons from PFS, protons from PDMSMA except SiCH_3, SiCH_2 and COOCH_2, C*H* and CH_3 from PhE-Br), 3.20−3.70 (m, COOCH_2 from PDMSMA), 6.80−7.25 (m, Ar*H* from PhE-Br); ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) δ −0.5−2.2, 14.0, 18.2, 22.6, 25.7, 26.6, 29.9, 32.3 34.9−40.5, 44.8, 65.9, 68.0, 113.9−117.4, 126.8, 136.0−146.3, 175.1; ^{19}F NMR (282.2 MHz, $CDCl_3$, ppm) δ −143.5 (m, 2F, *ortho*-F), −154.4 (m, 1F, *para*-F), −161.4 (m, 2F, *meta*-F).

Poly(PFS-*co*-PDMSMA), 1a. Sample **1a** was prepared from the polymerization mixture of PFS (3.60 g, 18.5 mmol), PDMSMA-870 (1.80 g, 2.07 mmol), PhE-Br (69.4 mg, 0.375 mmol), CuCl (37.0 mg, 0.375 mmol), Bipy (117 mg, 0.749 mmol), DMB (1.42 g, 10.3 mmol), and PhF (6.0 mL, 50 vol %) at 81 °C. Finally, the polymerization (~10.2 mL of reaction mixture remained) was quenched at 30 h, and the isolated yield was 3.26 g (87%; based on the relative amount of remaining reaction mixture and 78% conversion of PFS and 85% conversion of PDMSMA as measured by ^1H NMR spectroscopy). $M_n^{GPC} = 28.9$ kDa, $PDI^{GPC} = 1.32$. Anal. Calcd for $C_{1124}H_{1192}O_{122}F_{480}Si_{110}Cl$: C, 46.72; H, 4.16; F, 31.56; Si, 10.69. Found: C, 47.28; H, 3.97; F, 29.41; Si, 10.66. TGA in N_2: 25−330 °C, 1% mass loss; 330−475 °C, 97% mass loss.

Poly(PFS-*co*-PDMSMA), 1b. Sample **1b** was prepared from the polymerization mixture of PFS (1.00 g, 5.15 mmol), PDMSMA-870 (4.50 g, 5.17 mmol), PhE-Br (34.7 mg, 0.187 mmol), CuCl (18.5 mg, 0.187 mmol), Bipy (58.5 mg, 0.375 mmol), DMB (712 mg, 5.15 mmol), and PhF (6.0 mL, 50 vol %) at 81 °C. Finally, the polymerization (~10.2 mL of reaction mixture remained) was quenched at 30 h, and the isolated yield was 3.75 g (97%; based on the relative amount of remaining reaction mixture and 86% conversion of PFS and 81% conversion of PDMSMA as measured by ^1H NMR spectroscopy). $M_n^{GPC} = 49.2$ kDa, $PDI^{GPC} = 1.68$. Anal. Calcd for $C_{1758}H_{3657}O_{478}F_{241}Si_{432}Cl$: C, 42.92; H, 7.49; F, 9.31; Si, 24.66. Found: C, 42.97; H, 7.64; F, 9.14; Si, 25.22. TGA in N_2: 25−300 °C, 1% mass loss; 300−350 °C, 10% mass loss; 350−460 °C, 87% mass loss.

Poly(PFS-*co*-PDMSMA), 1c. Sample **1c** was prepared from the polymerization mixture of PFS (500 mg, 2.58 mmol), PDMSMA-870 (6.75 g, 7.76 mmol), PhE-Br (34.7 mg, 0.187 mmol), CuCl (18.5 mg, 0.187 mmol), Bipy (58.5 mg, 0.375 mmol), DMB (712 mg, 5.15 mmol), and PhF (8.2 mL, 50 vol %) at 81 °C. Finally, the polymerization (~14.6 mL of reaction mixture remained) was quenched at 30 h, and the isolated yield was 4.53 g (87%; based on the relative amount of remaining reaction mixture and 91% conversion of PFS and 79% conversion of PDMSMA as measured by ^1H NMR spectroscopy). $M_n^{GPC} = 52.9$ kDa, $PDI^{GPC} = 1.58$. Anal. Calcd for $C_{1850}H_{4361}O_{585}F_{107}Si_{529}Cl$: C, 42.00; H, 8.31; F, 3.84; Si, 28.09. Found: C, 41.64; H, 8.32; F, 4.57; Si, 28.05. TGA in N_2: 25−290 °C, 1% mass loss; 290−340 °C, 9% mass loss; 340−450 °C, 88% mass loss.

Poly(PFS-*co*-PDMSMA), 1d. Sample **1d** was prepared from the polymerization mixture of PFS (1.75 g, 9.02 mmol), PDMSMA-4400 (4.44 g, 1.01 mmol), PhE-Br (33.7 mg, 0.182 mmol), CuCl (18.0 mg, 0.182 mmol), Bipy (56.9 mg, 0.364 mmol), DMB (691 mg, 5.00 mmol), and PhF (6.2 mL, 50 vol %) at 81 °C. Finally, the polymerization (~10.8 mL of reaction mixture remained) was quenched at 45 h, and the isolated yield was 1.83 g (57%; based on the relative amount of remaining reaction mixture and 54% conversion of PFS and 61% conversion of PDMSMA as measured by ^1H NMR spectroscopy). $M_n^{GPC} = 46.7$ kDa, $PDI^{GPC} = 1.11$. Anal. Calcd for $C_{1485}H_{3040}O_{459}F_{309}Si_{449}Cl$: C, 38.14; H, 6.55; F, 12.55; Si, 26.97. Found: C, 36.73; H, 6.48; F, 12.52; Si, 27.52. TGA in N_2: 25−365 °C, 1% mass loss; 365−550 °C, 96% mass loss.

General Procedure for the Preparation of Poly(PFS-*co*-PDMSMA-*co*-CMS), 2. To a round-bottom flask with a magnetic stir bar was added PFS, PDMSMA, CMS, Bipy, DMB, and PhF. The flask was sealed with a rubber septum, and the mixture was frozen with liquid nitrogen bath. After the flask was pumped and refilled with nitrogen, it was opened, and CuCl (and also $CuCl_2$ in some trials) was added. After the flask was sealed again, the reaction mixture was degassed by at least three freeze−pump−thaw cycles and then heated at 72 or 82 °C with an oil bath. Aliquots (~0.2 mL) of the reaction mixture were withdrawn from the flask with a degassed dry syringe at time intervals during polymerization. A portion of each of these aliquots was analyzed directly by ^1H NMR spectroscopy to determine the extents of conversions of PFS, PDMSMA, and CMS, based on comparisons of the reference DMB methoxy proton intensity at 3.80 ppm with the intensities of the signals for β-vinylic protons at 5.69−5.85 (1 H for PFS, overlapped with 1 H for CMS), 5.58 (1 H for PDMSMA), and 5.31 ppm (1 H for CMS). A portion of each of these aliquots was passed through neutral alumina, concentrated in vacuo, and analyzed by GPC to monitor the formation of copolymer. After the polymerization time of 24 h (for trials using PDMSMA-870) or 30 h (for trials using PDMSMA-4400) was reached, the reminder of reaction mixture was allowed to cool to room temperature, diluted with THF, passed through a neutral alumina column, concentrated in vacuo, and precipitated 2−3 times in 1:9, THF:methanol (for trials using PDMSMA-870) or 1:2, THF:methanol (for trials using PDMSMA-4400). The polymer recovered by filtration was dried in vacuo for 1−2 days: IR (NaCl) 3150−2800, 1732, 1652, 1614, 1520, 1504, 1455, 1416, 1258, 1015, 791, 702, 681 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$, ppm) δ −0.90−4.10 (m, all aliphatic protons from PFS, PDMSMA, and CMS, except benzylic protons), 4.20−4.90 (br, all benzylic protons), 6.20−7.55 (m, Ar*H* from CMS); ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) δ −1.7−2.5, 14.0, 18.2, 22.5, 25.7, 26.6, 30.0, 32.0 37.3−46.2, 67.3, 114.0−119.8, 128.6, 135.1−147.2, 176.0; ^{19}F NMR (282.2 MHz, $CDCl_3$, ppm) δ −141.8 (m, 2F, *ortho*-F), −157.0 (m, 1F, *para*-F), −162.6 (m, 2F, *meta*-F).

Poly(PFS-*co*-PDMSMA-*co*-CMS), 2a. Sample **2a** was prepared from the polymerization mixture of PFS (971 mg, 5.00 mmol), PDMSMA-870 (4.35 g, 5.00 mmol), CMS (763 mg, 5.00 mmol), CuCl (148 mg, 1.50 mmol), $CuCl_2$ (20.2 mg, 0.15 mmol), Bipy (515 mg, 3.30 mmol), DMB (230 mg, 16.6 mmol), and PhF (6.7 mL, 50 vol %) at 72 °C. Finally, the polymerization (~12.6 mL of reaction mixture remained) was quenched at 24 h, and the isolated yield was 2.71 g (77%; based on the relative amount of remaining reaction mixture and 75% conversion of PFS, 54% conversion of PDMSMA, and 86% conversion of CMS, as measured by ^1H NMR spectroscopy). $M_n^{GPC} = 59.1$ kDa, $PDI^{GPC} = 1.89$. Anal. Calcd for $C_{2366}H_{4072}O_{447}F_{297}Si_{405}Cl_{68}$: C, 48.08; H, 6.94; F, 9.25; Si, 19.25; Cl, 4.08. Found: C, 47.30; H, 6.92; F, 10.03; Si, 20.45; Cl, 3.97. TGA in N_2: 25−305 °C, 1% mass loss; 305−355 °C, 10% mass loss; 355−450 °C, 73% mass loss; 450−550 °C, 4% mass loss.

Poly(PFS-*co*-PDMSMA-*co*-CMS), 2b. Sample **2b** was prepared from the polymerization mixture of PFS (1.94 g, 10.0 mmol), PDMSMA-870 (4.35 g, 5.00 mmol), CMS (763 mg, 5.00 mmol), CuCl (148 mg, 1.50 mmol), $CuCl_2$ (20.2 mg, 0.15 mmol), Bipy (515 mg, 3.30 mmol), DMB (230 mg, 1.66 mmol), and PhF (7.4 mL, 50 vol %) at 72 °C. Finally, the polymerization (~14.2 mL of reaction mixture remained) was quenched at 24 h, and the isolated yield was 3.02 g (75%; based on the relative amount of remaining reaction mixture and 61% conversion of PFS, 55% conversion of PDMSMA, and 84% conversion of CMS, as measured by ^1H NMR spectroscopy). $M_n^{GPC} = 63.8$ kDa, $PDI^{GPC} = 1.98$. Anal. Calcd for $C_{2555}H_{4037}O_{435}F_{463}Si_{393}Cl_{64}$: C, 48.09; H, 6.38; F, 13.78; Si, 17.30; Cl, 3.56. Found: C, 47.74; H, 6.36; F, 13.46; Si, 19.10; Cl, 3.86. TGA in N_2: 25−305 °C, 1% mass loss; 305−355 °C, 7% mass loss; 355−450 °C, 77% mass loss; 450−550 °C, 3% mass loss.

Poly(PFS-*co*-PDMSMA-*co*-CMS), 2c. Sample **2c** was prepared from the polymerization mixture of PFS (3.49 g, 18.0 mmol), PDMSMA-870 (1.74 g, 2.00 mmol), CMS (305 mg, 2.00 mmol), CuCl (59.4 mg, 0.60 mmol), $CuCl_2$ (8.1 mg, 0.06 mmol), Bipy (206 mg, 1.32 mmol), DMB (91.2 mg, 0.66 mmol), and PhF (4.9 mL, 50 vol %) at 72 °C. Finally, the polymerization (~9.2 mL of reaction mixture remained) was quenched at 24 h, and the isolated yield was 2.66 g (90%; based on the relative amount of remaining reaction mixture and 53% conversion of PFS, 59% conversion of PDMSMA, and 92% conversion of CMS, as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 84.1 kDa, PDI^{GPC} = 3.59. Anal. Calcd for $C_{3412}H_{3615}O_{329}F_{1270}Si_{298}Cl_{49}$: C, 48.72; H, 4.33; F, 28.68; Si, 9.95; Cl, 2.07. Found: C, 48.82; H, 4.32; F, 31.63; Si, 8.57; Cl, 2.01. TGA in N_2: 25−330 °C, 1% mass loss; 330−370 °C, 8% mass loss; 370−450 °C, 75% mass loss; 450−550 °C, 3% mass loss.

Poly(PFS-*co*-PDMSMA-*co*-CMS), 2d. Sample **2d** was prepared from the polymerization mixture of PFS (1.75 g, 9.02 mmol), PDMSMA-870 (7.83 g, 9.00 mmol), CMS (153 mg, 1.00 mmol), CuCl (29.7 mg, 0.30 mmol), Bipy (103 mg, 0.66 mmol), DMB (45.6 mg, 0.33 mmol), and PhF (9.6 mL, 50 vol %) at 82 °C. Finally, the polymerization (∼18.6 mL of reaction mixture remained) was quenched at 24 h, and the isolated yield was 4.88 g (82%; based on the relative amount of remaining reaction mixture and 65% conversion of PFS, 62% conversion of PDMSMA, and 93% conversion of CMS, as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 207 kDa, PDI^{GPC} = 3.06. Anal. Calcd for $C_{7497}H_{15330}O_{1971}F_{989}Si_{1783}Cl_{31}$: C, 43.50; H, 7.47; F, 9.08; Si, 24.19; Cl, 0.53. Found: C, 44.00; H, 7.14; F, 10.31; Si: 24.40, Cl, 0.6. TGA in N_2: 25−305 °C, 1% mass loss; 305−355 °C, 7% mass loss; 355−450 °C, 88% mass loss; 450−550 °C, 1% mass loss.

Poly(PFS-*co*-PDMSMA-*co*-CMS), 2e. Sample **2e** was prepared from the polymerization mixture of PFS (3.49 g, 18.0 mmol), PDMSMA-4400 (8.80 g, 2.00 mmol), CMS (305 mg, 2.00 mmol), CuCl (59.4 mg, 0.60 mmol), $CuCl_2$ (8.0 mg, 0.06 mmol), Bipy (207 mg, 1.32 mmol), DMB (91.2 mg, 0.66 mmol), and PhF (12.3 mL, 50 vol %) at 82 °C. Finally, the polymerization (∼24.0 mL of reaction mixture remained) was quenched at 30 h, and the isolated yield was 5.86 g (79%; based on the relative amount of remaining reaction mixture and 55% conversion of PFS, 62% conversion of PDMSMA, and 96% conversion of CMS, as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 132 kDa, PDI^{GPC} = 1.68. Anal. Calcd for $C_{4327}H_{8548}O_{1241}F_{848}Si_{1220}Cl_{33}$: C, 39.38; H, 6.53; F, 12.21; Si, 25.97; Cl, 0.89. Found: C, 38.45; H, 6.84; F, 11.77; Si, 25.90; Cl, 0.7. TGA in N_2: 25−360 °C, 1% mass loss; 360−525 °C, 94% mass loss.

General Procedure for the Preparation of HBFP—PDMS, 3. To a round-bottom flask with a magnetic stirring bar were added HBFP, PDMSMA, Bipy, DMB, and PhF. The flask was sealed with a rubber septum, and the mixture was frozen with liquid nitrogen bath. After the flask was pumped and refilled with nitrogen, it was opened, and CuCl and $CuCl_2$ were added. After the flask was sealed again, the reaction mixture was degassed by at least three freeze−pump−thaw cycles and then heated at 65 °C with an oil bath. Aliquots (∼0.2 mL) of the reaction mixture were withdrawn from the flask with a degassed dry syringe at time intervals during polymerization. A portion of each of these aliquots was analyzed directly by ^{1}H NMR spectroscopy to determine the extent of conversion of PDMSMA based on comparison of the reference DMB methoxy proton intensity at 3.80 ppm with the intensity of the signal for a methacrylic vinylic proton of PDMSMA resonating at 5.58 ppm. A portion of each of these aliquots was passed through neutral alumina, concentrated in vacuo, and analyzed by GPC to monitor the formation of copolymer. After the reaction time of 8−10 h (for trials using PDMSMA-870), the reaction mixture was allowed to cool to room temperature, diluted with THF, passed through a neutral alumina column, concentrated in vacuo, followed by precipitation 2−3 times in 1:9, THF:methanol (for trials using PDMSMA-870). The polymer recovered by filtration was dried in vacuo for 1−2 days: IR (NaCl) 3150−2800, 1732, 1652, 1520, 1504, 1455, 1418, 1298, 1260, 1091, 964, 800, 681 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ −0.40−0.65 (m, SiCH_3 and SiCH_2 from PDMSMA), 0.70−3.40 (m, all aliphatic protons from HBFP except benzylic protons, all protons from PDMSMA except SiCH_3, SiCH_2 and COOCH_2), 3.60−4.20 (s, COOCH_2 from PDMSMA), 4.20−4.80 (br, benzylic protons from HBFP), 6.20−7.45 (br m, all aromatic protons from HBFP); ^{13}C NMR (125.7 MHz, $CDCl_3$, ppm) δ −0.5−2.2, 14.0, 18.1, 22.3, 25.6, 26.6, 29.6, 32.1 33.7, 41.2, 45.9, 67.6, 115.7−117.5, 126.5−129.5, 136.0−147.1, 178.1; ^{19}F NMR (282.2 MHz, $CDCl_3$, ppm) δ −143.5 (m, 2F, *ortho*-F), −154.4 (m, 1F, *para*-F), −161.3 (m, 2F, *meta*-F).

HBFP—PDMS, 3a. Sample **3a** was prepared from the reaction mixture of HBFP-8600 (2.28 g, 0.266 mmol; containing 7.42 mmol of benzylic chlorides), PDMSMA-870 (8.70 g, 10.0 mmol), CuCl (297 mg, 3.0 mmol), $CuCl_2$ (40.3 mg, 0.30 mmol), Bipy (1.03 g, 6.6 mmol), DMB (456 mg, 3.3 mmol), and PhF (21 mL, 60 vol %) at 65 °C. Finally, the reaction (∼33.8 mL of reaction mixture remained) was quenched at 10 h, and the isolated yield was 3.10 g (51%; based on the relative amount of remaining reaction mixture and 46% conversion of PDMSMA as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 61.8 kDa, PDI^{GPC} = 2.18. Anal. Calcd for $C_{2475}H_{4316}O_{475}F_{287}Si_{430}Cl_{73}$: C, 48.11; H, 7.04; F, 8.82; Si, 19.54; Cl, 4.19. Found: C, 47.80; H, 6.88; F, 9.39; Si, 18.90; Cl: 4.29. TGA in N_2: 25−270 °C, 1% mass loss; 270−340 °C, 10% mass loss; 340−440 °C, 69% mass loss; 440−550 °C, 4% mass loss.

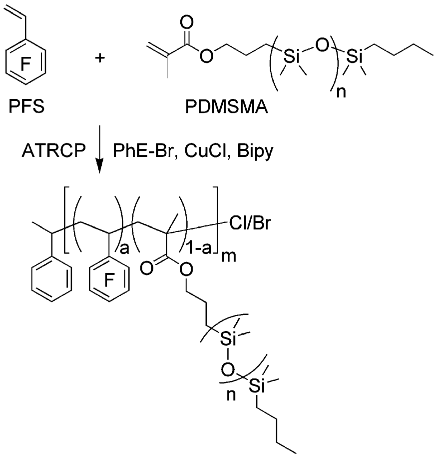
HBFP—PDMS, 3b. Sample **3b** was prepared from the reaction mixture of HBFP-8600 (2.28 g, 0.266 mmol; containing 7.44 mmol of benzylic chlorides), PDMSMA-870 (6.70 g, 7.70 mmol), CuCl (297 mg, 3.0 mmol), $CuCl_2$ (40.3 mg, 0.30 mmol), Bipy (1.03 g, 6.6 mmol), DMB (456 mg, 3.3 mmol), and PhF (23 mL, 66 vol %) at 65 °C. Finally, the reaction (∼33.8 mL of reaction mixture remained) was quenched at 10 h, and the isolated yield was 2.57 g (70%; based on the relative amount of remaining reaction mixture and 23% conversion of PDMSMA as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 29.3 kDa, PDI^{GPC} = 2.12. Anal. Calcd for $C_{1278}H_{1706}O_{145}F_{221}Si_{131}Cl_{57}$: C, 52.55; H, 5.83; F, 14.57; Si, 12.34; Cl, 6.93. Found: C, 54.53; H, 5.30; F, 16.38; Si, 11.70; Cl, 6.89. TGA in N_2: 25−240 °C, 1% mass loss; 240−320 °C, 10% mass loss; 320−450 °C, 57% mass loss; 450−550 °C, 5% mass loss.

HBFP—PDMS, 3c. Sample **3c** was prepared from the reaction mixture of HBFP-8600 (2.28 g, 0.266 mmol; containing 7.44 mmol of benzylic chlorides), PDMSMA-870 (1.67 g, 1.92 mmol), CuCl (297 mg, 3.0 mmol), $CuCl_2$ (40.3 mg, 0.30 mmol), Bipy (1.03 g, 6.6 mmol), DMB (456 mg, 3.3 mmol), and PhF (28 mL, 80 vol %) at 65 °C. Finally, the reaction (∼33.8 mL of reaction mixture remained) was quenched at 10 h, and the isolated yield was 1.87 g (75%; based on the relative amount of remaining reaction mixture and 18% conversion of PDMSMA as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 19.3 kDa, PDI^{GPC} = 2.03. Anal. Calcd for $C_{931}H_{835}O_{28}F_{219}Si_{25}Cl_{56}$: C, 57.88; H, 4.36; F, 21.54; Si, 3.63; Cl, 10.28. Found: C, 57.50; H, 3.94; F, 23.62; Si, 3.06; Cl, 9.55. TGA in N_2: 25−265 °C, 1% mass loss; 265−335 °C, 6% mass loss; 335−450 °C, 50% mass loss; 450−550 °C, 7% mass loss.

HBFP—PDMS, 3d. Sample **3d** was prepared from the reaction mixture of HBFP-258000 (3.47 g, 0.0134 mmol; containing 7.40 mmol of benzylic chlorides), PDMSMA-870 (8.70 g, 10.0 mmol), CuCl (297 mg, 3.0 mmol), $CuCl_2$ (40.3 mg, 0.30 mmol), Bipy (1.03 g, 6.6 mmol), DMB (456 mg, 3.3 mmol), and PhF (20 mL, 60 vol %) at 65 °C. Finally, the reaction (∼32.8 mL of reaction mixture remained) was quenched at 10 h, and the isolated yield was 6.85 g (84%; based on the relative amount of remaining reaction mixture and 57% conversion of PDMSMA as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 1560 kDa, PDI^{GPC} = 2.21. Anal. Calcd for $C_{61732}H_{100131}O_{1107}F_{1109}Si_{1001}Cl_{137}$: C, 47.53; H, 6.47; F, 13.51; Si, 18.02; Cl, 4.20. Found: C, 47.39; H, 6.12; F, 15.74; Si: 17.70, Cl, 3.17. TGA in N_2: 25−270 °C, 1% mass loss; 270−335 °C, 8% mass loss; 335−450 °C, 74% mass loss; 450−550 °C, 3% mass loss.

HBFP—PDMS, 3e. Sample **3e** was prepared from the reaction mixture of HBFP-258000 (3.47 g, 0.0134 mmol; containing 7.40 mmol of benzylic chlorides), PDMSMA-870 (6.70 g, 7.70 mmol), CuCl (297 mg, 3.0 mmol), $CuCl_2$ (40.3 mg, 0.30 mmol), Bipy (1.03 g, 6.6 mmol), DMB (456 mg, 3.3 mmol), and PhF (22 mL, 66 vol %) at 65 °C. Finally, the reaction (∼32.6 mL of reaction mixture remained) was quenched at 8 h, and the isolated yield was 5.97 g (83%; based on the relative amount of remaining reaction mixture and 60% conversion of PDMSMA as measured by ^{1}H NMR spectroscopy). M_n^{GPC} = 1040 kDa, PDI^{GPC} = 3.39. Anal. Calcd for $C_{61732}H_{100131}O_{1107}F_{1109}Si_{1001}Cl_{137}$: C, 49.19; H, 5.72; F, 17.83; Si, 13.98; Cl, 3.69. Found: C, 48.21; H, 6.03;

Scheme 1



F, 19.22; Si, 15.7; Cl, 3.19. TGA in N_2: 25−250 °C, 1% mass loss; 250−330 °C, 9% mass loss; 330−445 °C, 68% mass loss; 445−550 °C, 6% mass loss.

HBFP—PDMS, 3f. Sample **3f** was prepared from the reaction mixture of HBFP-258000 (3.47 g, 0.0134 mmol; containing 7.40 mmol of benzylic chlorides), PDMSMA-870 (1.67 g, 1.92 mmol), CuCl (297 mg, 3.0 mmol), $CuCl_2$ (40.3 mg, 0.30 mmol), Bipy (1.03 g, 6.6 mmol), DMB (456 mg, 3.3 mmol), and PhF (27 mL, 80 vol %) at 65 °C. Finally, the reaction (~32.6 mL of reaction mixture remained) was quenched at 8 h, and the isolated yield was 3.07 g (80%; based on the relative amount of remaining reaction mixture and 30% conversion of PDMSMA as measured by ^{1}H NMR spectroscopy). $M_n^{GPC} = 341$ kDa, $PDI^{GPC} = 4.96$. Anal. Calcd for $C_{61732}H_{100131}O_{1107}F_{1109}Si_{1001}Cl_{137}$: C, 54.54; H, 3.75; F, 28.68; Si, 2.99; Cl, 6.63. Found: C, 54.74; H, 3.29; F, 28.57; Si, 2.92; Cl, 6.55. TGA in N_2: 25−270 °C, 1% mass loss; 270−335 °C, 7% mass loss; 335−450 °C, 55% mass loss; 450−550 °C, 6% mass loss.

Results and Discussion

Synthesis of Poly(PFS-*co*-PDMSMA), 1. As shown in Scheme 1, poly(PFS-*co*-PDMSMA) **1**, as PDMS-grafted copolymers with linear fluorinated backbones, were prepared by ATRCP of PFS with PDMSMA, using PhE-Br together with CuCl and Bipy as initiator/catalyst/ligand system (($[PFS]_0 + [PDMSMA]_0$):$[PhE\text{-}Br]_0$:$[CuCl]_0$:$[Bipy]_0$ = 55:1.0:1.0:2.0), in 50 vol % of PhF at 81 °C. Either PDMSMA-870 (M_n = 870 Da) or PDMSMA-4400 (M_n = 4400 Da) was used as macromonomer, and the molar feed ratio of PFS to PDMSMA was 9:1, 1:1, or 1:3. When PDMSMA-870 was used, the polymerization time was 30 h for each trial; when PDMSMA-4400 was used, the polymerization time was 45 h for each trial.

To monitor the copolymerization process by ^{1}H NMR spectroscopy, for each trial, DMB ($[DMB]_0$:($[PFS]_0 + [PDMSMA]_0$) = 1:2) was also added to allow for the resonance of its methoxy protons at 3.80 ppm to be used as a reference for determination of the conversions of PFS and PDMSMA, based on the characteristic resonances of their β-vinylic protons at 5.75 and 5.58 ppm. No considerable conversions (<15%) of comonomers were observed for the two trials using PDMSMA-4400 with molar feed ratios of PFS to PDMSMA of 1:1 and 1:3. High comonomer conversions (>75%) were obtained for all the trials using PDMSMA-870, and significant comonomer conversions (>50%) were also obtained for the trial using PDMSMA-4400 with high molar feed ratio of PFS to PDMSMA-4400 of 9:1 (Table 1).

Kinetic analysis demonstrated that both PFS and PDMSMA were consumed almost simultaneously (Figure 2), indicating that the resulting copolymers had PDMS grafts well distributed along their backbones. The monomer reactivity ratios (r) were investigated. For copolymerization systems using PDMSMA-870, r_{PFS} of 0.75 ± 0.13 and $r_{PDMSMA-870}$ of 0.58 ± 0.07 were determined by using the Kelen−Tüdös method,[65,66] based on varying feed monomer compositions (Figure 3a). Using the Alfrey−Price equations,[67] with $Q_{PFS} = 0.87$ and $e_{PFS} = 0.75$ that were obtained from the PFS-MMA radical copolymerization system by Pryor and Huang,[68] $Q_{PDMSMA-870}$ of 0.58 and $e_{PDMSMA-870}$ of −0.16 were estimated. From the trial with a high molar feed ratio of PFS to PDMSMA-870 of 9:1, a r_{PFS} value of 0.80 ± 0.01 was also obtained through the Jaccks method[62,69] (Figure 3b). From the trial with high molar feed ratio of PFS to PDMSMA-4400 of 9:1, a r_{PFS} value of 0.85 ± 0.03 was obtained by using the Jaccks method (Figure 3c). The results of essentially consistent r_{PFS} values suggests that the reactivity of PDMSMA was not significantly influenced by its chain length, and the low molar concentrations of comonomers might be among the key factors responsible for the slow copolymerization rates, in those systems using PDMSMA-4400. Additionally, the considerable steric hindrance effect of PDMS-MA-4400 might also entropically disfavor its incorporation into copolymer structures.[15]

For all trials with significant occurrence of polymerization, copolymers **1** were obtained by passing the copolymerization solutions through alumina columns, followed by removal of remaining unreacted PDMSMA by precipitation 2−3 times in 1:9 THF:methanol (for PDMSMA-870) or 1:2 THF:methanol (for PDMSMA-4400). Quantitative composition determination of these copolymers was conducted through elemental analyses, based on mass percentages of characteristic elements of the comonomers (PFS has 48.96 mass % of F; PDMSMA-870 has 30.57 mass % of Si, and PDMSMA-4400 has 36.45 mass % of Si). With different initial feed ratios of comonomers, the successful synthesis of **1** with different molar fractions of comonomers was verified. Excellent agreements between theoretical and experimental values of molar fractions of comonomers were further established, indicating precise composition control in the ATRCP systems. Because molar fractions of PDMSMA in copolymers (F_{PDMSMA}) are also graft densities of copolymers, accurate control of F_{PDMSMA} correlates also with accurate control of graft densities in this "grafting through" system.

Besides elemental analysis, the compositions of copolymers **1** could also be investigated by quantitative ^{13}C NMR spectroscopy, based upon comparisons of the resonance intensities of five fluorinated aromatic carbons of each PFS unit at 136−148 ppm with the resonance intensities of silicated carbons of each PDMSMA unit observed from −2 to +6 ppm (Figure 4). For example, the quantitative ^{13}C NMR analysis of copolymer **1a** gave a molar fraction ratio of 0.90:0.10 for PFS units and PDMSMA-870 units (with 21 silicated carbons per unit), which was very close to the calculated value (0.89:0.11) and the experimental value (0.89:0.11) obtained by elemental analysis. As a note, ^{1}H NMR analysis of **1** could not provide accurate information on copolymer composition, because the resonances of aliphatic protons from PFS units were severely overlapped with resonances from PDMSMA units. ^{19}F NMR analysis of **1** detected only quantitative resonances of *ortho*-fluorines (concentrated at −143.5 ppm), *meta*-fluorines (concentrated at −161.4 ppm), and *para*-fluorines (concentrated at −154.4 ppm) on the pentafluorophenyl group of their PFS units but gave no information about PDMSMA units that had no fluorine atoms.

Table 1. Synthesis of Poly(PFS-*co*-PDMSMA) by ATRCP (M1 = PFS; M2 = PDMSMA)[a]

				conversion (%)[b]		F_1:F_2[c]		M_n (kDa)		
entry	$M_{n,M2}$[b] (Da)	$[M1]_0$:$[M2]_0$	*t* (h)	M1	M2	calcd[d]	exptl[e]	calcd[f]	exptl[g]	PDI[g]
1a	870	9:1	30	78	85	0.89:0.11	0.89:0.11	11.6	28.9	1.32
1b	870	1:1	30	86	81	0.51:0.49	0.50:0.50	24.0	49.2	1.68
1c	870	1:3	30	91	77	0.28:0.72	0.31:0.69	30.2	52.9	1.58
1d	4400	9:1	45	54	61	0.87:0.13	0.89:0.11	20.1	46.7	1.11

[a] ($[M1]_0$ + $[M2]_0$):[PhE-Br]$_0$:[CuCl]$_0$:[Bipy]$_0$:[DMB]$_0$ = 55:1.0:1.0:2.0:27.5; 50 vol % of PhF; 81 °C. [b] By ^{1}H NMR spectroscopy. [c] Molar ratios of PFS units to PDMSMA units in copolymer. [d] Calculated based on the molar feed ratios and conversions of comonomers. [e] By elemental analyses of F and Si. [f] Calculated based on the molar feed ratios of comonomers to initiator and conversions of comonomers. [g] By GPC with multiangle laser light scattering.

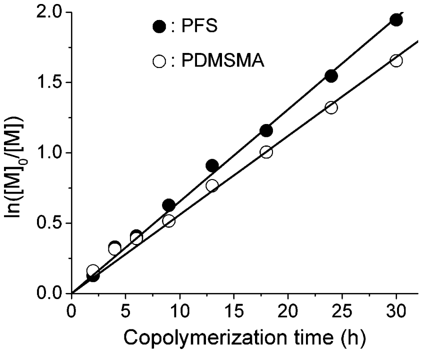


Figure 2. Representative kinetic plot for ATRCP of PFS and PDMSMA ([PFS]$_0$:[PDMSMA-870]$_0$:[PhE-Br]$_0$:[CuCl]$_0$:[Bipy]$_0$:[DMB]$_0$ = 27.5:27.5:1.0:1.0:2.0:27.5; 50 vol % of PhF; 81 °C; for the preparation of copolymer **1b**).

GPC analysis of copolymers **1** showed that they had M_n of 28.9−52.9 kDa, with PDI values of 1.11−1.68. These experimental M_n values were significantly higher than the calculated M_n values of 11.6−30.2 kDa. An appreciable occurrence of biradical coupling in the ATRCP system was considered as an important reason for the higher-than-expected M_n values and relatively high PDI values. GPC measurements of aliquots withdrawn from copolymerization systems at different copolymerization times showed that, with continuous consumption of comonomers, copolymers with increasing molecular weights were obtained; however, their molecular weight distributions became bimodal, suggesting increased occurrence of biradical coupling (Figure 5).

Synthesis of Poly(PFS-*co*-PDMSMA-*co*-CMS), 2. As shown in Scheme 2, PDMS-grafted copolymers with hyperbranched fluorinated backbones, poly(PFS-*co*-PDMSMA-*co*-CMS) **2**, were prepared by ATR−SCVCP of CMS, as a inimer, with PFS and PDMSMA comonomers, using CuCl and Bipy as the catalyst/ligand system, in 50 vol % of PhF (Table 2). Because Weimer et al. found that a high catalyst-to-inimer ratio was required for the preparation of hyperbranched polymers by CMS-based ATR−SCVCP systems,[33] 0.30 equiv of CuCl relative to the inimer was used for each trial. When PDMSMA-870 was used in copolymerization, copolymerization times were 24 h. For the trials with low initial feeds of PDMSMA-870, low radical concentrations were targeted by initial feeds of 10 mol % of $CuCl_2$ with respect to the copper(I) catalyst and with relatively low copolymerization temperature of 72 °C. For the trial using the highest initial feed of PDMSMA-870 ([PFS]$_0$:[PDMSMA-870]$_0$:[CMS]$_0$ = 9:9:1), because of relatively low initial molar concentration of CMS in the copolymerization system, the copolymerization was conducted at a higher temperature of 82 °C without a 10 mol % initial feed of $CuCl_2$ (a control experiment showed no significant occurrence of copolymerization, if 10 mol % of $CuCl_2$ relative to CuCl was added). PDMSMA-4400 was also used with a low initial feed in one trial ([PFS]$_0$:[PDMSMA-4400]$_0$:[CMS]$_0$ = 9:1:1), and the copolymerization was conducted at 82 °C for 30 h, with an initial feed of 10 mol % of $CuCl_2$ relative to CuCl.

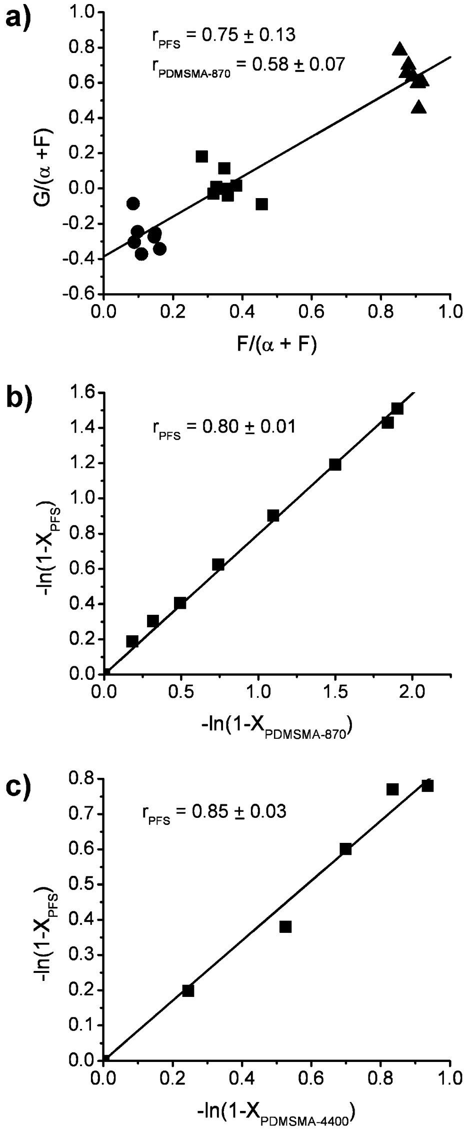


Figure 3. (a) Kelen−Tüdös plot for ATRCP of PFS and PDMSMA-870; (b) Jaccks plot of ATRCP with molar feed ratio of PFS to PDMSMA-870 of 9:1 (for the preparation of copolymer **1a**); (c) Jaccks plot of ATRCP with molar feed ratio of PFS to PDMSMA-4400 of 9:1 (for the preparation of copolymer **1d**).

To monitor the copolymerization process by ^{1}H NMR spectroscopy, for each trial, DMB ([DMB]$_0$:[CMS]$_0$ = 0.33:1) was also added to allow for the resonance of its methoxy protons at 3.80 ppm to be used as a reference for the determination of conversions of vinyl bonds of PFS, PDMSMA, and CMS, based on their characteristic resonances of β-vinylic protons at 5.69−5.85 (1 H for PFS, overlapped with 1 H for CMS), 5.58 (1 H for PDMSMA), and 5.31 ppm (1 H for CMS). Kinetic analysis

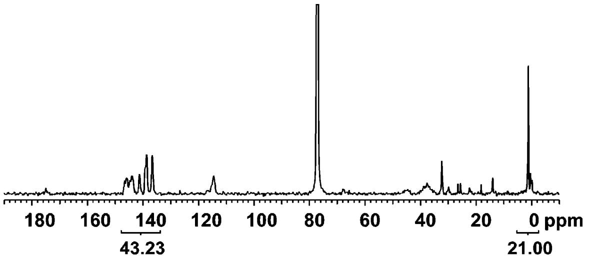


Figure 4. ^{13}C NMR spectrum (128.7 MHz, $CDCl_3$) of copolymer poly(PFS-*co*-PDMSMA), **1a**.

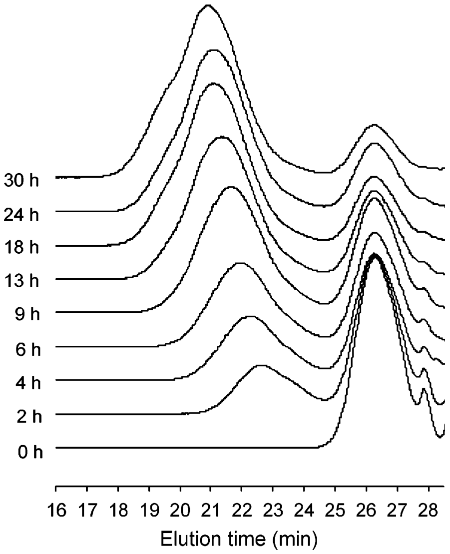


Figure 5. GPC traces for the showing graft copolymer growth during preparation of poly(PFS-*co*-PDMSMA), **1b**, ($[PFS]_0$:$[PDMSMA\text{-}870]_0$:$[PhE\text{-}Br]_0$:$[CuCl]_0$:$[Bipy]_0$ = 27.5:27.5:1.0:1.0:2.0; 50 vol % of PhF; 81 °C; the isolated copolymer was obtained after precipitation after 30 h of copolymerization).

demonstrated that, relative to PFS and PDMSMA, CMS had higher conversions of vinyl bonds during copolymerization for all trials, presumably due to its higher reactivity ($Q_{CMS} = 1.39$; $e_{CMS} = -0.38$).[70] Similar to PFS–PDMSMA ATRCP systems, copolymerization of PFS, PDMSMA, and CMS generally also exhibited comparable reactivity of PFS and PDMSMA. However, for trials with significant feeds of inimer CMS ($[PFS]_0$:$[PDMSMA\text{-}870]_0$:$[CMS]_0$ = 1:1:1 or 1:2:1), consumption of PDMSMA was found to be evidently slower than consumption of PFS after considerable conversions of comonomers and inimer were reached (Figure 6). This interesting phenomenon was ascribed to the steric effects caused by the hyperbranched architectures with significant degrees of branching. Because of initiation being slower than propagation, higher degrees of branching can be expected at late stages of copolymerizations of these trials with high inimer feeds, which exerted appreciable steric repulsion to macromonomer PDMSMA relative to small molecule PFS for chain propagation and resulted in increasing disparity in the rates of PFS vs PDMSMA incorporation.

The composition of poly(PFS-*co*-PDMSMA-*co*-CMS) copolymers **2** were characterized by elemental analyses for composition determinations, based on percentages of each characteristic element that originated from each comonomer and inimer (PFS has 48.96% of F; PDMSMA-870 has 30.57% of Si, and PDMSMA-4400 has 36.45% of Si; CMS has 23.23% of Cl). Excellent agreement between theoretical and experimental values of molar fractions of structural units from PFS, PDMSMA, and CMS were established for **2**. The well-controlled F_{PDMSMA} values in copolymers further indicate good control over graft density of the resulting copolymers by the ATR–SCVCP systems.

The composition of copolymers **2** could also be measured by quantitative ^{13}C NMR spectroscopy based on the resonance intensities for five fluorinated aromatic carbons per PFS unit at 136–148 ppm (the two aliphatic-substituted aromatic carbons from CMS units also resonated in this region, and their contributions were subtracted), four protonated aromatic carbons per CMS unit at about 128 ppm, and the silicated carbons of each PDMSMA unit at −2 to +6 ppm (Figure 7). For example, the quantitative ^{13}C NMR analysis of copolymer **2a** gave a molar fraction ratio of structural units from PFS, PDMSMA-870 (with 21 silicated carbons per unit), and CMS of 0.35:0.24:0.41, which was close to the calculated value of 0.35:0.25:0.40, based on the initial feed ratio and conversions of comonomers and inimer, and the experimental value of 0.36:0.26:0.38 obtained by elemental analysis. Similar to ^1H NMR analysis of **1**, ^1H NMR analysis of **2** could not provide accurate information on copolymer composition, because the resonances of aliphatic protons from PFS units were severely overlapped with resonances from PDMSMA units and CMS-based units. ^{19}F NMR analysis of **2** detected quantitative resonances of *ortho*-fluorines (concentrated at −141.8 ppm), *meta*-fluorines (concentrated at −162.6 ppm), and *para*-fluorines (concentrated at −157.0 ppm) on the pentafluorophenyl group of their PFS units, but gave no information about either PDMSMA units or CMS-based units because of their absence of fluorine atoms.

By GPC analysis, **2** had M_n values of 59.1–207 kDa, with PDI values of 1.68–3.59. The high PDI values are typical for hyperbranched polymers prepared by the SCVP method. As a note, because, theoretically, the degree of branching of hyperbranched polymers prepared by SCVCP can be adjusted through initial molar feed fractions of inimers and conversions of reactants, copolymers of **2** were expected to have different degrees of branching. However, currently there is lack of a general method to quantitatively determine degree of branching for these hyperbranched copolymers.

Synthesis of HBFP–PDMS, 3. As shown in Scheme 3, PDMS-grafted copolymers with hyperbranched fluorinated cores, HBFP–PDMS, were prepared by ATRP of PDMSMA, using HBFP with benzylic chloride-functionalized HBFP as initiator, together with CuCl, $CuCl_2$, and Bipy as catalyst/deactivator/ligand system ($[Cl_{HBFP}]_0$:$[CuCl]_0$:$[CuCl_2]_0$:$[Bipy]_0$ = 1.0:0.4:0.04:0.88), in 60–80 vol % of PhF. Two HBFP initiators were prepared by SCVCP of PFS and CMS. HBFP-8600 has a M_n of 8600 Da, a PDI of 2.23, and an average of 28 benzylic chlorides per macromolecule; HBFP-258000 has a M_n of 258000 Da, a PDI of 2.70, and an average of 550 benzylic chlorides per macromolecule. Because a polyfunctional ATRP macroinitiator was used in each trial, to avoid considerable occurrence of biradical coupling that could result in insoluble products, low radical concentrations were targeted by initial feeds of 10 mol % of $CuCl_2$ with respect to the copper(I) catalyst and with relatively low reaction temperature of 65 °C. To monitor the copolymerization process by ^1H NMR spectroscopy, for each trial, DMB ($[DMB]_0$:$[Cl_{HBFP}]_0$ = 0.44:1) was also added to allow for the resonance of its methoxy protons at 3.80 ppm to be used as a reference for the determination of conversions of vinyl bonds of PDMSMA based on its characteristic resonance of a vinylic proton at 5.58 ppm.

When PDMSMA-4400 was used as macromonomer, the initial molar feed ratios of macromonomer to benzylic chloride functionalities on HBFP were 0.26. A low macromonomer conversion of only 6% was observed in the reaction system

Scheme 2

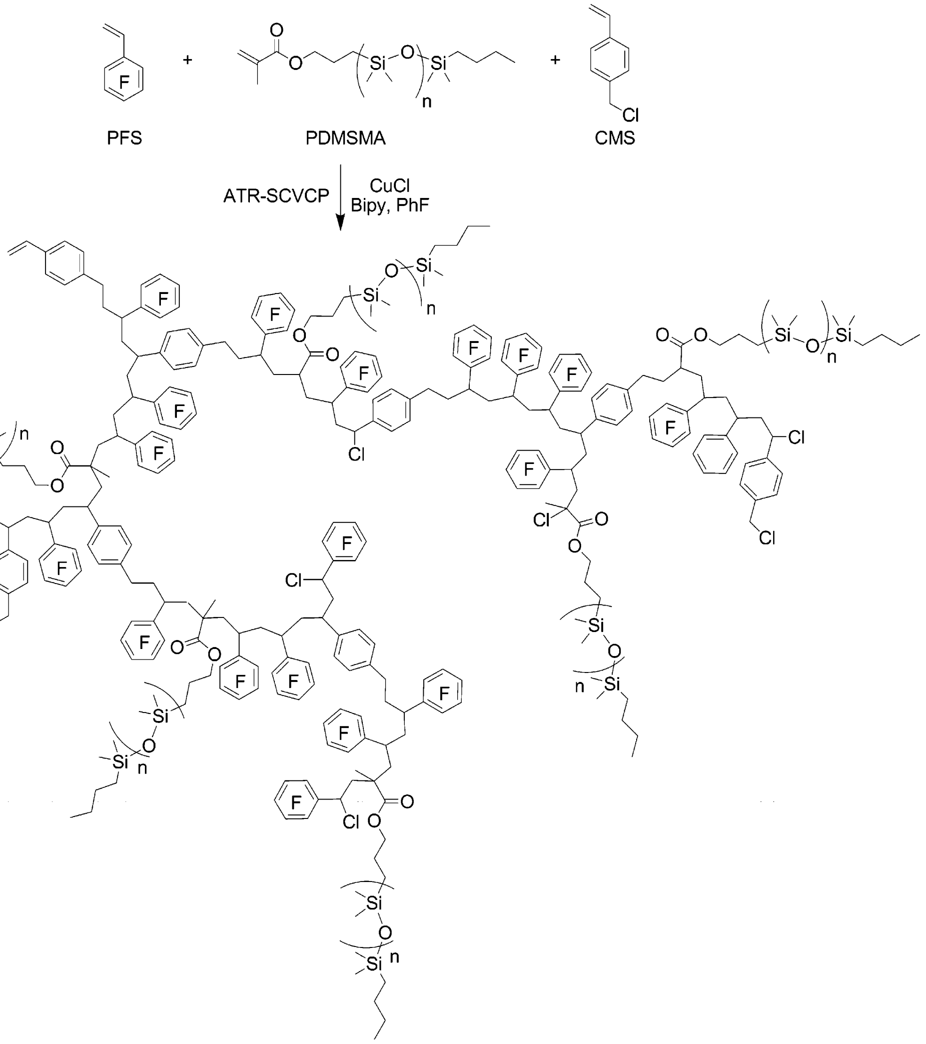


Table 2. Synthesis of Poly(PFS-*co*-PDMSMA-*co*-CMS) by ATR−SCVCP (M1 = PFS; M2 = PDMSMA; M3 = CMS)[a]

entry	$M_{n,M2}$[b] (Da)	$[M1]_0$:$[M2]_0$:$[M3]_0$	T (°C)	t (h)	conversion (%)[b] M1	M2	M3	F_1:F_2:F_3[c] calcd[d]	exptl[e]	M_n[f] (kDa)	PDI[f]
2a	870	1:1:1	72	24	75	54	86	0.35:0.25:0.40	0.36:0.26:0.38	59.1	1.89
2b	870	2:1:1	72	24	61	55	84	0.47:0.21:0.32	0.44:0.22:0.34	63.8	1.98
2c	870	9:1:1	72	24	53	59	92	0.76:0.09:0.15	0.79:0.08:0.13	84.1	3.59
2d	870	9:9:1	82	24	65	62	93	0.47:0.45:0.08	0.50:0.42:0.08	207	3.06
2e	4400	9:1:1	82	30	55	62	96	0.76:0.09:0.15	0.78:0.10:0.12	132	1.68

[a] $[M3]_0$:$[CuCl]_0$:$[Bipy]_0$:$[DMB]_0$ = 1:0.3:0.66:0.33; 50 vol % of PhF; for trials **2a**, **2b**, **2c**, and **2e**: 10 mol % initial feed of $CuCl_2$ relative to CuCl; for trial **2d**, no initial feed of $CuCl_2$. [b] By ^{1}H NMR spectroscopy. [c] Molar fraction ratios of units in copolymer that were originated from PFS, PDMSMA, and CMS. [d] Calculated based on the molar feed ratios and conversions of comonomers and inimer. [e] By elemental analyses of F, Si, and Cl. [f] By GPC with multiangle laser light scattering.

using HBFP-8600 as initiator with a reaction time of 15 h, presumably due to a very low molar concentration of vinyl bonds. With a theoretical average of 0.4 PDMS chains covalently attached on a HBFP core, a large fraction of unreacted HBFP remained in the reaction system. For the reaction system using HBFP-258000 as initiator with a reaction time of 15 h, a macromonomer conversion of 15% was observed, but the product was insoluble, presumably due to biradical coupling.

When PDMSMA-870 was used as macromonomer (Table 3), the initial molar feed ratios of macromonomer to benzylic chloride functionalities on HBFP were 1.35, 1.03, and 0.26, and polymerization times were 8−10 h. Considerable conversions of macromonomer (18−60%) were observed in all trials, and the resulting HBFP−PDMS copolymers were obtained by passing the reaction solutions through alumina columns, followed by precipitation 2−3 times in 1:9, THF:methanol. Kinetic analysis demonstrated that HBFP-258000 led to faster reaction with PDMSMA-870 than did HBFP-8600, under similar reaction conditions (Figure 8), presumably because of the high local concentrations of active polymerization sites relative to deactivator for reaction systems using HBFP-258000. A control experiment further showed that a small molecule structural analogue of the HBFP initiator sites, benzylic chloride, resulted in much slower polymerization of PDMSMA-870 ([PDMSMA-870]:[benzylic chloride]$_0$/$[CuCl]_0$/$[CuCl_2]_0$/$[Bipy]_0$/$[DMB]_0$ = 1.03/1.0/0.4/0.04/0.88/0.44; 74 vol % of PhF; 65 °C; 10 h; 9% conversion of PDMSMA-870).

With their core domains derived from HBFP, HBFP−PDMS copolymers **3** prepared from the same HBFP sample had consistent core structures but differed in F_{PDMSMA}. Therefore,

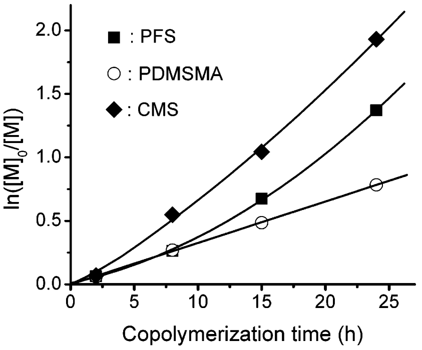


Figure 6. Kinetic plot for the PFS−PDMSMA−CMS ATR−SCVCP system with a high feed of CMS ($[PFS]_0:[PDMSMA\text{-}870]_0:[CMS]_0:[CuCl]_0:[CuCl_2]_0:[Bipy]_0:[DMB]_0 = 1:1:1:0.3:0.03:0.66:0.33$; 50 vol % of PhF; 72 °C; for the preparation of copolymer **2a**).

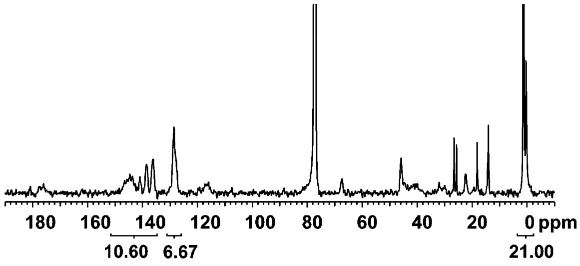


Figure 7. ^{13}C NMR spectrum (128.7 MHz, $CDCl_3$) of copolymer poly(PFS-*co*-PDMSMA-*co*-CMS), **2a**.

F_{PDMSMA} was an important structural parameter of **3**. Similar to composition determination of copolymers **1** and **2**, experimental F_{PDMSMA} values of **3** were also obtained through elemental analyses, based on percentages of Si, as well as F and Cl. For all samples of **3**, experimental F_{PDMSMA} values were slightly lower than the calculated values, presumably due to appreciable loss of copolymer species with rich PDMS contents during workup.

F_{PDMSMA} of **3** was also investigated by quantitative ^{13}C NMR spectroscopy, based upon comparison of the resonance intensities at 136−148 ppm for five fluorinated aromatic carbons of each PFS unit with the resonance intensities at −2−6 ppm for 21 silicated carbons of each PDMSMA-870 unit (Figure 9a). Alternatively, ^{1}H NMR analysis of **3** could also be employed to estimate F_{PDMSMA}, based upon the comparison of the resonance intensities at 6.20−7.45 ppm for four aromatic protons of each CMS-based unit with the resonance intensities from −0.40 to 0.40 ppm for 57 $SiCH_3$ protons of each PDMSMA-870 unit (Figure 9b). For example, the quantitative ^{13}C and ^{1}H NMR analyses of copolymer **3a** gave F_{PDMSMA} values of 0.23 and 0.25, respectively, which were close to the calculated value of 0.26 and were in excellent agreement with the experimental value of 0.24 obtained by elemental analysis. ^{19}F NMR analysis of **3** detected only quantitative resonances of *ortho*-fluorines (concentrated at −143.5 ppm), *meta*-fluorines (concentrated at −161.3 ppm), and *para*-fluorines (concentrated at −154.4 ppm) on the pentafluorophenyl group of their PFS units, but gave no information about PDMSMA units due to their absence of fluorine atoms.

As detected by GPC, **3** had M_n values ranging from 19.3 to 1560 kDa, with PDI of 2.03−4.96. These experimental M_n values were significantly higher than the calculated values, presumably due to appreciable occurrences of biradical coupling and polymerization of vinyl-functionalized head units from HBFP during reactions. On the basis of their experimental M_n values and mass fractions of PDMSMA units, average numbers of 2.2−1040 PDMS chains per HBFP−PDMS macromolecule were further obtained. Theoretically, it is possible that sample **3c** with only 2.2 PDMS chains per macromolecule might contain a significant portion of macromolecules without PDMS chains, i.e., unreacted HBFP species. As a note, we avoided the investigation of initiation efficiency for the preparation of **3** using HBFP as macroinitiators, due to a lack of quantitative determination method with sufficient accuracy.

Thermogravimetric Analysis. Thermogravimetric analysis of PDMS-grafted fluorocopolymers **1**, **2**, and **3** was conducted under nitrogen atmosphere, from 25 to 550 °C, with a heating rate of 10 °C per min, to investigate their thermal stabilities (Figure 10). Thermolytic profiles of their precursors, including PDMSMA macromonomers and HBFP macroinitiators, were also measured as references to evaluate the changes of thermal stability of polymers before and after synthetic reactions of these copolymers.

Poly(PFS-*co*-PDMSMA) copolymers **1a** (M_n = 28.9 kDa, $F_{PDMSMA-870}$: 11%), **1b** (M_n = 49.2 kDa, $F_{PDMSMA-870}$: 50%), **1c** (M_n = 52.9 kDa, $F_{PDMSMA-870}$: 69%), and **1d** (M_n = 46.7 kDa, $F_{PDMSMA-4400}$: 11%) had onset temperatures of thermal degradation (T_d) at 310, 285, 271, and 343 °C, respectively (Figure 10a). With increases of graft density, copolymers **1a**, **1b**, and **1c** with short PDMS grafts showed decreased thermal stability. Copolymer **1d** had better thermal stability than the others, due to its long PDMS grafts, as supported by the fact that PDMSMA-4400 (onset T_d: 380 °C) had much higher thermal stability than did PDMSMA-870 (onset T_d: 149 °C). Relative to their precursor PDMSMA-870, **1a**, **1b**, and **1c** had significantly higher thermal stabilities, but on the other hand, relative to its precursor PDMSMA-4400, **1d** had appreciably lower thermal stability. Thermal degradation of copolymers **1a**, **1b**, and **1c** completed at 450−470 °C. Thermal degradation of copolymer **1d** was near to completion at 550 °C.

Poly(PFS-*co*-PDMSMA-*co*-CMS) copolymers **2** exhibited onset T_d values similar to those for poly(PFS-*co*-PDMSMA) copolymers **1** (Figure 10b). Among copolymers with short PDMS grafts, **2c** (M_n = 84.1 kDa, $F_{PDMSMA-870}$, 8%; onset T_d, 320 °C), with the lowest graft density, showed higher thermal stability than **2a** (M_n = 59.1 kDa, $F_{PDMSMA-870}$, 26%; onset T_d, 295 °C), **2b** (M_n = 63.8 kDa, $F_{PDMSMA-870}$, 22%; onset T_d, 299 °C; not shown), and **2d** (M_n = 207 kDa, $F_{PDMSMA-870}$, 42%; onset T_d, 297 °C). With long PDMS grafts, **2e** (M_n = 132 kDa, $F_{PDMSMA-4400}$, 10%; onset T_d, 343 °C) had better thermal stability than copolymers **2a**−**d**, but was less thermally stable than its precursor PDMSMA-4400.

Samples **2a**, **2b**, and **2c**, with 9−17 wt % of units from CMS, showed two evident phases of thermal degradation. The first phase of fast degradation that occurred from onset T_d to about 450 °C for about 85% mass loss was ascribed to thermal degradation of all PDMS grafts and linear portions of the hyperbranched fluorinated backbones. The second phase of slow degradation that occurred after about 450 °C was ascribed mainly to thermal degradation of CMS-based branched portions of hyperbranched fluorinated backbones. Finally, at 550 °C, each of samples **2a**, **2b**, and **2c** had 12−13% mass remaining. On the other hand, samples **2d** and **2e** did not show two such phases of thermal degradation, due to their very low degree of branching, which was deduced from their very low compositions of CMS (∼3 wt %).

Similar to their precursors, HBFP-8600 and HBFP-258000, with onset T_d values of only 215 and 230 °C, HBFP−PDMS copolymers **3** exhibited low onset T_d values of 219−251 °C. The composition of **3** complicated their thermal stabilities.

Scheme 3

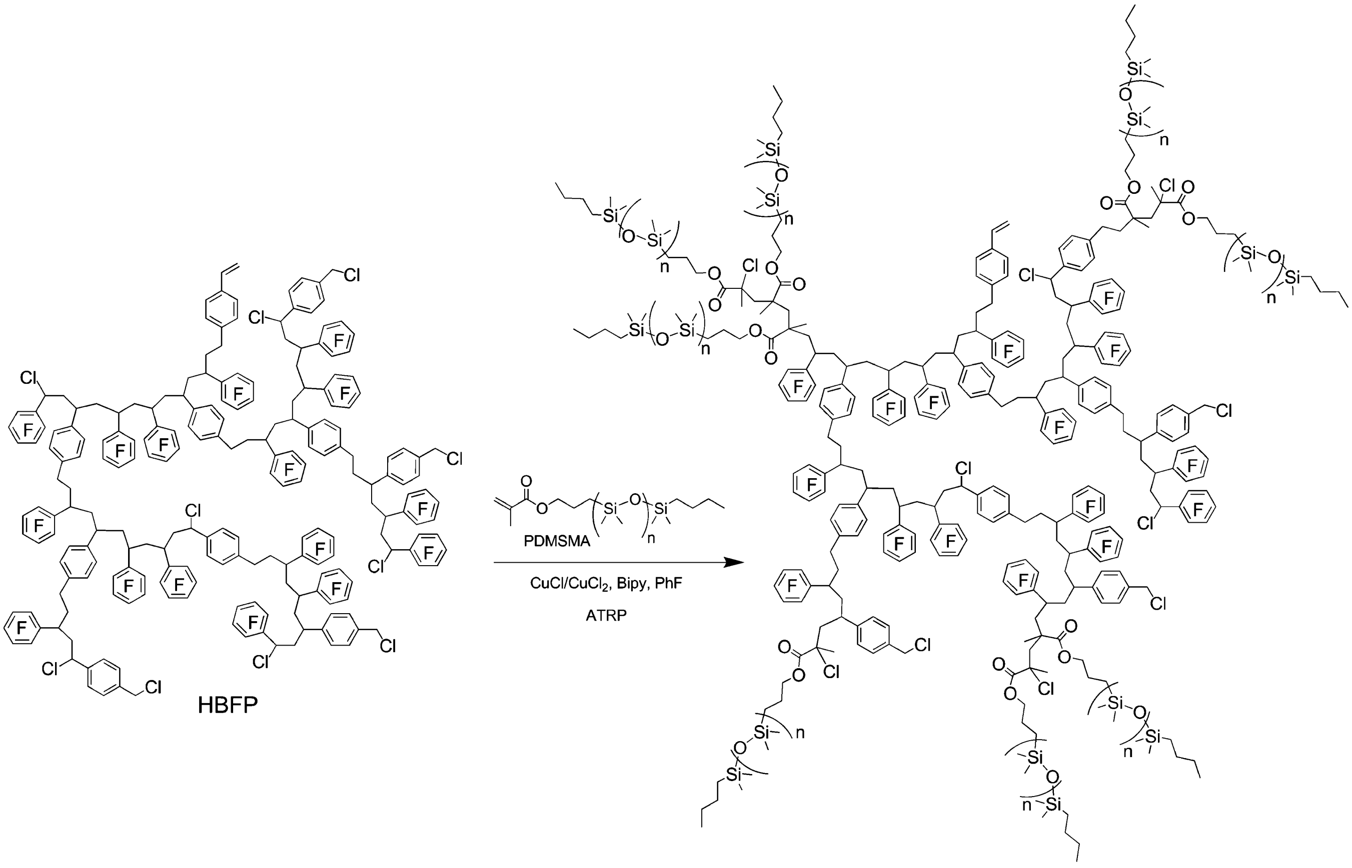


Table 3. ATRP of PDMSMA-870 Initiated by HBFP[a]

entry	HBFP M_n[b] (kDa)	HBFP PDI[b]	HBFP F_{PFS}:F_{CMS}[c]	HBFP N_{Cl}[d]	[PDMSMA-870]$_0$: [Cl$_{HBFP}$]$_0$[e]	t (h)	convn[f] (%)	F_{PDMSMA}[g] calcd[h]	F_{PDMSMA}[g] EA[i]	M_n (kDa) calcd[j]	M_n (kDa) GPC[b]	PDI[b]	N_{PDMSMA}[k]
3a	8.6	2.23	0.44:0.56	28	1.35	10	46	0.26	0.24	23.7	61.8	2.18	44
3b	8.6	2.23	0.44:0.56	28	1.03	10	23	0.12	0.11	14.4	29.3	2.12	13
3c	8.6	2.23	0.44:0.56	28	0.26	10	18	0.026	0.022	9.7	19.3	2.03	2.2
3d	258	2.70	0.62:0.38	550	1.35	10	57	0.23	0.21	626	1560	2.21	1040
3e	258	2.70	0.62:0.38	550	1.03	8	60	0.19	0.17	546	1040	3.39	630
3f	258	2.70	0.62:0.38	550	0.26	8	30	0.029	0.022	294	341	4.96	39

[a] [initiator site]$_0$/[CuCl]$_0$/[CuCl$_2$]$_0$/[Bipy]$_0$/[DMB]$_0$ = 1.0/0.4/0.04/0.88/0.44; 60−80 vol % of PhF; 65 °C. [b] By GPC with multiangle laser light scattering. [c] Molar ratios of PFS units to CMS-based units in HBFP. [d] Average number of benzylic chlorides (ATRP initiator sites) per HBFP macromolecule. [e] Initial molar feed ratio of PDMSMA-870 macromonomer to ATRP initiator site. [f] Conversion of macromonomer determined by ^{1}H NMR spectroscopy. [g] Molar fraction of PDMSMA units in copolymers **3**. [h] Calculated based on the molar feed fractions and conversions of PDMSMA, and compositions of HBFP. [i] Determined by elemental analysis. [j] Calculated based on the molar feed fractions and conversions of PDMSMA, and M_n of HBFP. [k] Average number of PDMSMA units per macromolecule of copolymers **3**, based on F_{PDMSMA} and M_n of **3**.

Samples **3a** (M_n = 61.8 kDa, $F_{PDMSMA-870}$, 24%; onset T_d, 243 °C), **3b** (M_n = 29.3 kDa, $F_{PDMSMA-870}$, 11%; onset T_d, 219 °C), and **3c** (M_n = 19.3 kDa, $F_{PDMSMA-870}$, 2.2%; onset T_d, 251 °C) had their cores derived from HBFP-8600, and differed with each other in PDMS content. Sample **3b**, with its PDMS content between those of **3c** and **3a**, showed the lowest onset T_d value among the three samples. A similar trend was also observed in samples **3d** (M_n = 1560 kDa, $F_{PDMSMA-870}$, 21%; onset T_d, 251 °C), **3e** (M_n = 1040 kDa, $F_{PDMSMA-870}$, 17%; onset T_d, 225 °C), and **3f** (M_n = 341 kDa, $F_{PDMSMA-870}$, 2.2%; onset T_d, 240 °C), which were prepared using HBFP-258000 (thermolytic profiles of **3d**, **3e**, and **3f** were not shown).

Thermal degradations of copolymers **3** were limited before 330 °C with 6−13% mass loss, became significant at 330−430 °C with 44−71% mass loss, and was low again at 430−550 °C with 6−15% mass loss. Their mass losses before 430 °C were ascribed mainly to thermal degradation of PDMS grafts, as well as benzylic chloride functionalities and linear portions of HBFP cores. Their mass losses after 430 °C were ascribed mainly to thermal degradation of CMS-based branched portions of their HBFP cores. For the samples derived from the same HBFP, those with high PDMS contents had lower final remaining mass percentages at 550 °C.

Both copolymers **2** and **3** were composed of structural units from PFS, CMS, and PDMSMA with different topological features, and their thermolytic profiles were compared. Because of their similar fractions of units from comonomers and inimer as detected by elemental analysis, the high onset T_d of **2a** relative to **3a** (295 vs 243 °C) suggested that the topological arrangement of structural units had significant influences on their thermal behaviors.

Solubility. Because PDMS-grafted fluorocopolymers **1**, **2** and **3** have different grafted architectures, solubility studies were focused on the influence of grafted features on solubility. Samples **1b**, **1d**, **2a**, and **3a**, with PDMS as the major component (56−74 wt %), have comparable M_n values (46.7−61.8 kDa),

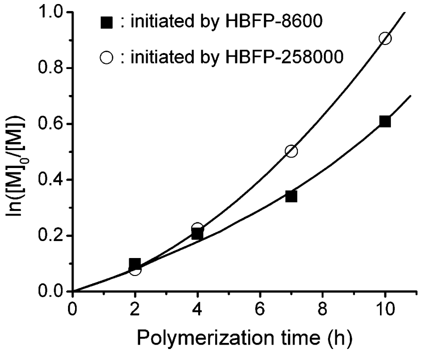


Figure 8. Kinetic plot for HBFP−PDMS synthetic systems ([PDMSMA-870]$_0$:[Cl$_{\mathrm{HBFP}}$]$_0$:[CuCl]$_0$:[CuCl$_2$]$_0$:[Bipy]$_0$:[DMB]$_0$ = 1.35:1.0:0.4:0.04:0.88:0.44; 60 vol % of PhF; 65 °C; for the preparations of copolymers **3a** and **3d**, from HBFP-8600 and HBFP-258000, respectively).

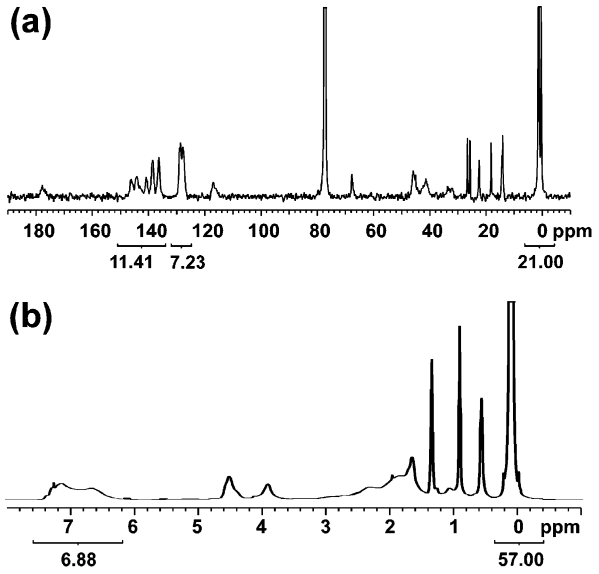


Figure 9. (a) ^{13}C NMR spectrum (128.7 MHz, CDCl$_3$) of copolymer HBFP−PDMS **3a**; (b) ^{1}H NMR spectrum (500 MHz, CDCl$_3$) of copolymer HBFP−PDMS **3a**.

and therefore, their solubilities were compared (Table 4). The solubilities of their precursors, including PDMSMA-870, PDMSMA-4400, and HBFP-8600, were also tested for references. At room temperature, each copolymer **1b**, **1d**, **2a**, and **3a** was soluble in hexane, cyclohexane, benzene, toluene, methylene chloride, chloroform, carbon tetrachloride, fluorobenzene, ethyl acetate, diethyl ether, tetrahydrofuran, and 1,4-dioxane and was insoluble in dimethyl sulfoxide (DMSO), ethanol, and methanol. At the same time, they had significantly different solubility in acetone, pyridine, 1-butanol, acetonitrile, *N*,*N*-dimethylformamide (DMF).

As copolymers with PDMS grafted on linear fluorinated backbones, sample **1b** (M_n = 49.2 kDa, 74 wt % of PDMS; $F_{\mathrm{PDMSMA-870}}$, 50%) exhibited better solubility than sample **1d** (M_n = 46.7 kDa, 74 wt % of PDMS; $F_{\mathrm{PDMSMA-4400}}$, 11%) in acetone, pyridine, 1-butanol, acetonitrile. Because they had very similar M_n and the same weight percent of PDMS, such results suggested that increased graft density and decreased graft length may lead to increasing solubility. High graft density may result in rigidified solution morphology of macromolecules and reduced intra-macromolecular attractive secondary forces. As supported by the fact that PDMSMA-870 has also better solubility than PDMSMA-4400 in solvents including pyridine, acetonitrile, and others, relative to long PDMS grafts of **1d**, short PDMS grafts of **1b** were expected to be dissolved easily due to minimized interchain entanglements.

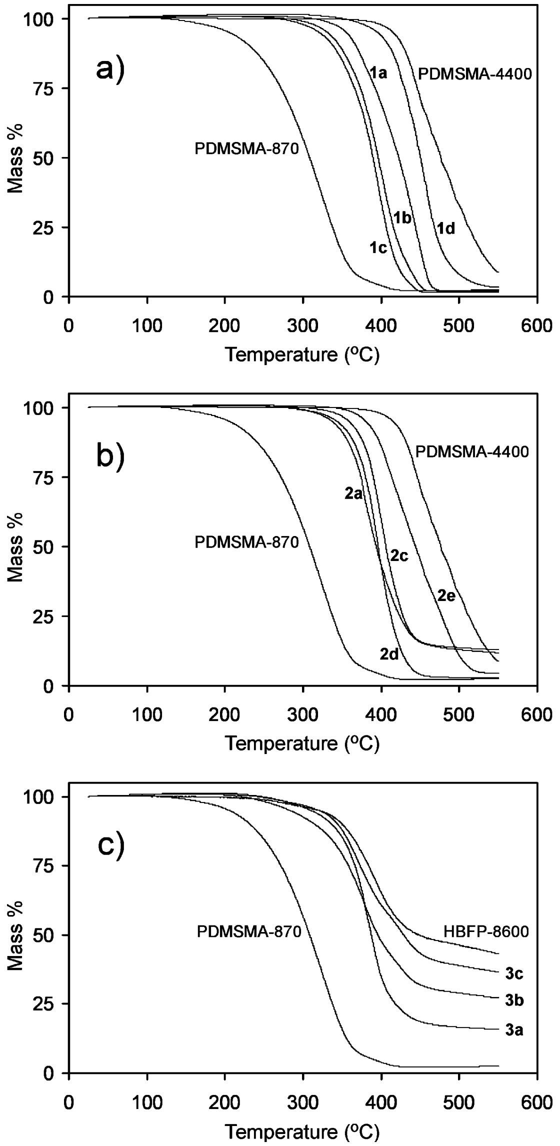


Figure 10. (a) Thermolytic profiles of poly(PFS-*co*-PDMSMA) copolymers **1**; (b) thermolytic profiles of poly(PFS-*co*-PDMSMA-*co*-CMS) copolymers **2**; (c) thermolytic profiles of HBFP−PDMS copolymers **3** (heating rate: 10 °C/min; nitrogen atmosphere; thermolytic profiles of precusors PDMSMA-870, PDMSMA-4400, and HBFP-8600 were presented for comparison).

Both of the copolymers **2a** (M_n = 59.1 kDa, 60 wt % of PDMS; $F_{\mathrm{PDMSMA-870}}$, 26%) and **3a** (M_n = 61.8 kDa, 56 wt % of PDMS; $F_{\mathrm{PDMSMA-870}}$, 24%) were prepared from PFS, CMS, and PDMSMA. They have similar M_n values, weight percent of PDMS, and molar fractions of PDMSMA-870 structural units. They also exhibited similar solubility in most solvents used, except acetonitrile and DMF. Copolymer **2a** was slightly soluble in both acetonitrile and DMF, whereas copolymer **3a** was insoluble in acetonitrile and soluble in DMF. Such solubility differences may have resulted from their different grafted features (PDMS chains of **2a** were grafted within a hyperbranched backbone, but PDMS chains of **3a** were grafted on HBFP cores).

Although copolymer **3a** had its core derived from HBFP-8600, it showed significantly different solubility. HBFP-8600 could not be dissolved by hexane, cyclohexane and 1-butane,

Table 4. Solubility Comparison of PDMS-Grafted Fluorocopolymers, PDMSMA and HBFP[a]

solvent	**1b**	**1d**	**2a**	**3a**	PDMSMA-870	PDMSMA-4400	HBFP-8600
hexane	s	s	s	s	s	s	i
cyclohexane	s	s	s	s	s	s	i
benzene	s	s	s	s	s	s	s
toluene	s	s	s	s	s	s	s
methylene chloride	s	s	s	s	s	s	s
chloroform	s	s	s	s	s	s	s
carbon tetrachloride	s	s	s	s	s	s	s
fluorobenzene	s	s	s	s	s	s	s
ethyl acetate	s	s	s	s	s	s	s
diethyl ether	s	s	s	s	s	s	s
tetrahydrofuran	s	s	s	s	s	s	s
1,4-dioxane	s	s	s	s	s	s	s
acetone	s	ss	s	s	s	s	s
pyridine	ss	i	s	s	s	i	s
1-butanol	s	ss	s	s	s	s	i
acetonitrile	ss	i	ss	i	ss	i	ss
N,*N*-dimethylformamide	ss	ss	ss	s	s	ss	s
methyl sulfoxide	i	i	i	i	i	i	s
ethanol	i	i	i	i	s	s	i
methanol	i	i	i	i	ss	i	i

[a] Room temperature, 10 mg/mL. Key: i, insoluble; s, soluble; ss, slightly soluble.

but **3a** was soluble in all three solvents; HBFP-8600 could be easily dissolved in DMSO, but **3a** was insoluble in this solvent. On the other hand, **3a** qualitatively agreed with PDMSMA-870 in solubility in these four solvents. Such results indicated that the solubility of **3a** was more dominated by its PDMS grafts, because they, with 56 wt % of **3a**, were attached predominantly on the shell domains and played a major role in polymer−solvent interaction. It should be noted that both **3a** and HBFP-8600 were insoluble in methanol and ethanol but PDMSMA-870 was slightly soluble in methanol and soluble in ethanol, indicating the core domain of **3a** still affected its solubility.

Conclusions

Three types of PDMS-grafted fluorocopolymers with different branching characteristics have been prepared based on ATRP technology via a “grafting through” approach using PDMSMAs as macromonomer. These three kinds of macromolecular architectures allowed for investigation of the effects of polymer composition and topology on their physical properties. However, even more importantly at this stage of the methodology development, we were able to study the effects of synthetic strategies on the polymerization efficiencies and the structures of the resulting materials.

Copolymers **1**, with a linear fluorinated backbone and linear PDMS grafts, were prepared by copolymerizations of PFS with PDMSMA. Comparable polymerization rates of PFS and PDMSMA were observed during their copolymerizations, and the reactivity of PDMSMA was not significantly affected by its chain length. The copolymers had well-controlled compositions, but their molecular weights and molecular weight distributions were affected by considerable occurrence of biradical coupling at the late stages of copolymerizations.

Copolymers **2**, with a hyperbranched fluorinated backbone and linear PDMS-based grafts, were prepared by SCVCP of PFS and PDMSMA, with inimer CMS. In the SCVCP process, the vinyl bonds of CMS showed higher reactivity than those of PFS and PDMSMA; the vinyl bonds of PDMSMA exhibited reactivity similar to those of PFS at initial stages of copolymerization, but the polymerization rate of PDMSMA appeared to be negatively affected by steric hindrance between the macromonomer and the resulting hyperbranched copolymers. The copolymers had well-controlled compositions, high molecular weights, and broad molecular weight distributions.

Copolymers **3**, with a hyperbranched fluorinated core and PDMS linear grafts, were prepared by ATRP of PDMSMA initiated by pre-established HBFP (obtained by SCVCP of PFS and CMS). HBFP with a high M_n led to faster reaction than HBFP with a low M_n under similar reaction conditions. The compositions of the copolymers were controlled through the conversions and initial feeds of PDMSMA. Biradical coupling was a major synthetic concern, and was controlled through the initial feeds of deactivator ($CuCl_2$).

The effects of grafting features on properties were investigated through thermogravimetric analysis and solubility tests of copolymers **1**, **2**, and **3**. With similar molar fraction of structural units, **2** exhibited significantly higher onset T_d values than **3**, indicating that properties of copolymers (in this example, thermal stability of copolymers) can be affected by topological arrangement of structural units. Solubility tests also supported the influence of grafting features on polymer properties.

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