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Synthesis and Properties of Semifluorinated Copolymers of Oligo(ethylene glycol) Methacrylate and 1*H*,1*H*,2*H*,2*H*-Perfluorooctyl Methacrylate

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ABSTRACT: Semifluorinated block copolymers of oligo(ethylene glycol) methacrylate (OEGMA) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyl methacrylate (FOMA) were prepared using group transfer polymerization via sequential monomer addition. Wide ranges of copolymers were obtained with good control over both molecular weight and composition by adjusting the monomer/initiator ratio. Analogous statistical copolymers were prepared using radical polymerization in supercritical CO_2. The micelle-like aggregates of the block copolymers in water and chloroform were characterized by quasi-elastic light scattering and transmission electron microscopy. The size and morphology of the aggregates were found to depend on the nature of solvent, temperature, and the copolymer composition. The solubility of copolymers and the formation of hydrated reverse micelles in CO_2 were investigated. The block copolymer showed a better ability of solubilizing water in CO_2 than the statistical copolymer.

1. Introduction

Semifluorinated copolymers have attracted much attention due to their unique properties such as low surface energy, chemical/biological inertness, and oil/water repellence. They may be utilized in a variety of applications such as micelle formation in liquid and supercritical carbon dioxide, biomaterials, membranes, coatings, etc.[1−4]

Living anionic,[5] living cationic,[6] controlled radical,[7] and group transfer polymerization (GTP)[8] have been used in the past to prepare well-defined fluorinated polymers. Solution properties of block copolymers are greatly influenced by the length and the ratio of block segments, so precise control over the chemical structure and the molecular weight is very important to manipulate their properties.

Recently, a graft copolymer composed of a fluorinated polymer backbone and poly (ethylene glycol) (PEG) grafts was used to solubilize water into CO_2.[9] The formation of reverse micelles in CO_2 with hydrophilic core was confirmed by small-angle X-ray scattering (SAXS) and small angle neutron scattering (SANS).[10] In these micelles, the poly (1,1-dihydroperfluorooctyl acrylates) backbone forms the shell of the micelle, while the PEG grafts form the hydrophilic core. Emulsions consisting of the environmentally benign solvents such as carbon dioxide and water, which are nontoxic, nonflammable, and inexpensive, may be substituted for toxic organic solvents in chemical processing. Applications include dry cleaning,[11] photoresist drying,[12] nanoparticle synthesis,[13] enzymatic catalysis,[14] and organometallic catalysis.[15]

More recently, we have reported on the synthesis of semifluorinated block copolymers containing PFOMA block and either poly (ethylene oxide) (PEO) or poly (2-(dimethylamino)ethyl methacrylate) (PDMAEMA) block by atom transfer radical polymerization (ATRP) and GTP, respectively.[16,17] It was demonstrated that the block copolymers formed micelles where PEO or PDMAEMA is the shell, PFOMA is the core in water and chloroform, and the micellar characteristic depended on the block ratio in the copolymers. The PEO-*b*-PFOMA could stabilize nanometer-sized water-in-CO_2 (W/C) miniemulsion droplet with large water/surfactant ratios.[18] PDMAEMA-*b*-PFOMA was able to form hydrated reverse micelles in CO_2 that were utilized to prepare TiO_2 nanoparticles with controlled hydrolysis of titanium tetraisopropoxide.[19]

The present article describes the synthesis of POEGMA-*b*-PFOMA copolymers via GTP. GTP has been extensively utilized for the preparation of acrylate and methacrylate based block copolymers with controlled molecular weight and narrow molecular weight distribution. A series of block copolymers were prepared by varying the ratio of monomers to an initiator, and the micellar characteristics of the copolymers were investigated by quasi-elastic light scattering (QELS) and transmission electron microscopy (TEM). On the other hand, an analogous random copolymer was prepared by radical polymerization in supercritical CO_2. The POEGMA-PFOMA copolymer has interesting structure with pendant hydrophilic oligo (ethylene glycol) (OEG) and lipophobic semifluorinated alkyl groups. In addition, the solubility of copolymers in dense carbon dioxide and the formation of hydrated reverse micelles with the copolymers were examined.

2. Experimental Procedures

2.1. Materials. Tetrahydrofuran (THF) was distilled from sodium naphthalide under reduced pressure prior to use. OEGMA (Aldrich) (M_n = 300 g/mol) was purified by passing through a neutral alumina column, to remove the inhibitor, stored over CaH_2 at below 0 °C, and distilled prior to use. The GTP catalyst, tetrabutylammonium bibenzoate (TBABB), was

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synthesized according to a procedure found in the literature.[20] The initiator, methyl trimethysilyl dimethyl ketene acetal (MTSDA) (Aldrich), was distilled under high vacuum and stored under argon atmosphere. 1*H*,1*H*,2*H*,2*H*-Perfluorooctyl methacrylate (FOMA) (SynQuest) was passed through a neutral alumina column, stored over CaH_2, and then vacuum distilled before use. 1,1,2-Trichlorotrifluoroethane (F-113) (Aldrich), petroleum ether, hexane, chloroform, titanium(IV) isopropoxide(TTIP) (Aldrich), and research grade CO_2 (Daeyoung Co., 99.99%) were used as received. Deionized water (IWD-2000D) (Sam Bo Scientific Co.) was used as indicated.

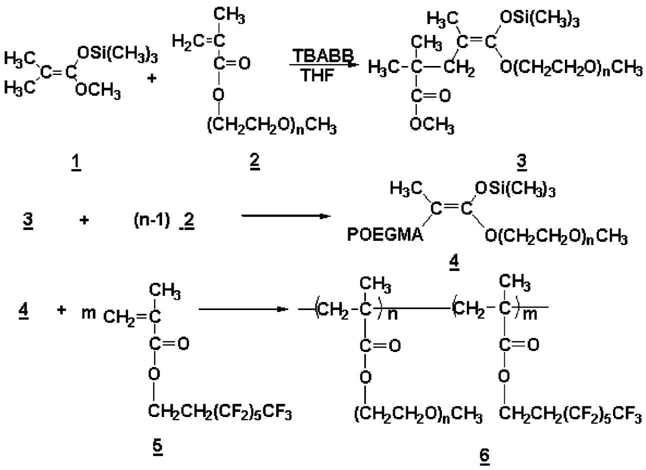
2.2. General Procedure of GTP for POEGMA-*b*-PFOMA. GTP was carried out under argon atmosphere in a previously flamed glass reactor. In a typical polymerization of POEGMA-*b*-PFOMA, 15 mL of THF and 4 mg (0.008 mmol) of TBABB were transferred into a reactor by means of a cannula. Then, 0.05 g (0.3 mmol) of MTSDA was added to the mixture via syringe. After 5 min of stirring, 1 g (5 mmol) of freshly distilled OEGMA was added slowly via syringe, and the polymerization proceeded for 30 min under argon. An aliquot of the reaction mixture was withdrawn for GPC analysis. For the block copolymerization, 1 g (2.3 mmol) of freshly distilled FOMA was added to the living POEGMA solution. The mixture was stirred for an additional hour and quenched with degassed methanol (2 mL). THF and methanol were removed by evaporation, and possible unreacted FOMA and POEGMA homopolymers were extracted with hexane and water, respectively. The product was collected, dried, and weighed to give 1.96 g of polymer. The molecular weights of POEGMA and PFOMA block of the copolymer were determined to be 1400 and 11 200, respectively. Control over the copolymer molar mass was achieved by varying monomers/initiator ratio.

2.3. Synthesis of POEGMA-*ran*-PFOMA in Supercritical CO_2. In a typical polymerization for statistical copolymer of POEGMA-*ran*-PFOMA, 0.2 g of OEGMA, 0.8 g of FOMA, and 0.01 g AIBN and a Teflon-coated stir bar were introduced into a stainless steel reactor (4 mL). The reactor was then closed and purged with argon prior to pressurization. The reactor was pressurized by ISCO syringe pump (Model 260D) containing compressed CO_2. Following pressurization, the reactor was heated to 65 °C by immersing the reactor in a water bath in which temperature was controlled by a thermostatic head (LABTECH).

The polymerization was conducted in supercritical CO_2 at 345 bar for 8 h. After polymerization, any unreacted monomers were extracted with ~20 mL of liquid CO_2 at 70 bar and ambient temperature. The product was collected and weighed. The molar composition and molecular weight of random copolymer were determined by ^{1}H NMR and GPC, respectively.

2.4. Characterization. Size-exclusion chromatography (SEC) was carried out with a HP1100 apparatus equipped with a set of four columns (10^5 to 10^4 to 10^3 to 10^2 Å: polymer standards service) with THF as the eluent. Polystyrene samples were used as standards to construct the calibration curve. ^{1}H NMR spectra were recorded using a JNM-ECP 400 (JEOL). ^{1}H NMR spectra of the POEGMA-*b*-PFOMA and random copolymers were obtained in a mixed solvent of F-113 and $CDCl_3$ ($V/V = 3.5{:}1$). QELS experiment was performed to measure the apparent hydrodynamic diameter of the POEGMA-*b*-PFOMA copolymer micelles. The sample solution (2 g/L) was purified by passing it through a 0.45 μm filter. The scattered light of a polarized diode laser (659 nm) was measured at 90° and collected on a Brookhaven BI 9000 AT autocorrelator. The hydrodynamic diameter (d_h) was calculated from the measured diffusion constant using the Stokes equation, $D = kT/3\pi\eta d_h$, where k, T, and η are the Boltzmann's constant, the absolute temperature, and the solvent viscosity, respectively. The polydispersity of the micelle is given by μ_2/Γ^2, where μ_2 is the second cumulant of the decay function, and Γ is the decay rate of the scattering correlation function.

Scheme 1. Synthesis of POEGMA-*b*-PFOMA



The TEM image was obtained using a Hitachi H-7500 instrument operated at 80 kV. A drop of polymer solution (2 g/L) was applied onto a copper grid coated with carbon, which was in contact with a soaking tissue to remove the solution immediately. The sample was used without any staining procedure. The cloud point was determined by simple visual inspection using a 28 mL stainless steel variable-volume view cell equipped with a sapphire window that permitted visual observation of reverse micelle formation and phase behavior.[21] A piston inside the view cell was used to vary the volume of sample of constant weight fraction and the pressure independently of temperature.

3. Results and Discussion

3.1. Polymerization. The synthesis of POEGMA-*b*-PFOMA copolymers by group transfer polymerization is illustrated in Scheme 1. Block copolymers of POEGMA and PFOMA of various block lengths were prepared by varying the ratio of monomer to initiator in the polymerization. OEGMA was polymerized first in all cases because of the low solubility of PFOMA in THF. A sample was picked out from the reactor before the addition of FOMA to analyze the molecular weight and the conversion. The POEGMA had a low polydispersity of 1.21 with unimodal shape in GPC trace, and no monomer could be detected in the ^{1}H NMR spectrum. Thus, the complete polymerization of OEGMA was confirmed before the addition of the second monomer, FOMA. The GTP of the second monomer proceeded successfully, but a small amount of unreacted FOMA (less than 10%) remained even after prolonged reaction time. This may be attributed to the micellization of block copolymer in the reaction solvent upon increasing of PFOMA content. A reactive center tends to be at the core of polymer coil as lipophobic PFOMA block chain grows longer; therefore, the possibility of propagation is inhibited.

After isolation of the block copolymer, it was extracted with hexane and water to remove unreacted FOMA and POEGMA, respectively. A trace of POEGMA in the extracted water solution was detected.

The GPC analysis has been attempted to characterize the molecular weight and molecular weight distribution of the block copolymer. Figure 1 depicts the GPC curves of the polymers. The peak of starting POEGMA shifts toward the higher molecular weight copolymer with slight decrease of polydispersity. There is a small molecular weight shoulder in the POEGMA peak, which is attributed to the polydispersity of the OEGMA monomer. These results indicate that the polymerization of FOMA proceeded efficiently by the living POEGMA.

The initiator's peak could not be identified in ^{1}H NMR spectra because of overlapping with methylene protons

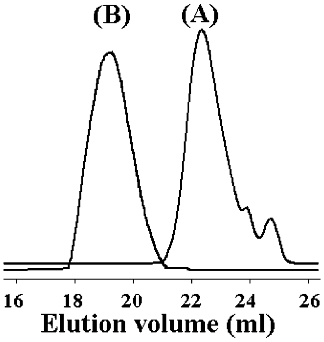
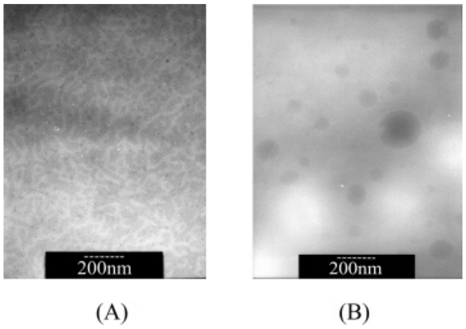


Figure 1. GPC trace of (A) starting $\text{POEGMA}_{1.4K}$ ($M_w/M_n = 1.21$) and (B) $\text{POEGMA}_{1.4k}$-*b*-$\text{PFOMA}_{11.2k}$ ($M_w/M_n = 1.09$).

of POEGMA; thus, the molecular weight of POEGMA was determined by GPC. The mole content of PFOMA with respect to POEGMA was calculated by comparing the peak integrals between the 1,1-dihydro protons (at 4.5 ppm) in the fluoroalkyl groups and the methylene protons (at 4.2 ppm) next to the ester moieties in OEGMA groups in the ^{1}H NMR spectra of copolymers. The molecular weight of the block copolymer was calculated from the copolymer composition based on the M_n of POEGMA by GPC. Table 1 summarizes the theoretical and observed number-average molecular weights (M_n) and compositions. Good yields (above 95%) were obtained in all copolymerizations with excellent control being achieved over both molecular weight and block copolymer composition.

Statistical copolymerizations of FOMA and OEGMA were conducted in supercritical CO_2 in the presence of AIBN. After 8 h of polymerization at 65 °C, the conversions fell in the range 75−80%. The solution was clear for 39:61 molar OEGMA-FOMA copolymer during the reaction. On the other hand, the solution became slightly cloudy at the end of polymerization for higher OEGMA copolymer of 65:35 molar composition due to a formation of aggregates. For most of copolymerizations, the conversion of OEGMA was found to be higher than FOMA. The discrepancy on the theoretical molar composition and observed molar composition for the random copolymer may result from the difference of monomer reactivity ratios and the incomplete polymerization.



(A) (B)

Figure 2. TEM picture of POEGMA-*b*-PFOMA aggregates made in chloroform: (A) $\text{POEGMA}_{6.5k}$-*b*-PFOMA_{20k} and (B) $\text{POEGMA}_{3.4k}$-*b*-PFOMA_{28k}.

3.2. Micellar Characteristics. Micellar characteristics of block copolymers in water and chloroform were studied by QELS. POEGMA is hydrophilic as well as lipophilic, and PFOMA is lipophobic, indicating amphiphilicity of POEGMA and amphiphobicity of PFOMA. Thus, the copolymer is expected to form micelles both in aqueous and organic media.

Characteristics of POEGMA-*b*-PFOMA micelles are given in Table 2. As expected, POEGMA-*b*-PFOMA copolymers were soluble in water and chloroform to form micelles consisting of a core of PFOMA and a shell of POEGMA within a range of block compositions. For the block copolymers whose FOMA content is lesser than 17 mol %, no micelles were detected, and the block copolymers existed as unimers in chloroform. On the contrary, those block copolymers formed micelles in water. The copolymers may have higher lyophobicity in water than chloroform. Large aggregates were formed in chloroform for block copolymers above 77 mol % PFOMA due to the insufficient steric stabilization of relatively short POEGMA blocks.[22]

The effect of temperature on the size of the micelles formed by $\text{POEGMA}_{6.6k}$-*b*-$\text{PFOMA}_{1.2k}$ copolymer in water was investigated. At temperatures between 30 °C and 50 °C, the average d_h of micelles was ca. 27.6 nm. However, at 60 °C, the d_h increased to 160.6 nm. It is likely that the POEGMA steric barriers collapse due to the decrease of solubility at higher temperature, as the

Table 1. GTP of POEGMA and FOMA via Sequential Monomer Addition

block copolymer	theor. Mn (g mol^{-1})	obs. Mn^a (g mol^{-1})	theor. molar composition (mol %)	obs. molar composition^b (mol %)
$\text{POEGMA}_{6.6k}$-*b*-$\text{PFOMA}_{1.2k}$	7000	7800	90:10	89:11
$\text{POEGMA}_{3.1k}$-*b*-$\text{PFOMA}_{0.9k}$	3900	4000	83:17	83:17
$\text{POEGMA}_{6.5k}$-*b*-PFOMA_{20k}	26000	26500	32:68	32:68
$\text{POEGMA}_{1.6k}$-*b*-$\text{PFOMA}_{7.7k}$	9000	9300	22:78	23:77
$\text{POEGMA}_{3.4k}$-*b*-PFOMA_{28k}	31000	31400	13:87	15:85
$\text{POEGMA}_{1.4k}$-*b*-$\text{PFOMA}_{11.2k}$	12000	12600	12:88	15:85
$\text{POEGMA}_{1.8k}$-*b*-$\text{PFOMA}_{23.2k}$	23500	25000	9:91	10:90
POEGMA-*ran*-PFOMA		34500^c	59:41	65:35
POEGMA-*ran*-PFOMA		60700^c	26:74	39:61

^{a} Calculated from GPC and ^{1}H NMR. ^{b} Determined by ^{1}H NMR. ^{c} Determined by GPC.

Table 2. Characteristics of POEGMA-*b*-PFOMA Micelles

block copolymer	mol % of FOMA	solvent^a	T (°C)	$d_h{}^b$ (nm)	polydispersity (μ_2/Γ^2)
$\text{POEGMA}_{1.4k}$-*b*-$\text{PFOMA}_{11.2k}$	85	chloroform	30	237.9	0.172
$\text{POEGMA}_{3.4k}$-*b*-PFOMA_{28k}	85	chloroform	30	276.4	0.296
$\text{POEGMA}_{1.6k}$-*b*-$\text{PFOMA}_{7.7k}$	77	chloroform	30	138.2	0.149
$\text{POEGMA}_{3.1k}$-*b*-$\text{PFOMA}_{0.9k}$	17	water	30	45.2	0.332
$\text{POEGMA}_{6.6k}$-*b*-$\text{PFOMA}_{1.2k}$	11	water	30	27.0	0.212
			50	28.2	0.178
			60	160.6	0.005

^{a} 0.2 wt % polymer solution. ^{b} Effective diameter at 30 °C.

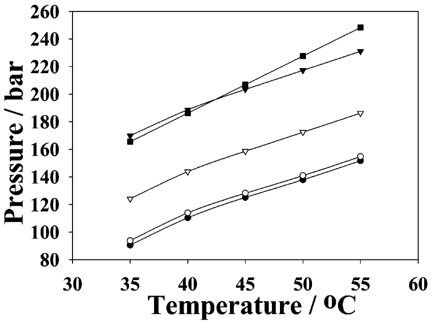


Figure 3. Cloud point profiles of POEGMA-PFOMA copolymers (0.5 wt %) in CO_2 ●: $POEGMA_{1.8k}$-*b*-$PFOMA_{23.2k}$; ○: $POEGMA_{1.4k}$-*b*-$PFOMA_{11.2k}$; ▼: $POEGMA_{6.5k}$-*b*-$PFOMA_{20k}$; ▽: $POEGMA_{1.6k}$-*b*-$PFOMA_{7.7k}$; and ■: POEGMA-*ran*-PFOMA (mole ratio = 39:61).

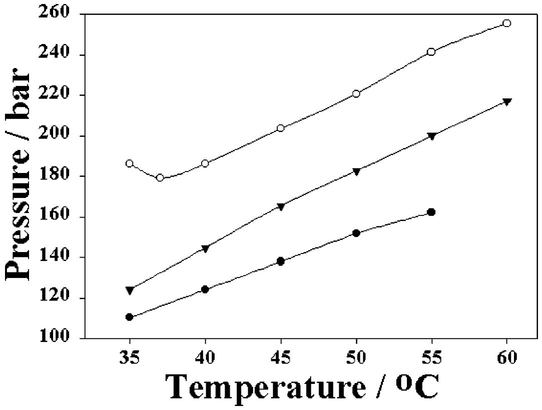


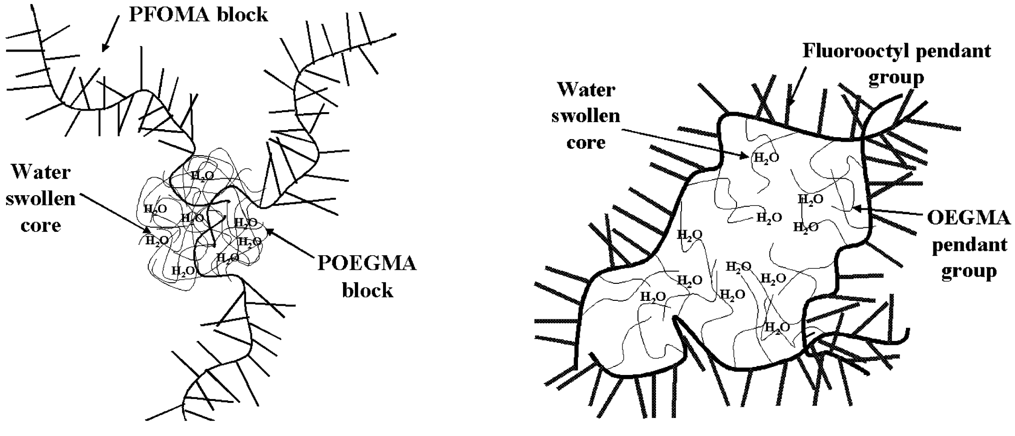
Figure 4. Phase behavior of the water/surfactant/CO_2 system as a function of w_o=12 at surfactant concentration of 0.25 wt % in CO_2 (●: $POEGMA_{1.4k}$-*b*-$PFOMA_{11.2k}$; ○: POEGMA-*ran*-PFOMA (39:61); and ▼: $POEGMA_{6.5k}$-*b*-$PFOMA_{20k}$).

lower critical solution temperature (LCST) for the POEGMA was measured to be ~65 °C.

The morphology of the block copolymer micelles was examined by TEM. Figure 2 shows the TEM images of the micellar aggregates of $POEGMA_{6.5k}$-*b*-$PFOMA_{20k}$ and $POEGMA_{3.4k}$-*b*-$PFOMA_{28k}$ in chloroform. The dark core regions correspond to the PFOMA in accordance with the higher electron density of the fluorinated block. $POEGMA_{6.5k}$-*b*-$PFOMA_{20k}$ showed cylindrical morphology, while large aggregates were formed for $POEGMA_{3.4k}$-*b*-$PFOMA_{28k}$. In the previous study, PEO_{5K}-*b*-$PFOMA_{4.5K}$ was predominantly spherical, but PEO_{5K}-*b*-$PFOMA_{12.5K}$ was cylindrical in chloroform. As the content of the soluble block in the block copolymer decreases, the morphology of the aggregates changes progressively from sphere to cylinders and eventually to large aggregates.[22]

3.3. Solubility and Reverse Micelle Formation of POEGMA-*b*-PFOMA in CO_2. The solubility of copolymers in dense CO_2 was studied in the temperature range 35−60 °C and at pressures up to 260 bar. The results in Figure 3 indicate that most surfactants are soluble in CO_2 in these conditions. The optically transparent one-phase region is above each curve in the plot. It is well-known that the PFOMA component is very CO_2-philic, so the solubility of block copolymers in CO_2 increases with the mole fraction of PFOMA. Furthermore, it is found that block and random copolymers of similar mole fraction feature comparable solubility when dissolved at similar pressure and temperature conditions (compare $POEGMA_{6.5k}$-*b*-$PFOMA_{20k}$ with POEGMA-*ran*-PFOMA). Conversely, the previous work on PDMAEMA-PFOMA copolymers showed that the block copolymer was more soluble than the random copolymer, possibly due to the micellar formation in CO_2 where PDMAEMA is the core and PFOMA is the shell.[17] In the case of POEGMA-PFOMA copolymers, the block structure does not have the advantage of statistical structure from the viewpoint of solubility in CO_2.

Past work demonstrated that stable water-in-carbon dioxide (W/C) microemulsions are formed with cationic or anionic perfluoropolyether surfactants.[23,24] The hydrophilic headgroups form a core while CO_2-philic tails interact with carbon dioxide, and the water partitions into the hydrophilic domain forming microscopic water pools. Above 77mol % of PFOMA composition, the bock copolymer is very soluble in CO_2 and has a low solubility in water; thus, it is expected to make W/C microemulsions. Cloud point studies confirmed that optically transparent and thermodynamically stable hydrated reverse micelles solutions were formed with the copolymer surfactants. Pressure−temperature phase behavior of reverse micelles formed by the $POEGMA_{1.4\ K}$-*b*-$PFOMA_{11.2K}$, $POEGMA_{6.5k}$-*b*-$PFOMA_{20k}$, and POEGMA-*ran*-PFOMA (39:61) at w_o=12 and 0.25 wt % in CO_2 are represented in Figure 4. w_o is the molar ratio of water to each EO unit in the OEG pendant groups ($[H_2O]/[EO]$) since water associates only with the polar EO groups of the polymer. Because a certain amount of



(A) (B)

Figure 5. Proposed structure of a POEGMA-*b*-PFOMA (A) and POEGMA-*ran*-PFOMA (B) micelle with a water-swollen core in CO_2.

water can dissolve in bulk CO_2, for example, 0.14 wt % at 276 bar and 25 °C, corrected values (w_o^c) of water-to-surfactant ratio excluding the bulk solubility are often quoted to represent the water contents in micellar cores. The w_o^c values for POEGMA$_{6.5k}$-*b*-PFOMA$_{20k}$ and POEGMA-*ran*-PFOMA (39:61) at 35 °C are calculated to be 2.7 and 3.6, respectively. The one-phase hydrated reverse micelle solution region is above the curve in the plot. As the pressure is lowered at constant temperature, the solution developed a characteristic orange tinge when viewed in the pressure cell. This color can be attributed to an increase in light scattering indicating an increase in the size of droplets and droplet clusters. The clusters result from increased droplet interactions prior to the cloud point pressure.[25,26] At the transition point, the samples rapidly became opaque. The phase transition due to micelle−micelle interactions results from a decrease in the density and solvent power of CO_2. Upon decreasing the solvent power of CO_2, solvent−tail interactions decrease, and tail−tail interactions increase resulting in the aggregation of micelles.[27] It is shown that the phase separation occurred at lower densities for block copolymer as compared with the statistical copolymer at similar chemical composition. It may be suggested that the block copolymer self-assembles more compactly than the random copolymer in the presence of water as shown in the proposed structure in Figure 5. The PFOMA chains extend into CO_2 phase more efficiently and reduce droplet−droplet interactions; thus, the block copolymer structure provides better stability to hydrated reverse micelles in CO_2 than the statistical copolymer.

4. Conclusions

Block copolymers that consist of POEGMA and PFOMA were synthesized by sequential addition of monomers using GTP. Precise control over molecular weight and copolymer composition was achieved by changing the monomer/initiator ratio. The statistical copolymers were also prepared in supercritical CO_2 with AIBN as an initiator. It has been demonstrated that the block copolymers formed micelles where POEGMA is the shell, and PFOMA is the core in both water and chloroform. The micellar sizes in water varied depending on the solution temperature. In chloroform, the micellar morphology was changed from cylinder to large aggregates with the increase of PFOMA mole fraction in the copolymers. The solubility of copolymers in CO_2 increased as the mole fraction of PFOMA increased. Stable hydrated reverse micelles of block and statistical copolymers were formed in CO_2 at relatively low pressure and temperature, with the block copolymer showing better ability to solubilize water in CO_2 than the random copolymer.

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Note Added after ASAP Publication. This article was published ASAP on 11/20/2004. The name of a copolymer has been changed in the caption of Figure 2. The correct version was posted on 11/24/2004.

References and Notes

(1) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999,** *99(2)*, 543−564.
(2) Riess, J. G. *Tetrahedron* **2002**, *58*, 4113−4131.
(3) Volkov, V. V.; Fadeer, A. G.; Plate, N. A.; Amaya, N.; Murata, Y.; Takahara, A.; Kajiyama, T. *Polym. Bull.* **1994**, *32*, 193−200.
(4) Verweire, I.; Schacht, E.; Qiang, B. P.; Wang, K.; de Scheerder, I. *J. Mater. Sci.: Mater. Med.* **2000**, *11*, 207−212.
(5) Ishizone, T.; Sugiyama, K.; Sakano, Y.; Mori, H.; Hirao A.; Nakahama, S. *Polym. J.* **1999**, *31*, 983−988.
(6) Matsumoto, K.; Kubota M.; Matsuoka, H.; Yamaoka, H. *Macromolecules* **1999**, *32*, 7122−7127.
(7) Betts, D. E.; Johnson, T.; LeRoux, D.; DeSimone, J. M. *ACS Symp. Ser.* **1998**, *685*, 418−432.
(8) Krupers, M. J.; Sheiko, S. S.; Möller, M. *Polym. Bull.* **1998**, *40*, 211−217.
(9) Fulton, J. L.; Pfund, D. M.; McClain, J. B.; Romack, T. J.; Maury, E. E.; Combes, J. R.; Samulski, E. T.; DeSimone, J. M.; Capel, M. *Langmuir* **1995**, *11(11)*, 4241−4249.
(10) Chillura-Martino, D.; Triolo, R.; McClain, J. B.; Combes, J. R.; Betts, D. E.; Canelas, D. A.; DeSimone, J. M.; Samulski, E. T.; Cochran, H. D.; Londono, J. D.; Wignall, G. D. *J. Mol. Struct.* **1996**, *383*, 3−10.
(11) DeSimone, J. M. *Science* **2002**, *297*, 799−803.
(12) Goldfarb, D. L.; de Pablo, J. J.; Nealey, P. F.; Simons, J. P.; Moreau, W. M.; Angelopoulos, M. J. *J. Vacuum Sci. Technol. B* **2000**, *18*, 3313−3317.
(13) Ohde, H.; Hunt, F.; Wai, C. M. *Chem. Mater.* **2001**, *13*, 4130−4135.
(14) Holmes, J. D.; Steytler, D. C.; Rees, G. D.; Robinson, B. H. *Langmuir* **1998**, *14*, 6371−6376.
(15) Jacobson, G. B.; Lee, C. T.; Johnston, K. P.; Tumas, W. *J. Am. Chem. Soc.* **1999**, *121*, 11902−11903.
(16) Lim, K. T.; Lee, M. Y.; Moon, M. J.; Lee, G. D.; Hong, S. S.; Dickson, J. L.; Johnston, K. P. *Polymer* **2002**, *43*, 7043−7049.
(17) Hwang, H. S.; Heo, J. Y.; Jeong, Y. T.; Jin, S.-H.; Cho, D.; Chang, T.; Lim, K. T. *Polymer* **2003**, *44*, 5153−5158.
(18) Dickson, J. L.; Psathas, P. A.; Salinas, B.; Ortiz-Estrada, C.; Luna-Barcenas, G.; Hwang, H. S.; Lim, K. T.; Johnston, K. P. *Langmuir* **2003**, *19*, 4895−4904.
(19) Lim, K. T.; Hwang, H. S.; Ryoo, W.; Johnston, K. P. *Langmuir* **2004**, *20(6)*, 2466−2471.
(20) Dicker, I. B.; Cohen, G. M.; Farnhan, W. B.; Hertler, W. R.; Laganis, E. D.; Sogah, D. Y. *Macromolecules* **1990**, *23*, 4034−4041.
(21) Psathas, P. A.; Sander, E. A.; Lee, M. Y.; Lim, K. T.; Johnston, K. P. *J. Dispersion Sci. Technol.* **2002**, *23(1−3)*, 65−80.
(22) Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1996**, *118*, 3168−3181.
(23) Clarke, M. J.; Harrison, K. L.; Johnston, K. P.; Howdle, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 6399−6406.
(24) Lee, C. T., Jr.; Psathas, P. A.; Ziegler, K. L.; Johnston K. P.; Dai, H. J.; Cochran H. D.; Melnichenko, Y. B.; Wingall, G. D. *J. Phys. Chem. B* **2000**, *104*, 11094−11102.
(25) Lee, C. T., Jr.; Johnston, K. P.; Dai, H. J.; Cochran, H. D.; Melnichenko, Y. B.; Wignall, G. D. *J. Phys. Chem. B* **2001**, *105*, 3540−3548.
(26) Fulton, J. L.; Blitz, J. P.; Tingey, J. M.; Smith, R. D. *J. Phys. Chem.* **1989**, *93*, 4198−4204.
(27) Ryoo, W.; Webber, S. E.; Johnston, K. P. *Ind. Eng. Chem. Res.* **2003**, *42*, 6348−6358.

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