Well-Defined Polymers Bearing Pendent Alkene Functionalities via Selective RAFT Polymerization

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ABSTRACT: A facile synthetic approach for the preparation of well-defined copolymers bearing pendent alkene functionalities was established by selective reversible addition–fragmentation chain transfer (RAFT) (co)polymerization. A divinyl monomer, 4-(3′-buten-1′-oxy)-2,3,5,6-tetrafluorostyrene (**1**), with a styrenyl group and a pendent alkene group was synthesized. Because of a very high reactivity of the styrenyl group relative to the alkene group in **1**, functional fluorocopolymers with both well-defined structures and pendent alkene groups were prepared by RAFT polymerization of **1** and copolymerization of **1** with pentafluorostyrene (PFS). Alkene-functionalized diblock copolymers were also prepared by RAFT copolymerizations of **1** with PFS or styrene, extending from a poly(styrene-*alt*-maleic anhydride) macrochain transfer agent. Hydrolysis and aminolysis of these copolymers resulted in amphiphilic diblock fluorocopolymers with alkene-functionalized hydrophobic segments, which were shown to form internally functionalized micelles in THF–water.

Introduction

The preparation of polymers with accurately controlled structures has become a research theme of modern polymer chemistry. Because properties and performances of polymers greatly depend on the kind and number of functional groups, the development of synthetic strategies that exert excellent control over functionalities of polymers has attracted increased interest.[1–8] Because of the broad applications of vinyl groups in polymerization,[9] cross-linking,[10–17] radical coupling,[18–22] postmodification, and transformations into other useful functionalities,[23] well-defined polymers with pendent vinyl groups have received significant attention.[20,24–35]

Similar to most types of polymers with functional side groups, those having multiple pendent vinyl groups have been synthesized by either postpolymerization functionalization or polymerization of vinyl-functionalized monomers. With high selectivity toward substituted vinyl groups, anionic polymerization of nonsymmetric divinyl monomers has provided a variety of well-defined vinyl-functionalized polymers. For example, as reported by Zhang and Ruckenstein,[25,26] anionic polymerizations of 4-(vinylphenyl)-1-butene and *trans,trans*-1-methacryloyloxy-2,4-hexadiene showed high selectivity, whereby only styrenyl and methacrylic groups underwent polymerization, and well-defined alkene-functionalized polystyrenes and polymethacrylates were afforded. The vinyl groups also exhibit little or no reactivity under the reaction conditions of most ring-opening polymerizations (except ring-opening radical polymerization). Ring-opening polymerizations,[20,28,29,36,37] including ring-opening metathesis polymerization,[38] of vinyl-functionalized cyclic monomers have yielded polymers with maintenance of side-chain vinylic groups. As illustrated by Coates and coworkers,[28] ring-opening polymerization using vinylcyclohexene oxide with other comonomers gave vinyl-functionalized polycarbonates, which were further converted into unimolecular nanoparticles through intramolecular cross-linking.

Throughout the past decade, controlled radical polymerization (CRP) has become one of the most powerful synthetic tools for the preparation of well-defined polymers. Three major CRP techniques have been developed, including nitroxide-mediated polymerization (NMP),[39] atom transfer radical polymerization (ATRP),[40] and reversible addition–fragmentation chain transfer (RAFT) polymerization.[41–47] With good functional group tolerance, CRP of functional monomers has readily provided a broad variety of polymers with terminal or side-chain functional groups. For instance, the syntheses of norbornenyl-based α-alkene macromonomers by ATRP or RAFT of vinylic monomers with high reactivity toward radical polymerization have been demonstrated using norbornene-functionalized initiators.[48,49] In such selective polymerizations, it is important to balance the relative reactivities of the multiple alkenyl groups in the system. The significant difference in reactivity between the norbornenyl units and styrenyl- or acrylate-based monomers provided for good control; however, there are situations in which the outcomes have not been as positive. Although, theoretically, methacrylate vinyl groups are more reactive than allyl groups toward ATRP, their difference is not sufficient. ATRP of allyl methacrylate (AMA) experienced cross-linking in early stages of polymerization, indicating that the selectivity between its two vinyl groups was not sufficient to afford well-defined allyl-functionalized polymers.[31–33]

Because CRP can provide polymers with C–C backbones under less stringent reaction conditions than typical anionic polymerization or ring-opening polymerization, we are interested in establishing selective CRP of nonsymmetrical divinyl monomers as an approach for the preparation of well-defined polymers with alkene functionalities. In this article, we report our recent research on selective RAFT polymerization of 4-(3′-buten-1′-oxy)-2,3,5,6-tetrafluorostyrene. As one of the major controlled/living polymerization techniques, RAFT polymerization provides homogeneous and metal-free controlled/living polymerization systems applicable to a wide variety of monomers under relatively mild temperature and therefore was chosen in this study.

Experimental Section

Materials. 2,3,4,5,6-Pentafluorostyrene (PFS) and styrene were purified by passing through a column packed with neutral alumina gel and were stored under argon at 4 °C. The chain transfer

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Chart 1. Various Divinyl Monomers Designed for Selective Radical Polymerization
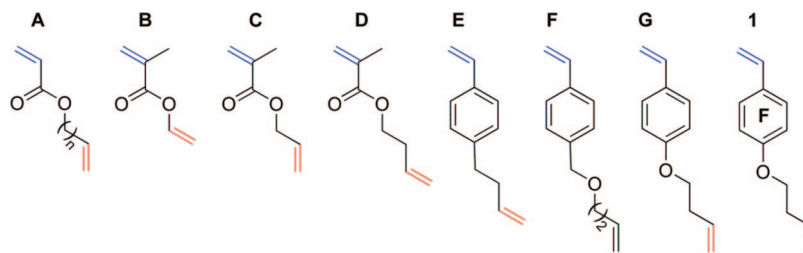
Table 1. Calculated Reactivity Ratios for Divinyl Monomers[a]

divinyl monomers[b]	(Q_1, e_1)	(Q_2, e_2)	r_1	r_2	r_1/r_2
A: MA vs BE	(0.45, 0.64)	(0.007, −0.06)	41	0.015	2800
B: MMA vs VAc	(0.78, 0.40)	(0.026, −0.88)	18	0.011	1700
C; MMA vs AAc	(0.78, 0.40)	(0.24, −1.07)	1.8	0.06	28
D: MMA vs BE	(0.78, 0.40)	(0.007, −0.06)	89	0.009	10 200
E/F: MSt vs BE[c]	(1.10, −0.60)	(0.007, −0.06)	110	0.007	17 000
G: MOSt vs BE	(1.53, −1.40)	(0.007, −0.06)	33	0.005	6800
1: PFS vs BE[d]	(0.86, 0.75)	(0.007, −0.06)	68	0.008	8800

[a] (Q, e) values are cited from *Polymer Handbook*,[52] and reactivity ratios were calculated on the basis of Alfrey−Price equations: $r_1 = (Q_1/Q_2) \cdot \exp[-e_1(e_1 - e_2)]$; $r_2 = (Q_2/Q_1) \cdot \exp[-e_2(e_2 - e_1)]$. [b] Individual vinylic functionalities within the divinyl monomer structures: MA, methyl acrylate; BE, 1-butene; MMA, methyl methacrylate; VAc, vinyl acetate; AAc, allyl acetate; MSt, *p*-methyl styrene; MOSt, *p*-methoxy styrene. [c] Both 4-(3-buten-1-yl)-styrene (**E**) and (3′-buten-1′-oxy) 4-vinylbenzyl ether (**F**) were approximated to the same copolymerization system as 4-methoxy styrene versus 1-butene. [d] 4-(3′-Buten-1′-oxy)-2,3,5,6-tetrafluorostyrene (**1**) was approximated to a copolymer pair of PFS with BE. (Q, e) of PFS is cited from the literature.[55]
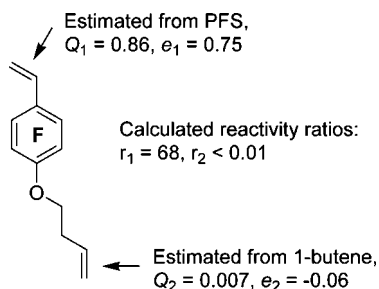

Figure 1. Structural design of nonsymmetrical divinyl monomer **1** for selective RAFT polymerization.

agent *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (DDMAT) was prepared following the published procedure.[50] All other chemicals and reagents were purchased from Aldrich Chemical and were used as received, unless otherwise noted.

　　Characterization Methods. ¹H NMR spectra were recorded at 300 MHz in CDCl₃, acetone-d_6, or DMSO-d_6 on a Varian Mercury 300 spectrometer with the solvent proton signal as standard. ¹³C NMR spectra were recorded at 150.8 MHz in CDCl₃ on a Varian Unity 600 spectrometer with the solvent carbon signal as standard. ¹⁹F NMR spectra were recorded at 282.2 MHz in CDCl₃ on a Varian Mercury 300 spectrometer with external CFCl₃ as standard. Infrared spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR system using diffuse reflectance sampling accessories and were analyzed by the use of FT-IR Spectrum v2.00 software (Perkin-Elmer, Beaconsfield, Bucks, England).

　　Size exclusion chromatography (SEC) was conducted on a Waters 1515 HPLC (Waters Chromatography) equipped with a Waters 2414 differential refractometer, a PD2026 dual-angle (15 and 90°) light scattering detector (Precision detectors), and a three-column series with PL gel 5 μm mixed C, 500 Å, and 10^4 Å (300 × 7.5 mm) columns (Polymer Laboratories). The system was equilibrated at 35 °C in 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

Scheme 1. Synthesis of 4-(3′-Buten-1′-oxy)-2,3,5,6-tetrafluorostyrene (1)
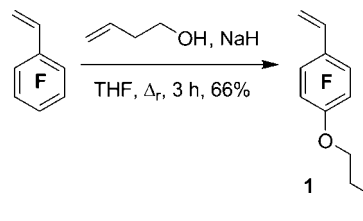
volume of 200 μL was used. Data collection and analysis were performed, respectively, with Precision Acquire software and Discovery 32 software (Precision Detectors). The interdetector delay volume and the light scattering detector calibration constant were determined by calibration using a nearly monodispersed polystyrene standard (Pressure Chemical, 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.

　　Samples for transmission electron microscopy (TEM) measurements were diluted with 1 wt % of phosphotungstic acid (PTA) stain solution (v/v 1:1). Carbon grids were exposed to oxygen plasma treatment to increase the surface hydrophilicity. Micrographs were collected at 100 000× magnification and were calibrated by the use of a 41 nm polyacrylamide bead from NIST. The number average particle diameters (D_{av}) and standard deviations were generated from the analysis of a minimum of 150 particles from at least 3 different micrographs.

　　Hydrodynamic diameters (D_h) and size distributions for the micelles in aqueous solutions were determined by dynamic light scattering (DLS). The DLS instrumentation consisted of a Brookhaven Instruments (Worcestershire, U.K.) system, including a model BI-200SM goniometer, a model BI-9000AT digital correlator, a model EMI-9865 photomultiplier, and a model 95−2 Ar ion laser (Lexel, Farmindale, NY) operated at 514.5 nm. Measurements were made at 20 ± 1 °C. Prior to analysis, solutions were filtered through a 0.22 μm Millex-GV PVDF membrane filter (Millipore, Medford, MA) and were then centrifuged in a model 5414 microfuge (Brinkman Instruments, Westbury, NY) for 10 min to remove dust particles. Scattered light was collected at a fixed angle of 90°. The digital correlator was operated with 522 ratio spaced channels, an initial delay of 5 μs, a final delay of 100 ms, and a duration of 10 min. A photomulitplier aperture of 400 μm was used, and the incident laser intensity was adjusted to obtain a photon counting of between 200 and 300 kcps. Only measurements in which the measured and calculated baselines of the intensity autocorrelation function agreed to within 0.1% were used to calculate particle size. The calculations of the particle size distributions and distribution averages were performed with the ISDA software package (Brookhaven Instruments), which employed single-exponential fitting, cumulants analysis, non-negatively constrained least-squares (NNLS), and CONTIN particle size distribution analysis routines. All determinations were made in triplicate.
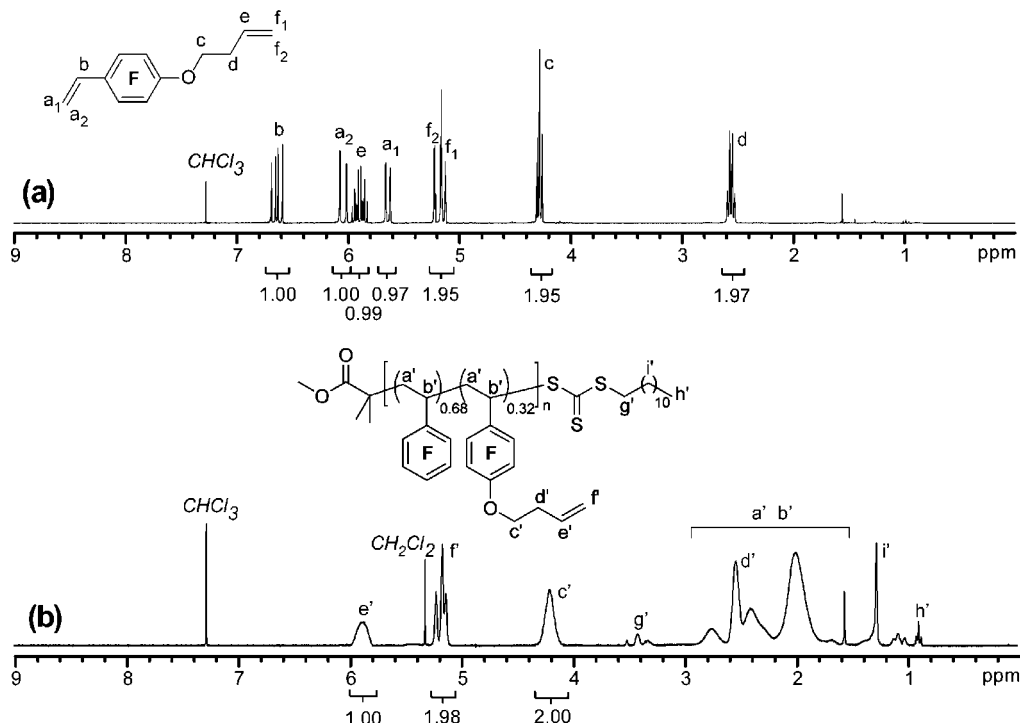
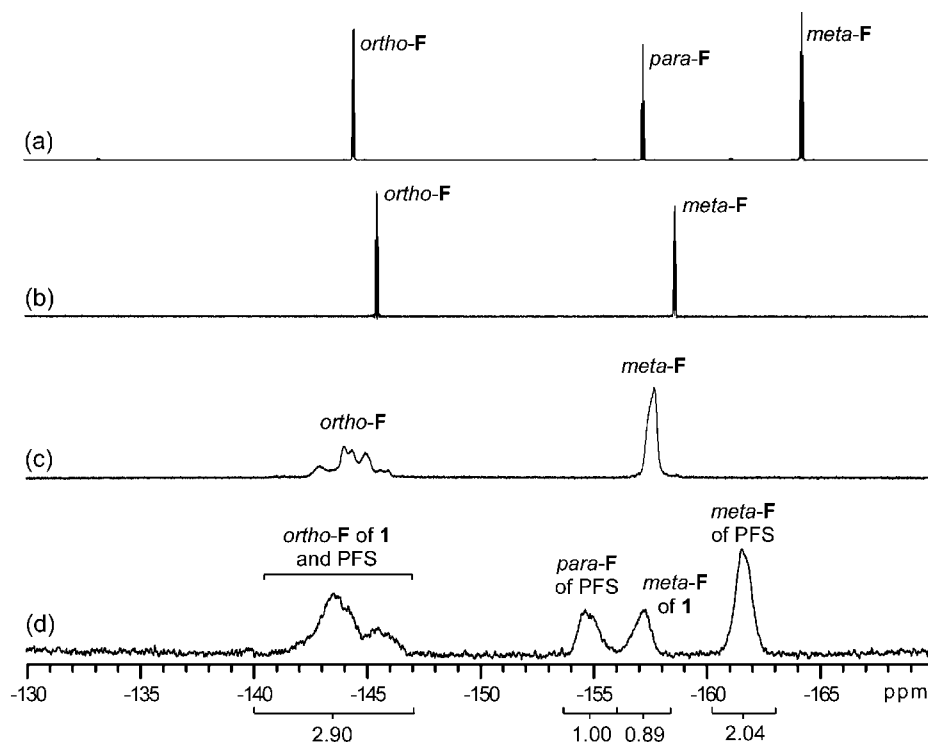**Figure 2.** ^{1}H NMR spectra of (a) the divinyl monomer **1** and (b) copolymer **3** (300 MHz, CDCl$_3$).

Figure 3. ^{19}F NMR spectra of (a) PFS, (b) divinyl monomer **1**, (c) polymer **2**, and (d) copolymer **3** (282 MHz, CDCl$_3$).

Synthesis of S-1-Dodecyl-S′-(α,α′-dimethyl-α″-methyl acetate)-trithiocarbonate (DDMMAT). DDMAT (2.92 g, 8.0 mmol), CH$_3$OH (0.79 g, 25 mmol), dicyclohexylcarbodiimide (DCC, 1.72 g, 8.4 mmol), and 4-dimethylaminopyridine (DMAP, 0.10 g, 0.80 mmol) were loaded in a 250 mL round-bottomed flask containing 100 mL of dry CH$_2$Cl$_2$. The reaction mixture was allowed to stir at room temperature under a nitrogen atmosphere for 40 h. The mixture was filtered, and the filtrate was concentrated in vacuo and separated by flash chromatography using CH$_2$Cl$_2$/hexane (1:4 v/v) as eluent to yield 2.85 g (94%) of DDMMAT as a yellow oil. IR (NaCl, cm^{-1}): 2924, 2852, 1740, 1465, 1382, 1363, 1263, 1193, 1154, 1128, 1067, 817. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 0.88 (t, *J* = 6.5 Hz, 3H, −(CH$_2$)$_{11}$C*H$_3$*), 1.26 (br, 18H, −SCH$_2$CH$_2$-(C*H$_2$*)$_9$CH$_3$), 1.66 (m, 2H, −SCH$_2$C*H$_2$*−), 1.70 (s, 6H, −SC(C*H$_3$*)$_2$COOCH$_3$), 3.28 (t, *J* = 7.5 Hz, 2H, −SC*H$_2$*CH$_2$−), 3.71 (s, 3H, −OC*H$_3$*). ^{13}C NMR (150.8 MHz, CDCl$_3$, δ): 14.1, 22.8, 25.1, 29.4, 31.9, 35.8, 52.5, 55.0, 174.5, 222.1. MS (ESI, M$^{·+}$): [C$_{18}$H$_{34}$O$_2$S$_3$ + H$^+$], calcd, 379.1793; found, 379.1784.

Scheme 2. RAFT Homopolymerization of 1 and RAFT Copolymerization of 1 and PFS[a]
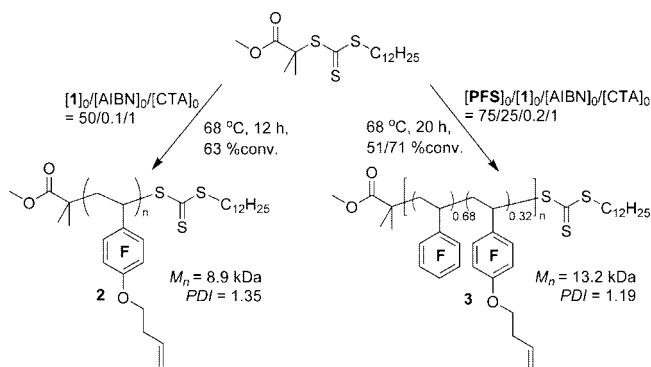
[a] Average *n* values were *n* = 32 and 57 for **2** and **3**, respectively.

Synthesis of 4-(3′-Buten-1′-oxy)-2,3,5,6-tetrafluorostyrene, 1. 3-Buten-1-ol (6.53 g, 90.5 mmol) was diluted with dry THF (60 mL) and deprotonated by the addition of NaH (2.71 g, 113 mmol) over 20 min at 0 °C. PFS (14.1 g, 72.4 mmol) in dry THF (30 mL) was then added dropwise. The reaction mixture was heated at reflux for 3 h, cooled to room temperature, and concentrated under reduced pressure. Saturated NH_4Cl solution (100 mL) was slowly added, and the organic products were extracted in CH_2Cl_2 (70 mL × 3), which was then washed with water (70 mL) and dried over $MgSO_4$. The organic phase was concentrated to give the crude product, which was purified by flash chromatography using CH_2Cl_2/hexane (1:19 v/v) as eluent to yield 11.8 g (66%) of product as a colorless liquid. IR (NaCl, cm^{-1}): 3080−2960, 1660−1620, 1530−1400, 1353, 1291, 1252, 1180−1060, 980−962, 944, 895, 847, 667. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 2.55 (td, *J* = 6.8 and 6.6 Hz, 2H, −OCH$_2$CH_2CH=CH$_2$), 4.28 (t, *J* = 6.8 Hz, 2H, −OCH_2CH$_2$CH=CH$_2$), 5.15 (dd, 1H, *J* = 18.0 and 2.8 Hz, *cis*-OCH$_2$CH$_2$CH=CH *H*), 5.11 (dd, *J* = 11.8 and 2.8 Hz, *trans*-OCH$_2$CH$_2$CH=C *H*H), 5.63 (d, *J* = 12.0 Hz, 1H, *cis*-C*H*H=CHAr), 5.89 (m, 1H, −OCH$_2$CH$_2$C*H*=CH$_2$), 6.04 (d, *J* = 17.6 Hz, 1H, *trans*-CH *H*=CHAr), 6.63 (dd, *J*$_1$ = 17.6 and 12.0 Hz, 1H, CH$_2$=C*H*Ar). ^{13}C NMR (150.8 MHz, CDCl$_3$, δ): 34.4, 74.4, 118.5, 122.2, 134.4, 136.2, 139.9, 143.3, 144.1, 147.2. ^{19}F NMR (282.2 MHz, CDCl$_3$, δ): −158.7 (m, 2F, *meta*-F), −145.6 (m, 2F, *ortho*-F). MS (ESI, M$^{•+}$): [C$_{12}$H$_{10}$OF$_4$ + H$^+$], calcd, 247.0741; found, 247.0690.

Synthesis of Poly(1), 2. A 10 mL Schlenk flask with a stir bar and sealed by a rubber septum was charged with **1** (1.24 g, 5.02 mmol), DDMMAT (37.9 mg, 0.10 mmol), 2,2′-azobisisobutyronitrile (AIBN, 1.6 mg, 0.010 mmol), and 0.60 mL of 2-butanone as the cosolvent. After three cycles of freeze−pump−thaw to degas the reaction mixture, the flask was placed in an oil bath at 69 °C to allow for polymerization under N$_2$. During polymerization, small aliquots (0.1 mL) of polymerization solution were withdrawn with a syringe and were analyzed by ^{1}H NMR spectroscopy for the determination of conversions of **1** and by SEC for the determination of molecular weights and polydispersities. Finally, after 12 h, the flask was immersed in liquid N$_2$ to quench the polymerization. The polymer solution was precipitated twice in 200 mL of methanol. The product was collected and dried in vacuo for 24 h at room temperature to afford **2** as a yellow solid. Yield: 0.35 g (53% based on the 63% conversion of **1**). M_n^{NMR} = 8.2 kDa, M_n^{GPC} = 8.9 kDa, PDI = 1.35, averaged degree of polymerization DP$_{ave}$ = 32. IR (NaCl, cm^{-1}): 3090−2900, 2360, 2343, 1649, 1540, 1493, 1459, 1384, 1144, 1098, 960, 921, 667. ^{1}H NMR (300 MHz, CDCl$_3$, 7.27 δ): 0.87 (br, −C*H$_3$* of DDMMAT), 1.25 (br, alkyl protons of DDMMAT), 2.51 (br, −OCH$_2$C*H$_2$*CH=CH$_2$ on polymer side chain), 2.80−1.40 (br, protons on polymer backbone), 3.39 (br, −SC*H$_2$*− of DDMMAT), 4.18 (br, −OC*H$_2$*CH$_2$−), 5.14 (br, −CH$_2$CH=C*H$_2$*), 5.87 (br, −CH$_2$C*H*=CH$_2$). ^{13}C NMR (150.8 MHz, CDCl$_3$, 77.2 δ): 19.2, 22.9, 29.1−32.3, 37.7, 74.4, 114.0, 115.2, 118.1, 135.2−144.1, 147.3. ^{19}F NMR (282.2 MHz, CDCl$_3$, δ): −158.9 (br, 2F, *meta*-F), −145.7 to −142.5 (br, 2F, *ortho*-F).

Synthesis of Poly(1$_{0.32}$-*co*-PFS$_{0.68}$)$_n$, 3. A 10 mL Schlenk flask with a stir bar and sealed by a rubber septum was charged with PFS (1.45 g, 7.5 mmol), **1** (0.62 g, 2.5 mmol), DDMMAT (37.0 mg, 0.10 mmol), AIBN (1.6 mg, 0.010 mmol), and 3 mL of 2-butanone as the cosolvent. After three cycles of freeze−pump−thaw, the mixture was allowed to stir for 10 min at room temperature to ensure that the mixture became homogeneous. The flask was then placed in an oil bath at 68 °C to allow for polymerization under N$_2$. During polymerization, small aliquots (0.1 mL) of polymerization solution were withdrawn with a syringe and were analyzed by ^{1}H NMR spectroscopy for the determination of conversion of each comonomer. Finally, after 20 h, the flask was immersed in liquid N$_2$ to quench the polymerization. The polymer solution was precipitated twice in 200 mL of methanol. The product was collected and dried in vacuo to afford **3** as a slightly green-yellow copolymer. Isolated yield: 1.02 g (83% based on 51% conversion of PFS and 71% conversion of **1**). M_n^{NMR} = 12.0 kDa, M_n^{GPC} = 13.2 kDa, PDI = 1.13, DP$_{ave}$ = 57. IR (NaCl, cm^{-1}): 3080−2850, 2358, 2332, 1646, 1540, 1493, 1455, 1381, 1224, 1136, 1082, 957, 922, 760, 702, 666. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 0.88 (br, −C*H$_3$* of DDMMAT), 1.26 (br, alkyl protons of DDM-MAT), 2.50 (br, −OCH$_2$C*H$_2$*CH=CH$_2$ on polymer side chain), 3.00−1.40 (br, protons on polymer backbone), 3.32 (br, −SC*H$_2$*− of DDMMAT), 4.17 (br, −OC*H$_2$*CH$_2$−), 5.14 (br, −CH$_2$CH=C*H$_2$*), 5.89 (br, −CH$_2$C*H*=CH$_2$). ^{13}C NMR (150.8 MHz, CDCl$_3$, δ): 22.4, 29.3−33.0, 38.2, 74.5, 115.3, 118.1, 136.2, 139.4−145.2, 147.1. ^{19}F NMR (282.2 MHz, CDCl$_3$, δ): −161.6 (br, *meta*-F of PFS units), −157.2 (br, *meta*-F of **1** units), −154.8 (br, *para*-F of PFS units), −147.0 (br, *ortho*-F of **1** units and PFS units).

Synthesis of Poly(St-*alt*-MAn)$_n$, 4. A 50 mL Schlenk flask with a stir bar and sealed by a rubber septum was charged with styrene (5.31 g, 51.0 mmol), maleic anhydride (5.00 g, 51.0 mmol), DDMMAT (387 mg, 10.2 mmol), AIBN (16.5 mg, 1.00 mmol), and 10 mL of 1,4-dioxane as the cosolvent. The reaction mixture was degassed by three cycles of freeze−pump−thaw and was then heated in an oil bath to 54 °C under N$_2$. The polymerization was quenched by cooling to room temperature and opening the flask to air. Dilution of the reaction mixture was carried out by the addition of THF at a polymerization time of 3 h with estimated conversions of both comonomers of 70%. The polymer solution was precipitated twice in 500 mL of diethyl ether and dried in vacuo to yield **4** as a pale-yellow powder. Isolated yield: 6.89 g (93% based on the 70% conversions of the comonomers). M_n^{NMR} = 7.8 kDa, M_n^{GPC} = 8.1 kDa, PDI = 1.16, DP$_{ave}$ = 38. IR (NaCl, cm^{-1}): 3090−2860, 2360, 2341, 1856, 1779, 1720, 1540−1410, 1371, 1224, 1081, 956, 924, 703, 667. ^{1}H NMR (300 MHz, acetone-*d$_6$*, δ): 0.85 (br, −C*H$_3$* of DDMMAT), 1.25 (br, alkyl protons of DDMMAT), 1.30−3.00 (br, backbone protons of styrene units), 3.00−3.90 (br, backbone protons of MAn units), 6.00−7.60 (br, Ar−*H*). ^{13}C NMR (150.8 MHz, CDCl$_3$, δ): 31.0−38.5, 40.2−46.4, 52.5, 127.0−131.2, 136.5, 140.2, 171.1−174.9.

Synthesis of Poly(St-*alt*-MAn)$_n$-*b*-P(St$_{0.55}$-*co*-1$_{0.45}$)$_n$, 5. A 10 mL Schlenk flask with a stir bar and sealed by a rubber septum was charged with St (0.79 g, 7.6 mmol), **1** (0.94 g, 3.8 mmol), macrochain transfer agent **4** (0.81 g, 0.10 mmol), AIBN (3.2 mg, 0.020 mmol) and 3 mL of 2-butanone as the cosolvent. The reaction mixture was degassed by three cycles of freeze−pump−thaw and was then heated in an oil bath to 70 °C for 5 h under N$_2$. The polymer solution was precipitated three times in 100 mL of pentane, and the product was collected and dried in vacuo to give **5** as a yellow powder. Isolated yield: 1.35 g (95% based on the 26% conversion of St and 43% conversion of **1**). M_n^{NMR} = 14.1 kDa, M_n^{GPC} = 13.6 kDa, PDI = 1.18, DP$_{ave,n}$ = 38, DP$_{ave,m}$ = 25. IR (NaCl, cm^{-1}): 3100−2900, 1858, 1782, 1735, 1648, 1492, 1454, 1382, 1332, 1225, 1136, 1082, 957, 923, 760, 702, 670. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 0.87 (br, −C*H$_3$* of DDMMAT), 1.26 (br, alkyl protons of DDMMAT), 2.51 (br, −OCH$_2$C*H$_2$*CH=CH$_2$ on polymer side chain), 1.30−3.00 (br, protons on polymer backbone except MAn units), 3.00−4.00 (br, backbone protons of MAn units), 4.15 (br, −OC*H$_2$*CH$_2$−), 5.13 (br, −CH$_2$CH=C*H$_2$*), 5.86 (br, −CH$_2$C*H*=CH$_2$), 6.00−7.80 (m, all aromatic protons). ^{13}C NMR
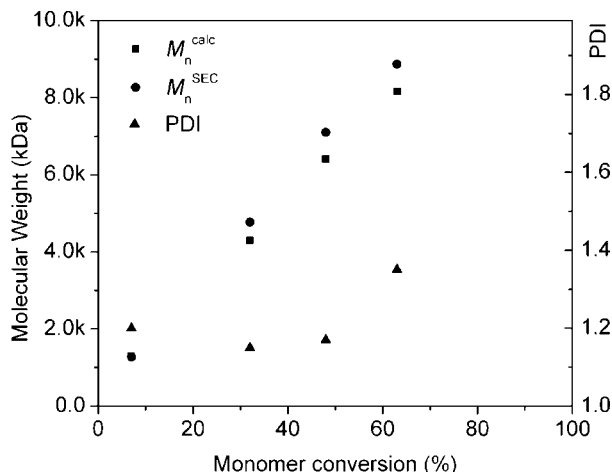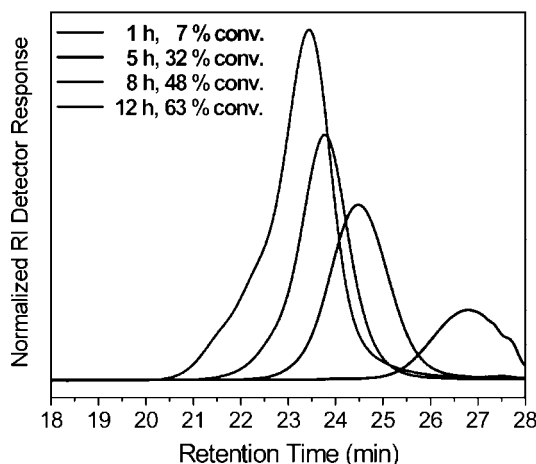
Figure 4. A composite of SEC curves collected during the RAFT polymerization of **1** (left) and a plot showing the dependency of M_n^{calcd}, M_n^{SEC}, and PDI of the resulting polymers on the monomer conversions (right).
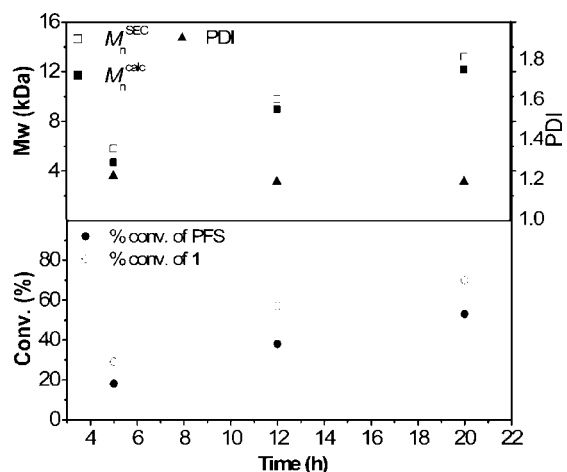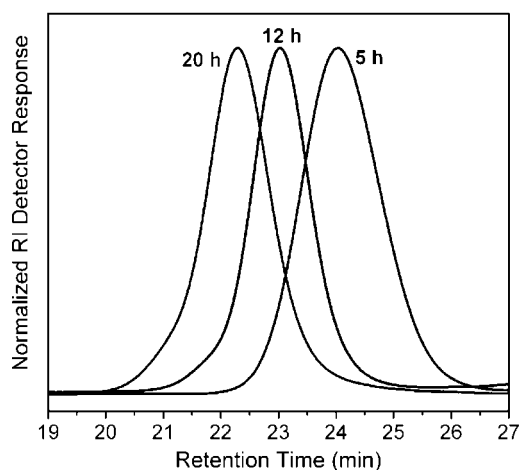

Figure 5. A composite of SEC traces collected during the RAFT copolymerization of **1** with PFS (left) and plots of molecular weights of polymers and conversions of comonomers versus polymerization time (right).

(150.8 MHz, CDCl$_3$, δ): 22.5, 29.2−33.1, 34.5−48.9, 51.3, 52.2, 53.5, 74.1, 115.0 118.1, 124.3, 137.9−145.0, 147.2, 171.0−175.0. ^{19}F NMR (282.2 MHz, CDCl$_3$, δ): −159.1 (br, 2F, *meta*-F), −145.0 to −141.9 (br, 2F, *ortho*-F).

Synthesis of Poly(St-*alt*-MAn)$_n$-*b*-P(FSt$_{0.60}$-*co*-1$_{0.40}$)$_n$, 6. A 10 mL Schlenk flask with a stir bar and sealed by a rubber septum was charged with PFS (1.48 g, 7.63 mmol), **1** (0.94 g, 3.8 mmol), macrochain transfer agent **4** (0.81 g, 0.10 mmol), AIBN (3.2 mg, 0.020 mmol), and 3 mL of 2-butanone as the cosolvent. The reaction mixture was degassed by three cycles of freeze−pump−thaw and was then heated in an oil bath to 70 °C for 5 h under N$_2$. The polymer solution was precipitated three times in 100 mL of pentane, and the product was collected and dried in vacuo to give **6** as a yellow powder. Isolated yield: 1.73 g (97% based on the 36% conversion of PFS and 48% conversion of **1**). M_n^{NMR} = 17.8 kDa, M_n^{GPC} = 18.5 kDa, PDI = 1.12, DP$_{ave,n}$ = 38, DP$_{ave,m}$ = 49. IR (NaCl, cm^{-1}): 3000−2850, 1859, 1782, 1735, 1653, 1523, 1501, 1457, 1419, 1383, 1303, 1225, 1142, 1088, 981, 959, 922, 870, 764, 703. ^{1}H NMR (300 MHz, acetone-*d*$_6$, δ): 0.88 (br, −C*H*$_3$ of DDMMAT), 1.26 (br, alkyl protons of DDMMAT), 2.51 (br, −OC*H*$_2$C*H*$_2$CH=CH$_2$ on polymer side chain), 1.30−3.00 (br, backbone protons of styrene units), 3.00−3.90 (br, backbone protons of MAn units), 4.18 (br, −OC*H*$_2$CH$_2$−), 5.15 (br, −CH$_2$CH=C*H*$_2$), 5.88 (br, −CH$_2$C*H*=CH$_2$), 6.00−7.70 (br, all aromatic protons). ^{13}C NMR (150.8 MHz, CDCl$_3$, δ): 22.9, 29.5−32.1, 33.8−47.1, 50.5−53.4, 74.3, 115.4, 118.2, 122.5, 136.3, 140.0−145.0, 147.2, 171.5−174.1. ^{19}F NMR (282.2 MHz, CDCl$_3$, δ): −161.6 (br, *meta*-F

of PFS units), −157.3 (br, *meta*-F of **1** units), −154.7 (br, *para*-F of PFS units), −147.0 and −141.0 (br, *ortho*-F of **1** units and PFS units).

Synthesis of 7. Copolymer **5** (71 mg, 5.8 × 10^{-3} mmol, 0.22 mmol of maleic anhydride units) was dissolved in 15 mL of THF, and the solution was stirred for 1 h at room temperature. KOH solution (1 mL, 30 mg/mL, 0.5 mmol) was added, and the mixture was stirred overnight. The solution was then adjusted with 1 N HCl solution to pH 4 and dialyzed against water (MWCO = 3500 Da) for 3 days. Water was removed by evaporation, and the product was then dried in vacuo for 24 h to yield 69 mg (93%) of **7** as a yellow solid. IR (KBr, cm^{-1}): 3550−2500, 1719, 1654, 1492, 1458, 1419, 1384, 1247, 1173, 1150, 1118, 960, 860, 810, 660, 604. ^{1}H NMR (300 MHz, DMSO-*d*$_6$, δ): 0.82 (br, −C*H*$_3$ of DDMMAT), 1.18 (br, alkyl protons of DDMMAT), 3.80−1.50 (br, protons on polymer backbone), 4.13 (br, −OC*H*$_2$CH$_2$−), 5.12 (br, −CH$_2$CH=C*H*$_2$), 5.82 (br, −CH$_2$C*H*=CH$_2$), 6.18−7.60 (m, all aromatic protons), 12.0 (br, −COO*H*).

Synthesis of 8. Copolymer **6** (152 mg, 8.22 × 10^{-3} mmol, 0.312 mmol of maleic anhydride units) was dissolved in 20 mL of THF and stirred for 30 min. An aqueous solution of NH$_4$OH (0.50 mL, 2 M) was added, and the reaction was allowed to stir for 30 h at room temperature. The mixture was allowed to dialyze against water (MWCO = 3500 Da) for 3 days. Water was removed by evaporation, and the product was dried in vacuo for 24 h to yield 125 mg (78%) of **8** as a yellow solid. IR (KBr, cm^{-1}): 3700−2500, 1718, 1656, 1560, 1493, 1457, 1398, 1216, 1148, 1076, 962, 861,

Scheme 3. Syntheses of Well-Defined Amphiphilic Diblock Copolymers with Pendent Alkene Functionalities[a]
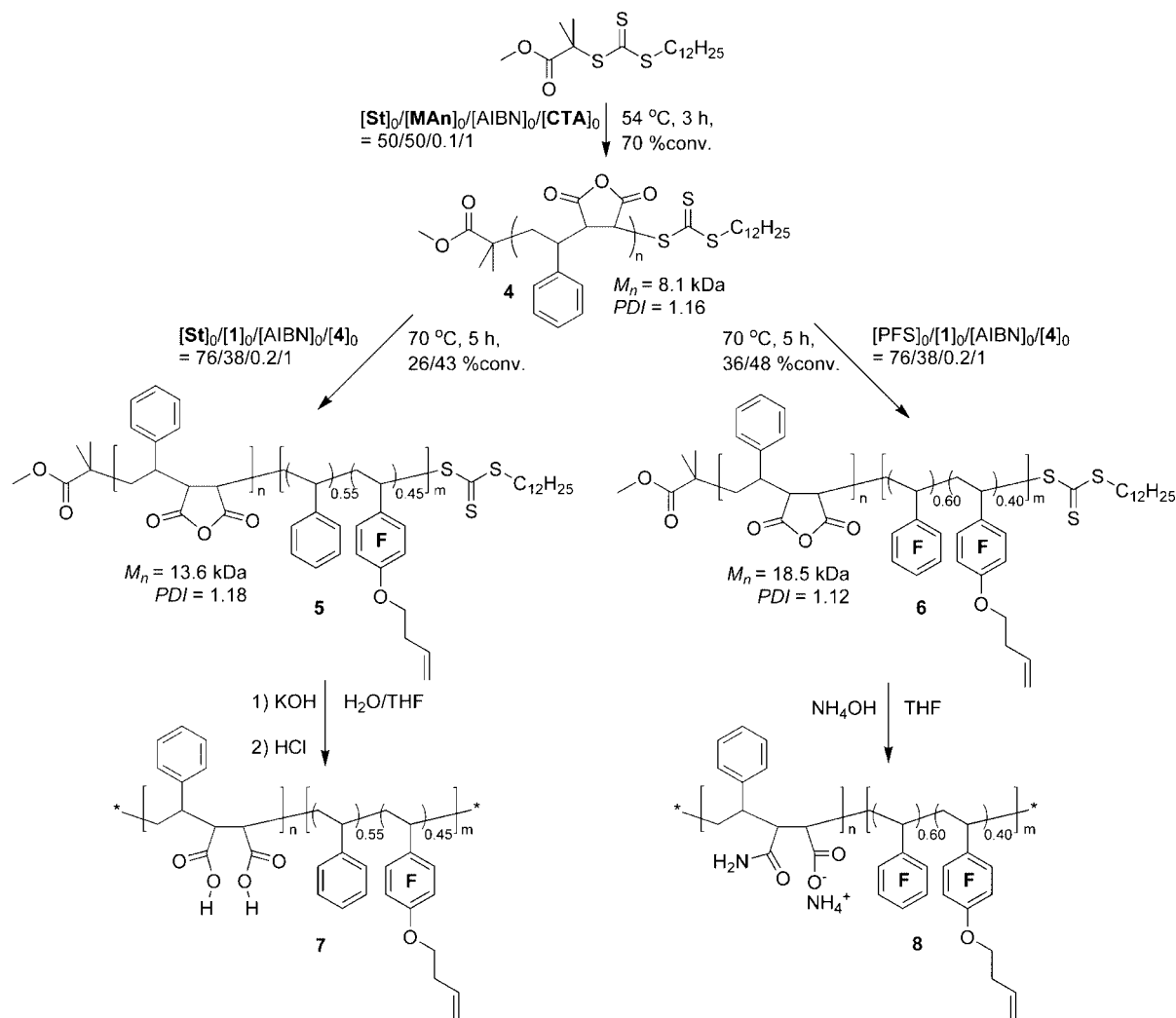
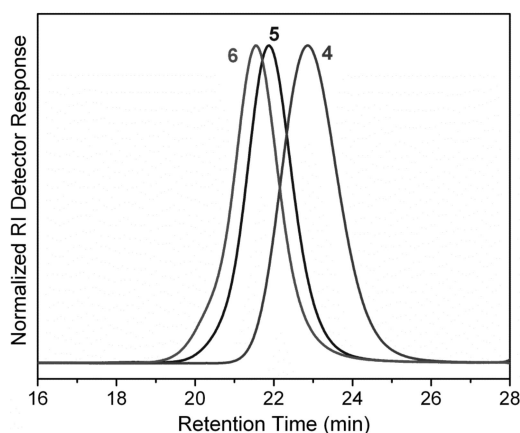[a] Average n and m values were $n = 38$ for **4**, $n = 38$ and $m = 25$ for **5**, and $n = 38$ and $m = 49$ for **6**.

Figure 6. SEC traces of copolymers poly(St-*alt*-MAn)$_n$ (**4**), poly(St-*alt*-MAn)$_n$-*b*-P(St$_{0.55}$-*co*-**1**$_{0.45}$)$_m$ (**5**), and poly(St-*alt*-MAn)$_n$-*b*-P(FSt$_{0.60}$-*co*-**1**$_{0.40}$)$_m$ (**6**).

763, 702, 660. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 0.83 (br, $-CH_3$ of DDMMAT), 1.20 (br, alkyl protons of DDMMAT), 4.00−1.20 (br, protons on polymer backbone), 4.08 (br, $-OCH_2CH_2-$), 5.03 (br, $-CH_2CH{=}CH_2$), 5.76 (br, $-CH_2CH{=}CH_2$), 6.00−7.50 (m, all aromatic protons).

Preparation of Micelle Solution from Copolymer 7. Copolymer **7** (10 mg) was dissolved in 10 mL of THF, and the solution

was stirred for 1 h at room temperature. DI water (10 mL) was added dropwise to the copolymer solution at a rate of 20 mL/h. The mixture was transferred to dialysis tubing (MWCO = 3500 Da) and was allowed to dialyze against DI water for 3 days to result in 37 mL of micelle solution. The concentration of the final micelle solution was 0.30 mg/mL. $(D_h)_n$ (DLS) = 8 ± 1 nm; $(D_h)_v$ (DLS) = 13 ± 1 nm; $(D_h)_i$ (DLS) = 137 ± 19 nm (bimodal with populations at 13 and 228 nm); D_{av} (TEM) = 10 ± 1 nm.

Preparation of Micelle Solution from Copolymer 8. A procedure similar to that for the preparation of micelle solution **7** was followed. The final micelle solution of copolymer **8** (24 mL) was obtained at a concentration of 0.21 mg/mL. $(D_h)_n$ (DLS) = 11 ± 1 nm; $(D_h)_v$ (DLS) = 14 ± 1 nm; $(D_h)_i$ (DLS) = 155 ± 24 nm (bimodal with populations at 21 and 387 nm); D_{av} (TEM) = 10 ± 2 nm.

Results and Discussion

Monomer Design and Synthesis. Initially, a variety of potential divinyl monomers was considered from both radical polymerization and organic chemistry aspects (Chart 1). As shown in Table 1, each divinyl monomer can be viewed as a copolymerization system of two vinylic monomer units.[51] On the basis of the (Q, e) values[52] from Alfrey−Price theory,[52−54] the reactivity ratios (r_1 and r_2) of each pair of vinyl groups within each divinyl monomer were calculated (Table 1). For this treatment, vinylic unit 1 was designated as having a higher
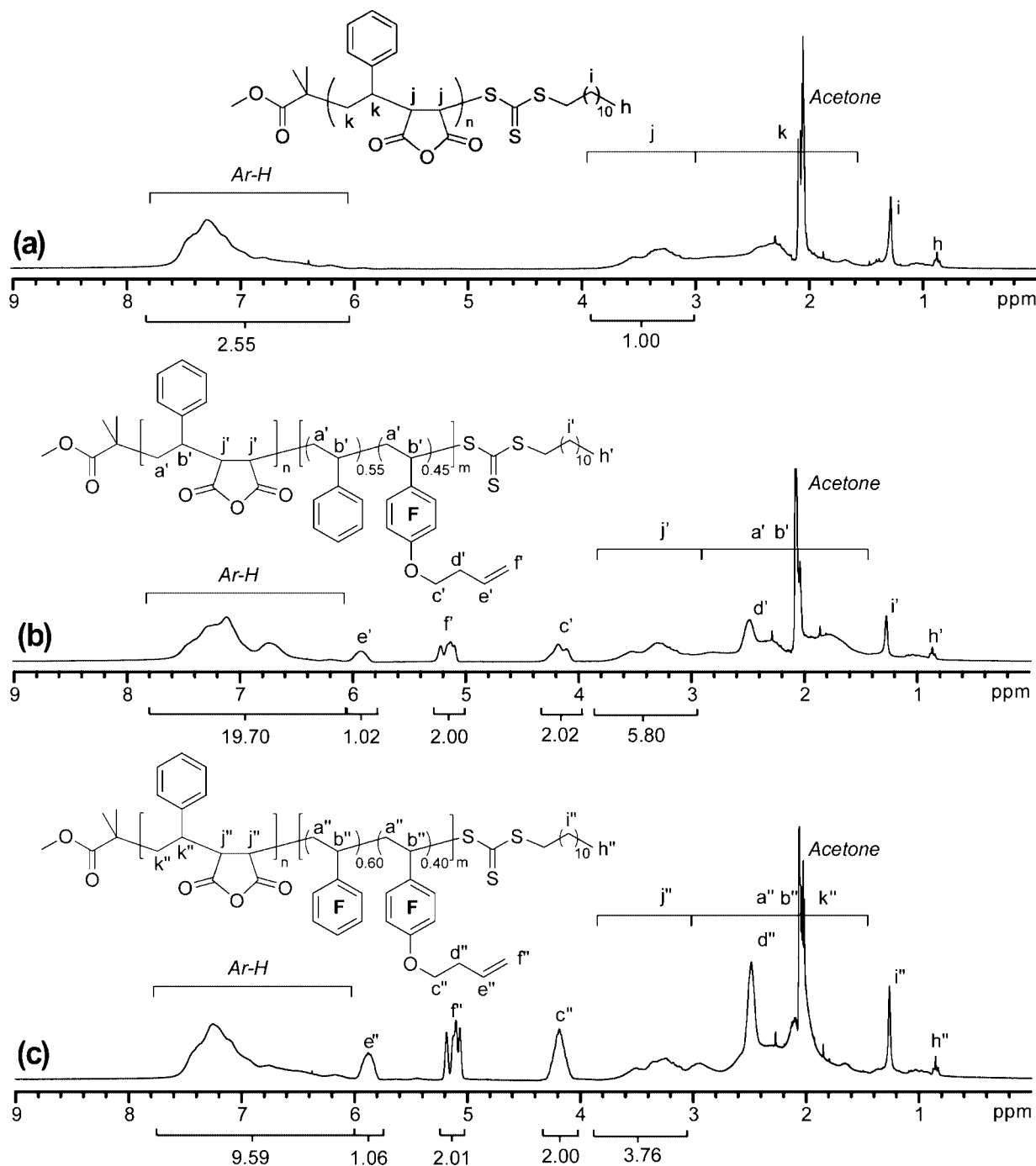
Figure 7. ^{1}H NMR spectra of (a) copolymer **4**, (b) copolymer **5**, and (c) copolymer **6** (300 MHz, acetone-d_6).

tendency toward polymerization, whereas vinylic unit 2 was expected to be retained. A divinyl monomer that is capable of undergoing polymerization with good selectivity between the two vinylic bonds should have a significant difference between r_1 and r_2. (i.e., r_1 with a large value, r_2 with a value close to 0, and a high ratio of r_1/r_2).

Because of the low intrinsic reactivity of the acrylate unit ($Q = 0.45$), the acrylate-based divinyl monomer (**A**) is expected to have poor selectivity between the two vinyl groups; therefore, it might be potentially used for the synthesis of branched polymers or cross-linked networks under radical polymerization conditions. Although the methacrylate moieties in vinyl methacrylate (VMA, **B**) and allyl methacrylate (AMA, **C**) are highly reactive ($Q = 0.78$), the vinyl acetate (VAc) moiety in **B** and allyl acetate (AAc) moiety in **C** also have noticeable reactivities ($Q_{VAc} = 0.026$, $Q_{AAc} = 0.24$), which could be reflected by the

relatively low r_1 values (18 and 1.8 for **B** and **C**, respectively). Moreover, the allylic protons of **C** have appreciable tendency to undergo chain transfer reactions in radical polymerization because of contributions from both the allyl and ester groups. Therefore, both **B** and **C**, although commercially available, were not considered to be ideal candidates for selective radical polymerization. Each of the monomers **D**, **E**, **F**, **G**, and **1** exhibit characteristic reactivity ratios that suggest they would allow for the CRP-based preparation of well-defined linear polymers bearing side-chain vinylic groups. 4-(3′-Buten-1′-oxy)-2,3,5,6-tetrafluorostyrene (**1**) was selected to be the nonsymmetrical divinyl monomer for these initial studies of selective RAFT polymerization (Figure 1) because of the expected high contrast of radical polymerization reactivity of its two vinyl groups and its synthetic feasibility. In other work,[56] a monomer that at first glance appears to be similar to **1** yet has a nonfluorinated
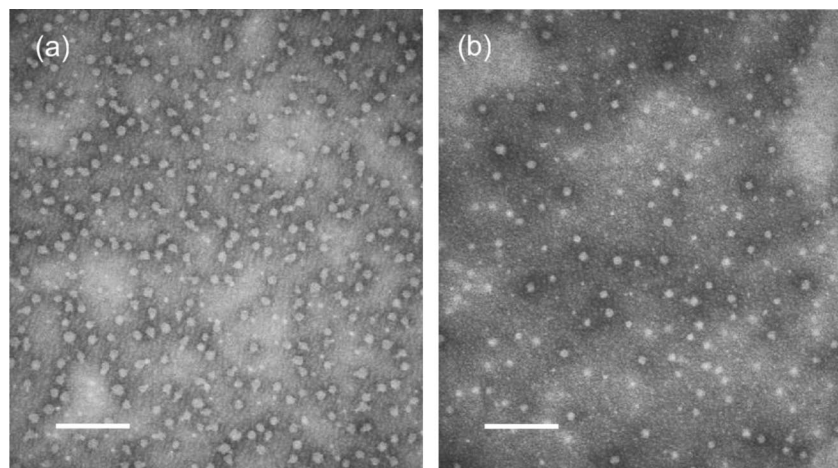
Figure 8. TEM images of the self-assembled micelles of diblock copolymers (a) **7** and (b) **8** in aqueous media. Scale bars = 100 nm.

styrenyl ring and, significantly, a benzylic ether linkage to the butenyl unit was studied for the preparation of branched polystyrenes via RAFT at high temperatures. In contrast with that work and our earlier exploitation of nonreactive 1-alkenes,[9] our current interest is in linear polymers that are prepared via selective RAFT polymerization that does not involve the side-chain vinylic groups.

On the basis of structural similarity, the reactivity of the substituted styrenyl group and alkene group in **1** can be estimated through PFS ($Q_1 = 0.86$, $e_1 = 0.75$) and 1-butene ($Q_2 = 0.007$, $e_2 = -0.06$), respectively. The calculated reactivity ratios, r_1 of 68 and r_2 of <0.01, indicate that the styrenyl group has significantly higher reactivity than does the alkene group and further suggest that the polymerization of **1** might be conducted as a homopolymerization of its styrenyl group until a high molar ratio of alkene group to styrenyl group is reached.

The nonsymmetric divinyl monomer **1** was synthesized by the nucleophilic aromatic substitution[57] of PFS with the commercially available 3-butenyl-1-ol. The reaction was conducted with a slight excess of the alcohol (1.25 equiv relative to PFS, to drive the complete consumption of PFS) in dry THF heated at reflux for 3 h to afford **1** in 66% yield after chromatographic purification (Scheme 1). The chemical structure of **1** was verified by IR and ^{1}H, ^{13}C, and ^{19}F NMR spectroscopies. As shown in Figure 2a, the three styrenyl protons resonated at 6.63, 6.04, and 5.63 ppm, whereas the three protons of the other vinyl group protons resonated at 5.89, 5.15, and 5.11 ppm. Their resonance intensity ratios were in excellent agreement with their proton number ratios. The signal for the methyleneoxy protons ($-OCH_2-$) at 4.28 ppm confirmed the covalent connection between the two vinyl-group-containing units. Furthermore, the ^{19}F NMR spectra of PFS and **1** allowed for the confirmation that the nucleophilic substitution occurred in the para position because the *para*-F signal of PFS (-157.4 ppm) coincidentally disappeared with the introduction of two new *ortho*- (-145.6 ppm for **1** vs -144.5 ppm for PFS) and *meta*-F (-158.7 ppm for **1** vs -164.4 ppm for PFS) resonances upon the formation of **1** (Figure 3).

RAFT Homopolymerization. With two different types of vinyl groups on monomer **1**, selective RAFT homopolymerization of **1** was investigated using AIBN as the thermal initiator and DDMMAT as the RAFT agent in 2-butanone (∼50 vol %) at 68 °C ($[1]_0/[AIBN]_0/[DDMMAT]_0 = 50:0.1:1$). DDMMAT was prepared by the esterification reaction of DDMMAT,[50] a widely used RAFT agent, with methanol. At time intervals during polymerization, small aliquots were withdrawn from the polymerization solution and analyzed by ^{1}H NMR spectroscopy for the determination of monomer conversions and by SEC for

the determination of molecular weights and polydispersities of the resulting polymers.

The comparison of the resonance intensities of the styrenyl protons at 6.63, 6.04, and 5.63 ppm with the resonance intensities of methylene protons ($-OCH_2-$) at 4.20 to 4.35 ppm gave 7, 32, 48, and 63% conversions of the styrenyl groups of **1** at 1.2, 5, 8, and 12 h, respectively. The resonance intensities of the protons of the pendent alkene groups remained consistent during the polymerization, indicating that essentially only the styrenyl groups were polymerized under the reaction conditions. SEC monitoring showed that with the increase in polymerization times and monomer conversions the molecular weights (MW) of the resulting polymers increased (Figure 4). Narrow MW distributions (PDI < 1.20) were observed for the polymers at monomer conversions below ca. 50%. The final polymer **2**, obtained with 63% monomer conversion after 12 h of polymerization, had a number-average molecular weight (M_n) of 8.87 kDa and a PDI of 1.35. The experimental M_n value of **2** by SEC was in agreement with the theoretical value of 8.2 kDa. However, the broadened molecular weight distribution of **2** suggested a slight occurrence of reactions of the pendent alkene functionalities in the later polymerization stage. Although not detectable by ^{1}H NMR spectroscopy, the consumption of a small fraction of the side-chain vinylic groups could occur as the molar ratio of the alkene group increased relative to the remaining styrenyl group at higher conversions, resulting in a broadening of the MW distribution.

A conventional radical polymerization of **1** was performed under conditions similar to those of RAFT polymerization, for which apparent cross-linking was observed when the conversion of styrenyl groups reached 43% after 5 h of polymerization. After the reaction mixture was precipitated in methanol, a material that was insoluble in organic solvents was obtained.[58] These results further support the controlled characteristics of the RAFT polymerization process.

RAFT Copolymerization. To improve the conversions of **1** while maintaining the suppression of the reactions of the pendent alkene groups, we studied copolymerization of **1** with PFS under polymerization conditions similar to those employed for the homopolymerizations ($[PFS]_0/[1]_0/[AIBN]_0/[DDMMAT]_0 = 75:25:0.1:1$; 60 vol % of 2-butanone; 68 °C). With PFS as the comonomer, the initial molar ratio of reactive styrenyl group to the pendent alkene group for this copolymerization system was 4:1, which is much higher than the ratio of 1:1 for the RAFT homopolymerization of **1**. As detected by ^{1}H NMR spectroscopic analysis of polymerization solutions, on the basis of the intensities of the resonances of unreacted styrenyl protons at 5.72 ppm for PFS and at 5.63 ppm for **1**, the conversions of

the comonomers increased with the copolymerization time and finally reached 51 and 71%, respectively, for PFS and **1** after 20 h. SEC analysis showed that the resulting copolymer **3** had an M_n of 13.2 kDa, which agreed with the calculated M_n (12.2 kDa), and a narrow MW distribution (PDI = 1.19) was obtained. As shown in the ^{1}H NMR spectrum (Figure 2b) of **3** (poly-(**1**-*co*-PFS)), the resonances of the pendent vinyl protons at ~5.8 and ~5.2 ppm had the same intensities as the methylene protons (−CH$_2$O−) at 4.25 ppm (Figure 2), indicating maintenance of the pendent alkene functionality of **3**. The well-defined structure of **3** could also be verified by the methyl protons at 0.84 ppm and methylene protons (−SCH$_2$−) at 3.31 ppm of the RAFT agent chain end functionality. The unit ratio of PFS and **1** in copolymer **3** was calculated to be 0.68:0.32 on the basis of the comonomer conversions, which indicates that >30 mol % of **1**, bearing the pendent alkenyl functionalities, was incorporated in the copolymer.

The ^{19}F NMR spectra (Figure 3c) for fluorocopolymer **3** showed four broad resonance peaks in the area from −140 to −165 ppm, which, according to the literature,[47] were assigned to the *ortho*-fluorines of **1**- and PFS-based repeat units (−144.0 ppm), the *para*-fluorines of PFS units (−154.8 ppm), the *meta*-fluorines of repeat units from **1** (−157.2 ppm), and the *meta*-fluorines of PFS units (−161.6 ppm), respectively. The ratio of ^{19}F NMR resonance intensities from the peaks at −154.8 and −157.2 ppm was calculated to be 1:0.89, indicating the molar ratio of the PFS/**1** repeat units to be 69:31 (2.00:0.89), which is in good agreement with the theoretical ratio on the basis of the feed ratio and the comonomer conversions.

RAFT Block Copolymerization. With the importance of amphiphilic block copolymers and their ability to afford well-defined nanoscale objects, our interest has been directed toward the use of amphiphilic block copolymers for the construction of functional nanoscale materials. Therefore, our final goal in this current work was to investigate the potential of this selective RAFT polymerization methodology for the preparation of alkene-functionalized amphiphilic block copolymers, extending from an initial macro-RAFT agent as a hydrophilic precursor. The alternating copolymer poly(St-*alt*-MAn)$_{38}$ (**4**, M_n = 8.1 kDa, PDI = 1.16) was prepared by RAFT copolymerization of styrene with an equal amount of MAn at 54 °C using DDMMAT as the CTA following a literature method.[59] Starting from the resulting poly(St-*alt*-MAn)$_n$-based macro-CTA, two types of alkene-functionalized diblock copolymers **5** and **6** were successfully synthesized (Scheme 3). RAFT copolymerization of styrene and **1** ([St]$_0$/[**1**]$_0$/[AIBN]$_0$/[**4**]$_0$ = 76:38:0.2:1) was conducted at 70 °C in 50 vol % of 2-butanone. The polymerization was allowed to proceed for 5 h, and as a result, 26% conversion of styrene and 43% conversion of **1** were obtained. (The intensities of ^{1}H NMR resonances of the unreacted styrenyl protons at 5.22 ppm for styrene and at 5.63 ppm for **1** were used for conversion determination.) Under the same reaction conditions, RAFT copolymerization of PFS and **1** ([PFS]$_0$/[**1**]$_0$/[AIBN]$_0$/[**4**]$_0$ = 76:38:0.2:1) was found to reach conversions of 36 and 48% for PFS and **1**, respectively. (The intensities of ^{1}H NMR resonances of the unreacted styrenyl protons at 6.09 ppm for PFS and at 5.63 ppm for **1** were used for conversion determination.) The formations of diblock copolymers poly(St-*alt*-MAn)$_n$-*b*-poly(St$_{0.55}$-*co*-**1**$_{0.45}$)$_m$ (**5**, M_n^{SEC} = 13.6 kDa, PDI = 1.18, n_{ave} = 38, m_{ave} = 25) and poly(St-*alt*-MAn)$_n$-*b*-poly(FSt$_{0.60}$-*co*-**1**$_{0.40}$)$_m$ (**6**, M_n^{SEC} = 18.2 kDa, PDI = 1.12, n_{ave} = 38, m_{ave} = 49) by chain extension from the poly(St-*alt*-MAn)$_n$ macro-CTA were verified by SEC analysis. Moreover, the good agreement between the experimental and calculated molecular weights (M_n^{calcd} = 14.0 kDa for **5** and 17.9 kDa for **6**) and monomodal molecular weight distributions of the diblock copolymers illustrates the quantitative chain transfer efficiency of the macro-CTA.

The block ratios of the diblock copolymers **5** and **6** were also analyzed by ^{1}H NMR spectroscopy (Figure 7) on the basis of comparisons of the intensities of characteristic resonances of MAn units (for protons j′ and j″ at 3.05 to 4.00 ppm), styrene units (for aromatic protons at 6.00 to 7.75 ppm), and repeat units of **1** (for protons f′ and f″ at 5.02 to 5.34 ppm). The molar ratio of repeat units of MAn/St/**1** of 2.90:3.94:1.00 was determined for copolymer **5**, indicating that the ratio of the degree of polymerization for the block segments of poly(St-*alt*-MAn)$_n$ and poly(St-*co*-**1**)$_m$ was 1.45:1, which agrees with the theoretical value of 1.52:1. A molar fraction of 0.49 for **1** was further obtained for the poly(St-*co*-**1**)$_m$ block of **5**, and it agrees with the theoretical value of 0.45 calculated from conversions and the molar feed ratio of comonomers. A molar ratio of repeat units of MAn/St/**1** of 1.88:1.91:1.00 was obtained for copolymer **6**. This ratio, coupled with the theoretical molar fraction of 0.40 for **1** within the poly(PFS-*co*-**1**)$_m$ block segment, indicates that the ratio of the degree of polymerization for block segments of poly(St-*alt*-MAn)$_n$ and poly(PFS-*co*-**1**)$_m$ is 0.76:1.00, which is close to the theoretical value of 0.78:1.00. Additionally, the molar fraction of **1** in the poly(PFS-*co*-**1**)$_m$ block segment of **6** was also determined by ^{19}F NMR spectroscopy. In terms of the intensities of resonances of *para*-fluorines of PFS centered at −154.7 ppm and *meta*-fluorines of **1** at −157.3 ppm, the experimental value of 0.42 was obtained, which is in excellent agreement with the theoretical value of 0.40.

Amphiphilic Block Copolymers. By transformations of the MAn units in the poly(St-*alt*-MAn) blocks into hydrophilic acid and amide units, **5** and **6** could be further converted into amphiphilic block copolymers **7** and **8**, respectively. Hydrolysis of **5** was first attempted under neutral conditions in 10% water−THF, but no reaction was observed by ^{1}H NMR spectroscopy after stirring overnight. However, hydrolysis readily proceeded at room temperature under basic conditions using 1 M KOH(aq) solution to promote the reaction.[59] Aminolysis−hydrolysis was carried out by treating **6** with an excess amount of 2 M NH$_4$OH(aq) solution for 6 h at room temperature.[60] ^{1}H NMR and FT-IR spectroscopic characterizations were used to verify the chemical structures of **7** and **8**. Resonances of carboxylic protons centered at 12.0 ppm were observed by ^{1}H NMR measurement of **6** in DMSO-d_6, which indicated the formation of carboxylic acids by hydrolysis of **5**. According to the consistent intensities of the resonances of the pendent alkene protons at ~5.8 and ~5.1 ppm for these polymers before and after the chemical transformations, the pendent alkene groups remained intact. Precursors **5** and **6** both showed two strong C=O stretching absorptions at 1855 and 1772 cm^{-1} for their cyclic anhydride groups, with absences of any O−H or N−H stretching absorptions. In comparison with **5**, polymer **7** had only one C=O stretching absorption at 1719 cm^{-1} and a broad O−H stretching absorption at 3500−2500 cm^{-1}, which indicated functional group transformation from the anhydrides to carboxylic acid groups. Copolymer **8** had N−H stretching absorptions at 3700−3400 cm^{-1} with a C=O stretching mode at 1656 cm^{-1}, which verified the formation of amides.

Amphiphilic copolymers **7** and **8** could undergo self-assembly in THF−water mixtures. Upon the slow addition of nanopure water to a dilute solution of **7** or **8** in THF (ca. 1 mg/mL), followed by dialysis against nanopure water, water-dispersible micelles were formed. As detected by DLS measurements, the micelles of **7** had a number-average hydrodynamic diameter $(D_h)_n$ of 8 ± 1 nm and a volume-average hydrodynamic diameter $(D_h)_v$ of 13 ± 1 nm, and the micelles of **8** had a $(D_h)_n$ of 11 ± 1 nm and a $(D_h)_v$ of 14 ± 1 nm. In each case, only the intensity-

weighted DLS data indicated a population of larger aggregates, together with the well-defined micellar assemblies. The micelles were further characterized by TEM. As shown in Figure 8, micelles from both **7** and **8** had average diameters of 10 nm and relatively narrow size distributions. These particles are expected to have a core-shell structure, potentially with an ability to adopt unusual multicompartment morphologies[61] and the core domains functionalized with alkene groups. Further study of the postmodification of these domain-specific alkene functionalities is in progress.

Conclusions

In summary, a facile synthetic approach for the preparation of well-defined copolymers with pendent alkene functionalities has been established by selective RAFT polymerization. Well-defined fluorocopolymers bearing vinylic side-chain functionalities were prepared by RAFT homopolymerization of a divinyl monomer **1** and by its copolymerization with PFS. Alkene-functionalized diblock fluorocopolymers were prepared by RAFT copolymerizations of **1** together with styrene or PFS, extending from a poly(styrene-*alt*-maleic anhydride) macrochain transfer agent. Hydrolysis and aminolysis of these copolymers resulted in amphiphilic fluorocopolymers with alkene-functionalized hydrophobic block segments, which generated functional micelles upon supramolecular assembly of the amphiphilic block copolymers in aqueous solution. These functionalized polymers are expected to have significant applications for the preparation of advanced polymer architectures by cross-linking, grafting, or other chemical transformations via the pendent alkene groups.

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