Macromolecules **2008**, *41*, 6089–6093

Novel Fluorinated Block Copolymer Stabilizers for Dispersion Polymerization of Cross-Linked Poly(2-ethylhexyl methacrylate-*stat*-chloromethylstyrene) in Fluorinated Solvents

Yan Zhu and Warren T. Ford*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

Received January 16, 2008; Revised Manuscript Received June 16, 2008

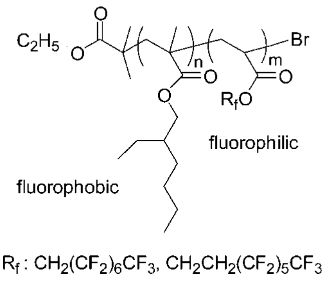
ABSTRACT: Amphiphilic block copolymers of 2-ethylhexyl methacrylate (EHMA) and 1*H*,1*H*-perfluorooctyl acrylate (FOA) and of EHMA and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl acrylate (THFOA) were synthesized by atom transfer radical polymerization (ATRP) in trifluorotoluene/tetrahydrofuran (THF) mixtures and characterized by ^{1}H NMR, IR, and SEC analyses. Control of ATRP of the fluoropolymer block required a fluoroalkyl-substituted 2,2′-bipyridine ligand for the Cu(I) catalyst. Dynamic light scattering detected 66–426 nm aggregates of the block copolymers in THF solution. Dispersion polymerizations of cross-linked poly(2-ethylhexyl methacrylate-*stat*-chloromethylstyrene) in the fluorinated solvent HFE-7200 (an isomeric mixture of nonafluorobutyl ethyl ethers) using the block copolymers as stabilizers produced 0.3–1.5 μm colloidal particles. The most effective stabilizers had block lengths of $(EHMA)_{30}$ and $(FOA)_{45}$ or $(EHMA)_{30}$ and $(THFOA)_{50}$. Particle sizes decreased with increasing concentration of stabilizer.

Introduction

For catalytic decomposition of toxic organic chemicals in fluorous solvents, we are investigating polymer colloids as phase transfer catalysts for hydrolysis of organophosphates. The target polymer particles are cross-linked copolymers of 2-ethylhexyl methacrylate (EHMA) and vinylbenzyl chloride (VBC) dispersed in the solvents perfluorobutyl methyl ether (HFE-7100) and perfluorobutyl ethyl ether (HFE-7200). The VBC units are converted to quaternary ammonium ions, and the ionic polymer particles are used as catalysts in the fluorous solvent without any intermediate isolation of the particles. Because the polymers are fluorophobic, amphiphilic fluorophilic/fluorophobic dispersants are needed to stabilize the colloidal dispersions in fluorous solvents. We are not aware of any examples of emulsion or dispersion polymerizations at ambient pressure in fluorous solvents to prepare such polymer colloids. The most closely related examples are copolymerizations of mixtures of butyl methacrylate and perfluoroalkyl methacrylate monomers in aqueous emulsions,[1,2] dispersion polymerization of styrene in 1,1,1,2-tetrafluoroethane at elevated pressure,[3] and dispersion polymerizations of methyl methacrylate,[4–7] acrylonitrile,[8,9] *N*-vinylpyrrolidinone,[10–12] vinyl acetate,[13] styrene,[14,15] and other methacrylic esters[16–19] in supercritical carbon dioxide ($scCO_2$).

Fluorous solvents and $scCO_2$ have similar properties of low solubility parameters and low cohesive energy density. Consequently, the stabilizers most useful for dispersion polymerizations in $scCO_2$ are amphiphilic fluorophilic/fluorophobic block and graft copolymers. Spherical micrometer-size polymer particles have been produced by dispersion polymerization in $scCO_2$ using semifluorinated block and graft copolymers and poly(perfluorooctyl acrylate) (PFOA) as stabilizers. Block copolymer stabilizers for radical chain polymerizations in $scCO_2$ include poly(styrene-*b*-perfluorooctyl acrylate)[20] and Krytox perfluoropolyether-*b*-PMMA.[4] The Krytox polymers with low molecular weight fluorophobic end groups such as alcohol, acetate, and methacrylate also enabled dispersion polymerization of MMA.[4] Graft copolymer stabilizers used in $scCO_2$ include poly(perfluoropropylene oxide) grafted to poly(methyl methacrylate-*stat*-2-hydroxyethyl methacrylate)[6] and the adducts of perfluoroalkyl alcohols to poly(methyl vinyl ether-*alt*-maleic anhydride) and to poly(hexadecyl vinyl ether-*alt*-maleic anhydride).[5] Even the fluorophilic homopolymer PFOA apparently grafts to the fluorophobic polymer during radical polymerization in $scCO_2$ and therefore is another example of a graft copolymer stabilizer.[10]

Scheme 1. Structures of the Block Copolymers



In this paper we report the synthesis of semifluorinated amphiphilic block copolymers by atom transfer radical polymerization (ATRP) and their application as stabilizers for the dispersion polymerization of cross-linked poly(EHMA-*stat*-VBC) in HFE-7200 solvent. An ATRP route to semifluorinated block copolymers in supercritical CO_2 has been reported for poly(FOMA-*b*-MMA) and poly(FOMA-*b*-2-(dimethylamino)-ethyl methacrylate).[21] ATRP syntheses of block copolymers of butyl methacrylate with very short blocks of mixed perfluoroalkyl acrylates[22] and of poly(styrene-*r*-acrylonitrile) with 1,1,2,2-tetrahydroperfluorooctyl methacrylate[13] also are known. Our block copolymer stabilizers for dispersion polymerization in HFE-7200 are comprised of a PEHMA block and a fluorinated block (PFOA or PTHFOA), as shown in the general structure of Scheme 1.

Experimental Section

Materials. All chemicals were used as received unless noted otherwise. 4,4′-Dinonyl-2,2′-dipyridyl (97%), Cu(I)Br (99.999%), Cu(0) (powder, 99.9%), ethyl 2-bromoisobutyrate (98%), and THF (anhydrous, inhibitor free, 99.9%) were from Aldrich. THF (HPLC grade, inhibitor free, 99.9%) was from Acros. 1,1,1,3,3-Pentafluorobutane (BuF_5, Solkane 365 MFC) was from Microcare. HFE-7100 and HFE-7200 (3M Novec Engineered Fluids) were distilled

* Corresponding author. E-mail: warren.ford@okstate.edu.

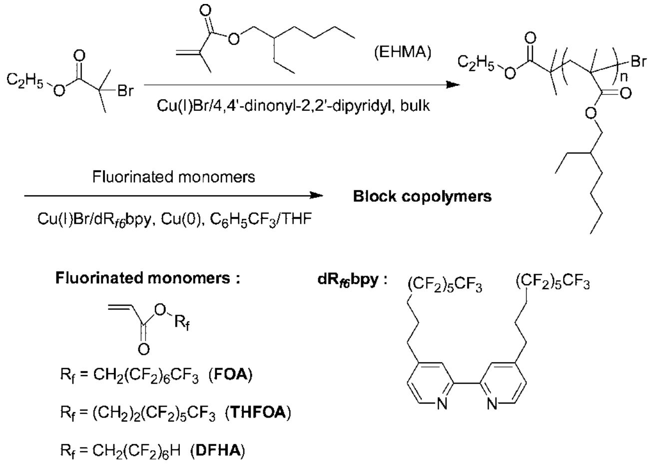
10.1021/ma800111t CCC: $40.75

Table 1. Properties of the Block Copolymers

block copolymer[a]	M_n (SEC)[b] PEHMA	PDI (SEC)[b] PEHMA	conv[c] (%)	$M_{n,cal}$[d] total	M_n(NMR)[e] total
$(EHMA)_{38}$-*b*-$(FOA)_{36}$	7500	1.20	61	21 400	23 900
$(EHMA)_{30}$-*b*-$(FOA)_{45}$-1	5950	1.33	66	21 000	26 400
$(EHMA)_{30}$-*b*-$(FOA)_{45}$-2[f]	5950	1.33	76	23 300	26 400
$(EHMA)_{31}$-*b*-$(FOA)_{18}$	6220	1.24	64	12 000	14 300
$(EHMA)_{15}$-*b*-$(FOA)_{45}$	2900	1.09	62	17 000	23 400
$(EHMA)_{17}$-*b*-$(FOA)_{17}$	3340	1.11	44	7 400	11 100
$(EHMA)_{30}$-*b*-$(THFOA)_{50}$	5950	1.33	75	21 700	26 900
$(EHMA)_{17}$-*b*-$(THFOA)_{42}$	3340	1.11	58	15 600	20 900
$(EHMA)_{17}$-*b*-$(THFOA)_{25}$	3340	1.11	67	8 900	13 800

[a] All reactions were conducted in $C_6H_5CF_3$/THF (4:1 v/v) at 100 °C for 3 days using fluorinated ligand $dR_{f6}bpy$, $[I]_0/[Cu(0)]_0/[Cu(I)Br]_0/[dR_{f6}bpy]_0 = 1/1/1/2$. [b] Determined by SEC in THF solution against PMMA standards. [c] Monomer conversions were obtained gravimetrically after purification and drying of the polymer product. [d] Calculated according to the following equation: $M_{n,cal} = ([M]_0/[I]_0) \times (MW)_0 \times (conv\%/100) + MW_i$, where $[M]_0$ and $[I]_0$ are the initial concentrations of monomer and initiator, $(MW)_0$ is the molecular weight of the monomer, and MW_i is the molecular weight of the initiator fragment. [e] Determined from ^1H NMR and M_n of the PEHMA. [f] 7-day reaction.

Scheme 2. Synthesis of Block Copolymers by ATRP



at atmospheric pressure under N_2 and stored under N_2. α,α,α-Trifluorotoluene (99.5%, Fluka) was dried over CaH_2, distilled, and stored under N_2. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from methanol.

The monomers 2-ethylhexyl methacrylate (EHMA, 98%, Aldrich), chloromethylstyrene (VBC, 98%, 60% meta, 40% para isomers, Scientific Polymer Products), divinylbenzene (DVB, 55−60%, Polysciences), 1*H*,1*H*-perfluorooctyl acrylate (FOA, 97%, Synquest), 1*H*,1*H*,2*H*,2*H*-perfluorooctyl acrylate (THFOA, 97%, Synquest), and 1*H*,1*H*,7*H*-dodecafluoroheptyl acrylate (DFHA, 97%, Synquest) were purified by passing through a column of activated basic alumina (~150 mesh, 58 Å, Aldrich).

Instrumentation. ^1H NMR (400 MHz) spectra were recorded on solutions in $CDCl_3$ or $CDCl_3$/Freon-113. Chemical shifts in ppm are relative to Me_4Si. Size exclusion chromatography (SEC) was performed on an Agilent series 1100 chromatograph using THF as eluant at 1 mL/min at 40 °C with two Polymer Laboratories PLgel 10 μm mixed bed columns, a refractive index detector, and a diode array UV detector (using the integrated absorbance from 190 to 350 nm for molecular weight calculations). The samples injected were 20 μL of a 5 mg/mL THF solution. The samples were passed through a 0.2 μm polypropylene w/GMF syringe filter (Whatman) before injection. Molecular weights were calibrated with PMMA standards (Polymer Laboratories). Particle sizes were measured at 25 °C using a Malvern model 3.3 dynamic light scattering (DLS) particle sizer equipped with a 633 nm He−Ne laser. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6400 instrument. Samples were mounted on mica sheets attached to aluminum stubs and sputter-coated with gold. Mean particle diameter was measured using the software Image-Pro Plus (Media Cybernetics, Silver Spring, MD) by counting and measuring at least 100 particles in the SEM images. IR spectra were recorded using KBr pellets for solid samples and NaCl plates for liquid samples.

PEHMA-Br Macroinitiators. (1) PEHMA ($M_n \sim 6000$). In a typical reaction, Cu(I)Br (0.097 g, 0.676 mmol) and 4,4′-dinonyl-2,2′-dipyridyl (0.553 g, 1.35 mmol) were added to a dry 25 mL Schlenk flask equipped with a stirring bar under argon. The flask was degassed and purged with argon for 20 min. Deoxygenated EHMA (6.05 mL, 27.0 mmol) was added. The flask was subjected to one freeze−pump−thaw cycle. Ethyl 2-bromoisobutyrate (0.100 mL, 0.674 mmol) was added at −78 °C, followed by two more freeze−pump−thaw cycles. The reaction mixture was kept at 23 °C for 3 h; stirring stopped after 20 min due to high viscosity. Monomer conversion was determined by ^1H NMR to be 90% by comparison of the $-OCH_2-$ peak area of monomer at 4.02 and 4.05 ppm to the $-OCH_2-$ peak area of polymer at 3.84 ppm. The reaction mixture was diluted with THF (75 mL) and passed through a column of neutral alumina (~150 mesh, 58 Å, Aldrich) to remove the catalyst. The column was washed with two 75 mL portions of THF. The filtrate was concentrated under reduced pressure. The residue was precipitated into excess methanol. The liquid was decanted. The precipitate was washed several times with methanol and dried under vacuum to give 5.0 g of a gummy solid. SEC analysis (RI detector): $M_n = 5950$, $M_w/M_n = 1.33$.

(2) PEHMA ($M_n \sim 3000$). The preceding method was followed but with THF added before the EHMA to dilute the mixture and slow the polymerization. A typical reaction used Cu(I)Br (0.290 g, 2.02 mmol), 4,4′-dinonyl-2,2′-dipyridyl (1.65 g, 4.04 mmol), 15 mL of anhydrous THF, EHMA (4.50 mL, 20.0 mmol), and ethyl 2-bromoisobutyrate (0.300 mL, 2.02 mmol). The reaction mixture was stirred at 23 °C for 3 h. The product was 1.64 g of a gummy solid. Monomer conversion was determined by ^1H NMR to be 31%. SEC analysis (RI detector): $M_n = 3340$, $M_w/M_n = 1.11$.

Poly(EHMA-*b*-FOA) and Poly(EHMA-*b*-THFOA). In a typical reaction, PEHMA-Br macroinitiator ($M_n = 5950$) (0.80 g, 0.134 mmol), 4,4′-di(tridecafluoro-1,1,2,2,3,3-hexahydrononyl)-2,2′-bipyridine ($dR_{f6}bpy$) (0.141 g, 0.268 mmol, synthesized by a literature procedure, purity confirmed by mp and ^1H NMR),[21] Cu(0) (8.5 mg, 0.134 mmol), FOA (2.18 mL, 6.73 mmol), and 4 mL of $C_6H_5CF_3$/THF (4:1 v/v) were added to a 25 mL Schlenk flask equipped with a stirring bar under argon. The reaction flask was subjected to one freeze−pump−thaw process. Cu(I)Br (0.019 g, 0.132 mmol) was added at −78 °C. After two more freeze−pump−thaw cycles, the mixture was left in an oil bath at 100 °C for 3 days. After cooling, the reaction mixture was diluted with 25 mL of THF and passed through a column of neutral alumina to remove the catalyst. The column was washed with two 20 mL portions of THF and 20 mL of BuF_5. The filtrate was concentrated under reduced pressure. The remaining solution was precipitated into excess methanol, filtered, and dried under vacuum to give a solid powder (2.8 g). The monomer conversion was determined gravimetrically after purification and drying. The number-average composition was calculated to be $(EHMA)_{30}$-*b*-$(FOA)_{45}$ from the molecular weight of the EHMA block and the ^1H NMR spectrum by comparing the signal areas of the $-OCH_2-$ protons in the PFOA block (4.6 ppm) and the $-OCH_2-$ protons in the PEHMA block (3.9 ppm).

Dispersion Polymerization of EHMA, VBC, and DVB in HFE-7200. All glassware was oven-dried and purged with nitrogen. In a typical polymerization, stabilizer $(EHMA)_{38}$-*b*-$(FOA)_{36}$ (0.254 g, 10 wt % of monomers) was dissolved in 26 mL of HFE-7200 in a 50 mL Schlenk flask. Argon-purged EHMA (2.26 mL, 10.08 mmol), VBC (0.48 mL, 3.42 mmol), DVB (19.4 μL, 0.136 mmol), and solid AIBN (26 mg) were added sequentially under argon. The reaction mixture was degassed by three freeze−pump−thaw cycles. Polymerization was carried out at 65 °C for 24 h with continuous stirring. After cooling, the product was filtered through cotton to remove a small amount of coagulated polymer. The filtrate was stored in a brown bottle, and the solids on the cotton were collected,

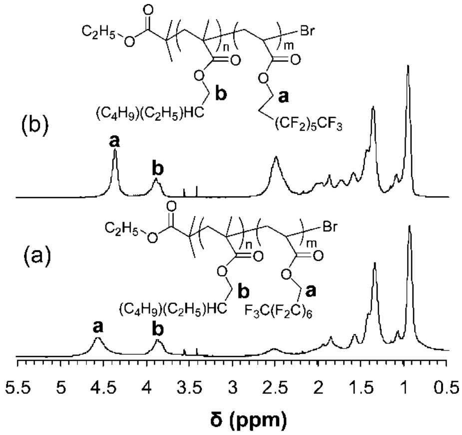


Figure 1. ^{1}H NMR spectra of (a) $(EHMA)_{30}$-*b*-$(FOA)_{45}$−1 and (b) $(EHMA)_{30}$-*b*-$(THFOA)_{50}$. NMR solvent is $CDCl_3$/Freon-113.

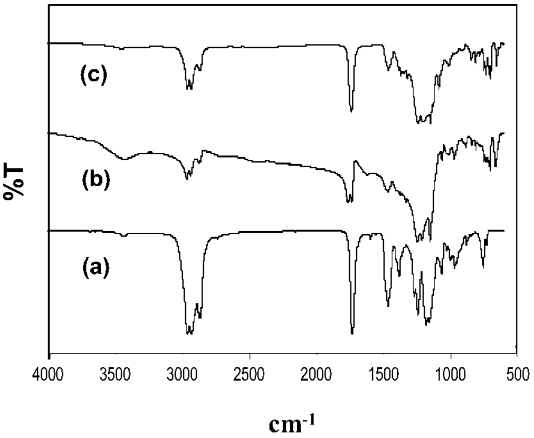


Figure 2. IR spectra of (a) PEHMA-Br, (b) $(EHMA)_{38}$-*b*-$(FOA)_{36}$, and (c) $(EHMA)_{30}$-*b*-$(THFOA)_{50}$.

washed with HFE-7200, and dried under vacuum. The yield of solids in the filtrate was 93%, and the yield of coagulum was 5%. All of the other stable dispersions gave similar results.

Results and Discussion

Synthesis of Block Copolymers by ATRP. The block copolymers reported in Table 1 were prepared in two steps, as shown in Scheme 2. First, the bromide-terminated macroinitiator PEHMA-Br was prepared by ATRP at 23 °C using ethyl 2-bromoisobutyrate as initiator and Cu(I)Br/4,4′-dinonyl-2,2′-dipyridyl as catalyst. Then the PEHMA-Br macroinitiator was used to polymerize a fluorinated monomer as the second block by ATRP. We prepared two different molecular weights of PEHMA-Br macroinitiators (M_n = ~3000 and $M_n \geq 6000$, respectively). The synthesis of the higher molecular weight PEHMA-Br proceeded in bulk at 23 °C with well-controlled molecular weight and molecular weight distribution. In order to attain the lower molecular weight PEHMA-Br, THF was used as a solvent to dilute the mixture and slow the polymerization.

The rate of polymerization by ATRP of the fluorinated monomers with PEHMA-Br macroinitiator was surprisingly slow even at 100 °C. Others also have reported slow ATRP of perfluoroalkyl acrylates.[13,22] The synthesis of the block copolymer $(EHMA)_{38}$-*b*-$(FOA)_{36}$ was monitored by ^{1}H NMR analysis. High monomer conversion required as long as 3 days. Extending the reaction time up to 7 days did not increase the degree of polymerization. The syntheses of the fluorinated block of the other copolymers were left for 3 days without NMR monitoring. Trifluorotoluene was selected as reaction solvent because of its high boiling point. A small amount of THF was added as cosolvent to improve the solubility of the catalyst. Cu(0) was added to increase the polymerization rate.[23] Two different ligands for the catalyst system were investigated: 4,4′-dinonyl-2,2′-dipyridyl and the corresponding fluorinated 4,4′-di(tridecafluoro-1,1,2,2,3,3-hexahydrononyl)-2,2′-bipyridine($dR_{f6}bpy$).[21] The fluorinated ligand gave the higher yield, probably due to greater solubility of this catalyst/ligand complex. Three fluorinated monomers were investigated: 1*H*,1*H*-perfluorooctyl acrylate (FOA), 1*H*,1*H*,2*H*,2*H*-perfluorooctyl acrylate (THFOA), and 1*H*,1*H*,7*H*-dodecafluoroheptyl acrylate (DFHA). It was dem-

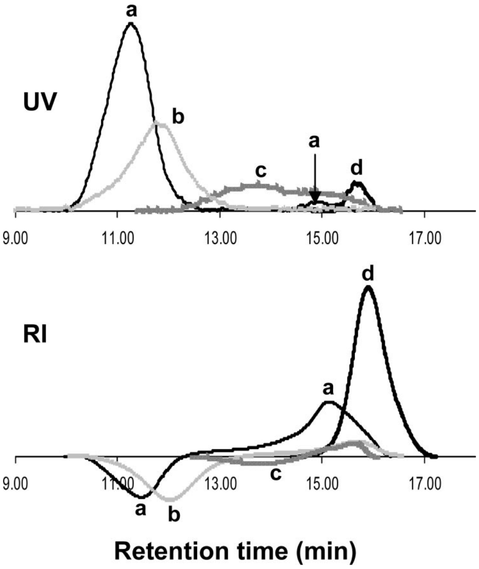


Figure 3. SEC traces of the PEHMA macroinitiator and the block copolymers. UV and RI chromatograms were recorded at the same time. Data are not corrected for the flow time from the UV detector to the RI detector. (a) $(EHMA)_{38}$-*b*-$(FOA)_{36}$; (b) $(EHMA)_{30}$-*b*-$(FOA)_{45}$-1; (c) $(EHMA)_{30}$-*b*-$(THFOA)_{50}$; (d) PEHMA-Br (M_n: 6220; DP = 31).

Table 2. Sizes of the Block Copolymers in THF

block copolymer	M_n (SEC)[a] total	PDI (SEC)[a] total	D_z[b] (nm)
$(EHMA)_{38}$-*b*-$(FOA)_{36}$	1.70×10^6 (1.88×10^4)	1.35(1.21)	103
$(EHMA)_{30}$-*b*-$(FOA)_{45}$-1	7.89×10^5 [c]	1.73	80
$(EHMA)_{30}$-*b*-$(FOA)_{45}$-2	1.33×10^6 (1.10×10^4)	1.44 (1.11)	95
$(EHMA)_{31}$-*b*-$(FOA)_{18}$	1.15×10^4	1.05	426
$(EHMA)_{17}$-*b*-$(FOA)_{17}$	2.11×10^6 (9.08×10^3)	1.41 (1.05)	335
$(EHMA)_{30}$-*b*-$(THFOA)_{50}$	1.07×10^5 (1.16×10^4)	1.24 (1.20)	66
$(EHMA)_{17}$-*b*-$(THFOA)_{25}$	8.14×10^3	1.13	367

[a] Determined by SEC in THF solution (5 mg/mL) relative to PMMA standards with a UV detector. Two values are for aggregated and unaggregated components in bimodal distributions. [b] D_z is the *Z*-average diameter determined by DLS measurement in THF (5 mg/mL). For each block copolymer, the value reported is the average of three measurements. [c] Lower molecular weight peak too small to analyze.

Table 3. Polymerizations of EHMA, VBC, and DVB in HFE-7200[a]

entry	stabilizer	stabilizer (wt %)[b]	diameter (nm) SEM[c]	diameter (nm) DLS[d]
1	$(EHMA)_{38}$-*b*-$(FOA)_{36}$	5	540	700
2	$(EHMA)_{38}$-*b*-$(FOA)_{36}$	10	300	410
3	$(EHMA)_{38}$-*b*-$(FOA)_{36}$	15	376	370
4	$(EHMA)_{30}$-*b*-$(FOA)_{45}$-1	10	1380	1450
5	$(EHMA)_{30}$-*b*-$(FOA)_{45}$-2	10	1020	1010
6	$(EHMA)_{30}$-*b*-$(TFOA)_{50}$	10	755	845

[a] Polymerizations were carried out at 65 °C for 24 h using 1 wt % of AIBN with respect to monomers. [b] Wt % with respect to monomers. [c] From measurement of at least 100 particles. [d] Mean hydrodynamic diameter of particles measured by DLS. The value reported is the average of three measurements.

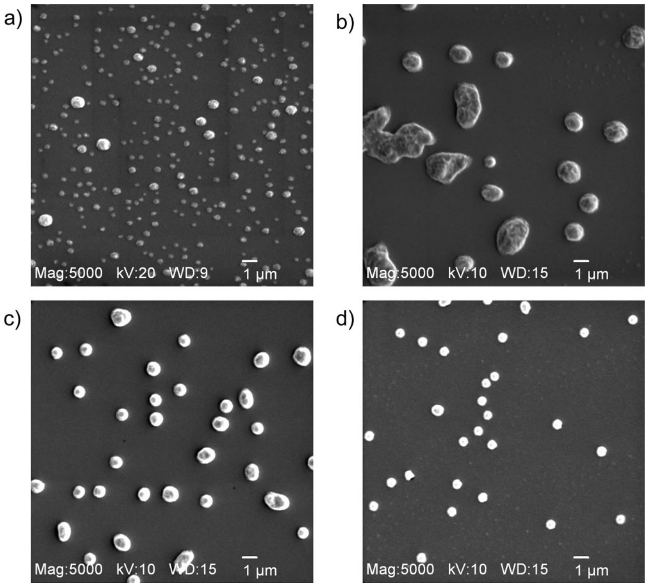


Figure 4. SEM images of polymer colloids made with 10 wt % of block copolymers: (a) $(EHMA)_{38}$-*b*-$(FOA)_{36}$; (b) $(EHMA)_{30}$-*b*-$(FOA)_{45}$-1; (c) $(EHMA)_{30}$-*b*-$(FOA)_{45}$-2; (d) $(EHMA)_{30}$-*b*-$(THFOA)_{50}$.

onstrated previously that the fluorinated acrylate homopolymer PFOA[24] and its corresponding block copolymers are effective stabilizers for dispersion polymerizations in $scCO_2$.[8,10,18,21] The ATRP of FOA and of THFOA gave good yields, but attempts to synthesize block copolymers from PEHMA and DFHA for unknown reason resulted in low DFHA conversion.

Characterization of the Block Copolymers. Typical ^1H NMR spectra, shown in Figure 1, confirm the formation of block copolymers. The number-average compositions of block copolymers were calculated by comparing the relative intensities of the signal for $-OCH_2-$ protons of the fluorinated block (4.6 ppm for PFOA or 4.4 ppm for PTHFOA) and of the PEHMA block (3.9 ppm).

Figure 2 depicts the IR spectra of PEHMA-Br macroinitiator and the corresponding block copolymers. The C=O signals can be identified distinctly in Figure 2b at 1760 cm^{-1} for PFOA block and at 1728 cm^{-1} for PEHMA block. The CF vibrations make the 1100−1300 cm^{-1} region much stronger relative to the C−H stretching and the C=O stretching regions in the spectra of the block copolymers than in the spectrum of PEHMA.

SEC analyses of fluorinated copolymers in common solvents such as THF are difficult because of low solubility of the fluorinated components and aggregation.[25,26] We have analyzed the block copolymers only qualitatively by SEC. Representative chromatograms of the PEHMA macroinitiator and the block copolymers in THF using both UV and refractive index (RI) detectors are shown in Figure 3. Earlier elution indicates higher molecular weight of the block copolymers than of the PEHMA macroinitiator. Only small overlap of the block copolymer chromatograms with that of the PEHMA macroinitiator indicates that most of the macroinitiator chains started fluoroacrylate blocks. However, chromatograms a and b in Figure 3 are bimodal with larger peaks at hydrodynamic sizes for $\sim 10^6$ Da than for the expected molecular weights from NMR spectra of 21 000−27 000 Da. We interpret the bimodal distributions as due to mixtures of large aggregates of block copolymers at 10−13 min retention time and individually dissolved block copolymers at 14−16 min retention time. The UV chromatograms indicate that the aggregates are the larger fraction of material. The RI chromatograms show inverted peaks for the high molecular weight species due to the high content of fluoroalkyl acrylate units of the polymers, which have a lower refractive index than that of THF. The high molecular weight peaks are due to copolymer that is rich in fluoropolymer units, not to homopolymer, because independently synthesized PFOA homopolymer is completely insoluble in THF. The lower molecular weight species have normal RI peaks and therefore are due to polymer richer in PEHMA than are the high molecular weight peaks. Because of the refractive index differences between fluoroalkyl acrylate and EHMA units, the sizes of the peaks in the RI chromatograms cannot be interpreted. No SEC data could be obtained for the block copolymers of lower EHMA content, such as $(EHMA)_{15}$-*b*-$(FOA)_{45}$ and $(EHMA)_{17}$-*b*-$(THFOA)_{42}$, because of their poor solubility in THF. The molecular weights in Table 1 calculated from NMR spectra are consistently higher than the molecular weights in Table 2 measured by SEC for the unaggregated components of the samples probably because the fluorinated block of the copolymer has a smaller hydrodynamic volume per unit mass than the PEHMA block.

Aggregation of the block copolymers in THF was confirmed by dynamic light scattering measurements, which are reported in Table 2. Average aggregate sizes from 66 to 426 nm were detected. The aggregation is likely due to association of the fluorinated blocks, which are much less soluble in THF than the PEHMA blocks. Because of the aggregation of the block copolymers in THF, the ^1H NMR analyses of the relative molar amounts of the EHMA and fluoroalkyl acrylate units combined with the SEC analyses of the PEHMA macroinitiators give the most reliable molecular weights.

Block Copolymers as Stabilizers in Dispersion Polymerization. The block copolymers were used as stabilizers for the dispersion copolymerization of EHMA, VBC, and DVB in the semifluorinated ether solvents HFE-7100 and HFE-7200 at atmospheric pressure. To decrease solvent evaporation, HFE-7200 (bp 76 °C) is preferred over HFE-7100 (bp 61 °C). Results are reported in Table 3. Freshly purified EHMA, VBC, and DVB are soluble in HFE-7200 at 23 °C, and the initiator AIBN is soluble at 65 °C. Stabilizers $(EHMA)_{15}$-*b*-$(FOA)_{45}$ and $(EHMA)_{30}$-*b*-$(THFOA)_{50}$ formed clear solutions in HFE-7200 at 23 °C. $(EHMA)_{38}$-*b*-$(FOA)_{36}$, $(EHMA)_{30}$-*b*-$(FOA)_{45}$-1, $(EHMA)_{30}$-*b*-$(FOA)_{45}$-2, $(EHMA)_{31}$-*b*-$(FOA)_{18}$, $(EHMA)_{17}$-*b*-$(FOA)_{17}$, $(EHMA)_{17}$-*b*-$(THFOA)_{42}$, and $(EHMA)_{17}$-*b*-$(THFOA)_{25}$

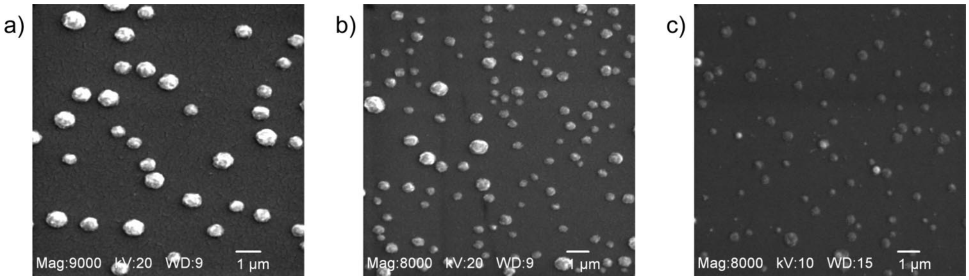


Figure 5. Effect of $(EHMA)_{38}$-*b*-$(FOA)_{36}$ concentration on product morphology: (a) 5 wt % (to monomers); (b) 10 wt %; (c) 15 wt %.

were not completely soluble in HFE-7200 at 23 °C. However, the addition of EHMA monomer to the HFE-7200 mixtures gave clear solutions either at 23 °C or upon heating at 65 °C ($(EHMA)_{17}$-*b*-$(FOA)_{17}$). Thus, EHMA acts as a cosolvent for the block copolymers. This phenomenon was also observed for enhanced solubility of Krytox perfluoropolyether-*b*-PMMA in $scCO_2$ by addition of MMA.[4]

Polymerizations conducted with the copolymers $(EHMA)_{38}$-*b*-$(FOA)_{36}$, $(EHMA)_{30}$-*b*-$(FOA)_{45}$-1, $(EHMA)_{30}$-*b*-$(FOA)_{45}$-2, and $(EHMA)_{30}$-*b*-$(THFOA)_{50}$ over 24 h formed remarkably stable colloidal dispersions with a milky white appearance. In contrast, the polymerizations conducted with $(EHMA)_{31}$-*b*-$(FOA)_{18}$, $(EHMA)_{15}$-*b*-$(FOA)_{45}$, $(EHMA)_{17}$-*b*-$(FOA)_{17}$, $(EHMA)_{17}$-*b*-$(THFOA)_{42}$, and $(EHMA)_{17}$-*b*-$(THFOA)_{25}$ started as stable dispersions for 1−3 h, and then the polymers precipitated. Polymerizations with no stabilizer and with Krytox and other commercial perfluoropolyethers intended as stabilizers also produced only precipitated polymer.

Comparing $(EHMA)_{15}$-*b*-$(FOA)_{45}$ with $(EHMA)_{30}$-*b*-$(FOA)_{45}$ shows that a longer PEHMA block is required to stabilize the polymer colloid. Comparing $(EHMA)_{31}$-*b*-$(FOA)_{18}$ with $(EHMA)_{30}$-*b*-$(FOA)_{45}$ shows that an efficient stabilizer must also contain a longer fluorophilic group. Table 3 also indicates that a fluorophile/fluorophobe balance of at least 0.5 mole fraction fluorophile and block lengths of ≥30 of both fluorophile and fluorophobe are required to obtain stable poly(EHMA−VBC−DVB) colloids.

SEM micrographs were recorded to determine the effect of stabilizer composition on the morphology of the polymer dispersions. Discrete spherical particles were observed for dispersions stabilized by $(EHMA)_{38}$-*b*-$(FOA)_{36}$, $(EHMA)_{30}$-*b*-$(FOA)_{45}$-1, $(EHMA)_{30}$-*b*-$(FOA)_{45}$-2, and $(EHMA)_{30}$-*b*-$(THFOA)_{50}$ (Figure 4). From stabilizer $(EHMA)_{30}$-*b*-$(FOA)_{45}$-1 (Figure 4b), some aggregated particles were detected in the SEM images. The particles stabilized by $(EHMA)_{38}$-*b*-$(FOA)_{36}$ were smaller and less uniform in size than the others. The diameters of the particles from SEM are equal to or less than the diameters from DLS measurements reported in Table 3. Somewhat larger differences were observed for entries 1 and 2 because the images of the polymer particles were not perfectly circular.

The block copolymer concentration in the polymerization mixtures affected polymer particle sizes and size distributions, as shown in Figure 5. The average particle sizes decreased from 700 to 410 nm when the concentration of stabilizer $(EHMA)_{38}$-*b*-$(FOA)_{36}$ increased from 5 to 10 wt % of monomers, which is consistent with previous literature results.[4,7,18] The 5 wt % of stabilizer yielded a narrower size distribution. However, the polymer colloid formed with 10 wt % stabilizer was more stable during storage over 5 months. Further increasing the concentration to 15 wt % had little effect on yield and particle size but resulted in increased coagulation.

Conclusions

A series of block copolymers of PEHMA and a fluorinated block (PFOA or PTHFOA) were prepared by ATRP. The block copolymers, $(EHMA)_{38}$-*b*-$(FOA)_{36}$, $(EHMA)_{30}$-*b*-$(FOA)_{45}$, and $(EHMA)_{30}$-*b*-$(THFOA)_{50}$, were effective stabilizers for the dispersion copolymerization of EHMA, VBC, and DVB in the fluorinated solvent HFE-7200, leading to stable colloidal dispersions of discrete particles. Variations of the lengths of both blocks of the amphiphilic copolymers indicate that $(EHMA)_{\geq 30}$ and $(FOA)_{>30}$ are necessary for the formation of stable cross-linked poly(EHMA-*stat*-VBC) colloidal dispersions.

Acknowledgment. We thank the Defense Threat Reduction Agency for financial support administered through the US Army Research Office.

References and Notes

(1) Zhang, Q.; Zhan, X.; Chen, F.; Shi, Y.; Wang, Q. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1585–1594.
(2) Zhou, X.; Ni, P.; Yu, Z.; Zhang, F. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 471–484.
(3) Wood, C. D.; Cooper, A. L. *Macromolecules* **2003**, *36*, 7534–7542.
(4) Woods, H. M.; Nouvel, C.; Licence, P.; Irvine, D. J.; Howdle, S. M. *Macromolecules* **2005**, *38*, 3271–3282.
(5) Giles, M. R.; Griffiths, R. M. T.; Aguiar-Ricardo, A.; Silva, M. M. C. G.; Howdle, S. M. *Macromolecules* **2001**, *34*, 20–25.
(6) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745–756.
(7) Christian, P.; Giles, M. R.; Griffiths, R. M. T.; Irvine, D. J.; Major, R. C.; Howdle, S. M. *Macromolecules* **2000**, *33*, 9222–9227.
(8) Shiho, H.; DeSimone, J. M. *Macromolecules* **2000**, *33*, 1565–1569.
(9) Wang, Z.; Yang, Y.; Dong, Q.; Liu, T.; Hu, C. *Polymer* **2006**, *47*, 7670–7679.
(10) Carson, T.; Lizotte, J.; DeSimone, J. M. *Macromolecules* **2000**, *33*, 1917–1920.
(11) Berger, T.; McGhee, B.; Scherf, U.; Steffen, W. *Macromolecules* **2000**, *33*, 3505–3507.
(12) Galia, A.; Giaconia, A.; Iaia, V.; Filardo, G. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 173–185.
(13) Yang, Y.; Wang, Z.; Gao, Y.; Liu, T.; Hu, C.; Dong, Q. *J. Appl. Polym. Sci.* **2006**, *102*, 1146–1151.
(14) Baran, N.; Deniz, S.; Akgün, M.; Uzun, I. N.; Dinçer, S. *Eur. Polym. J.* **2005**, *41*, 1159–1167.
(15) Shiho, H.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 1146–1153.
(16) Ma, Z.; Lacroix-Desmazes, P. *Polymer* **2004**, *45*, 6789–6797.
(17) Shiho, H.; DeSimone, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3783–3790.
(18) Shiho, H.; DeSimone, J. M. *Macromolecules* **2001**, *34*, 1198–1203.
(19) Wang, W.; Giles, M. R.; Bratton, D.; Irvine, D. J.; Armes, S. P.; Weaver, J. V. W.; Howdle, S. M. *Polymer* **2003**, *44*, 3803–3809.
(20) Guan, Z.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 5527–5532.
(21) Xia, J.; Johnson, T.; Gaynor, S. G.; Matyjaszewski, K.; DeSimone, J. *Macromolecules* **1999**, *32*, 4802–4805.
(22) Li, K.; Wu, P.; Han, Z. *Polymer* **2002**, *43*, 4079–4086.
(23) Matyjaszewski, K.; Coca, S.; Gaynor, S. G.; Wei, M.; Woodworth, B. E. *Macromolecules* **1997**, *30*, 7348–7350.
(24) DeSimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356–359.
(25) Krupers, M.; Möller, M. *Macromol. Chem. Phys.* **1997**, *198*, 2163–2179.
(26) Wang, J.; Mao, G.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1997**, *30*, 1906–1914.

MA800111T