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Synthesis of Emulsion-Templated Poly(acrylamide) Using CO_2-in-Water Emulsions and Poly(vinyl acetate)-Based Block Copolymer Surfactants

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ABSTRACT: We present here a simple and generic method for producing inexpensive and biodegradable polymer surfactants for use in supercritical CO_2. Low molecular weight (M_w < 7000 g/mol) hydroxyl-terminated poly(vinyl acetate) (PVAc−OH) was synthesized using optimized reaction conditions and isopropyl ethanol (IPE) as the chain transfer agent. Oligomeric PVAc−OH (OVAc−OH, M_w < 3000 g/mol) was then obtained by supercritical fluid fractionation. The OVAc−OH species was converted to the imidazole ester by reaction with carbonyl diimidazole (CDI) and CO_2-soluble surfactants were produced by coupling these reactive blocks with poly(ethylene glycol) methyl ethers or poly(ethylene glycol) diols. The surfactants found to be extremely effective in the production of stable CO_2-in-water (C/W) emulsions, which were then used as templates to produce emulsion-templated materials with unprecedentedly high levels of porosity for materials produced by this route. It was shown that these hydrocarbon surfactants can out-perform perfluorinated species in applications of this type.

Introduction

Emulsion templating is a versatile method for the preparation of highly porous organic polymers,[1−6] inorganic materials,[7−11] and inorganic−organic composites.[12] In general, the technique involves forming a high internal phase emulsion (HIPE) (>74.05% v/v internal droplet phase) and locking in the structure of the continuous phase, usually by reaction-induced phase separation (e.g., free-radical polymerization, sol−gel chemistry). Subsequent removal of the internal phase gives rise to a porous replica of the emulsion.

In principle, the polymerization of concentrated oil-in-water (O/W) emulsions can lead to novel, porous hydrophilic materials for applications such as separation media, catalyst supports, biological tissue scaffolds, and controlled release devices. However, a significant disadvantage is that concentrated O/W emulsion techniques are very solvent intensive. The internal oil phase (often an organic solvent) constitutes between 75 and 90% of the total reaction volume, and it may be difficult to remove this solvent from the material at the end of the reaction. For inorganic materials, purification tends to involve heating the sample to high temperatures (>600 °C), thus completely removing any organic residues.[7−11] This is clearly not practical for most organic polymers, biomaterials, or inorganic−organic hybrid materials that decompose at relatively low temperatures. In such cases, complete removal of the template phase may be much more problematic, particularly for applications such as biomaterials, where organic solvent residues are undesirable.

Supercritical carbon dioxide ($scCO_2$) has been promoted recently as a sustainable solvent because it is nontoxic, nonflammable, and naturally abundant.[13] In particular, $scCO_2$ has been shown to be a versatile solvent for polymer synthesis and processing.[14−17] Carbon dioxide has been exploited quite widely for the preparation of porous materials:[18] for example, $scCO_2$ has been used for the production of microcellular polymer foams,[19,20] biodegradable composite materials,[21] macroporous polyacrylates, and fluorinated microcellular materials.[22] We have developed a new approach to the synthesis of porous materials which involves the polymerization of high internal phase CO_2-in−water emulsions (C/W HIPEs).[23,24] This technique has wide appeal because it allows the synthesis of materials with well-defined porous structures without the use of any volatile organic solvents—just water and CO_2. Removal of the droplet phase is simple because the CO_2 reverts to the gaseous state upon depressurization. In our initial studies, the polymers were derived from acrylamide (AM) and a cross-linker, *N*,*N*-methylene bis(acrylamide) (MBAM). We employed a perfluoropolyether (PFPE) ammonium carboxylate surfactant since it is known that this surfactant can form both W/C and C/W macroemulsions[25] and microemulsions[26,27] and that the macroemulsions[25] can exhibit kinetic stability.

However, there are some key limitations associated with this initial approach,[24] particularly with respect to the potential for synthesizing biomaterials. The method involves a fluorinated surfactant, which is expensive and nonbiodegradable. Likewise, a similar method reported by Darr and co-workers employs highly fluorinated emulsion stabilizers.[28] We have demonstrated recently that it is possible to generate C/W emulsion-templated structures using a range of ionic and nonionic *hydrocarbon* surfactants that are much less expensive than fluorinated surfactant.[24] None of these hydrocarbon surfactants, however, gave rise to pore volumes as high as those obtained for samples using the PFPE surfactant, despite the fact that water solubility (and not CO_2 solubility) is the main criterion for C/W emulsion formation. For potential biomaterials, it proved very difficult to form stable C/W HIPEs and the materials produced exhibited low levels of porosity and partial templating of the emulsion structure.[24]

Carbon dioxide is a relatively weak solvent: for example, important classes of materials which tend to exhibit low solubility in $scCO_2$ include polar biomolecules, pharmaceutical actives, and high molecular weight polymers.[14,16,17] This problem is not unique to CO_2—indeed, an enormous variety of surfactants and phase transfer agents have been developed to disperse poorly

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soluble molecules in water. A technical barrier to the use of scCO_2 is the lack of an equivalent range of inexpensive CO_2-soluble (and preferably biodegradable) surfactants, ligands, and phase transfer agents. The majority of systems reported so far have been highly fluorine-substituted,[16,17] and the associated costs and low biodegradability may prohibit industrial-scale use in key applications. The discovery of inexpensive CO_2-soluble materials or "CO_2-philes" is therefore an important challenge.[29,30] Inexpensive poly(ether carbonate) (PEC) copolymers have been reported to be soluble in CO_2 under moderate conditions.[31] Similarly, sugar acetates are highly soluble and have been proposed as renewable CO_2-philes.[32,33] Such materials could, in principle, function as CO_2-philic building blocks for inexpensive ligands and surfactants, but this potential has not yet been realized and numerous practical difficulties remain. For example, CO_2 solubility does not in itself guarantee performance in the various applications of interest. Effective surfactants, in particular, tend to require specific asymmetric topologies such as diblock copolymers.[34,35] This in turn necessitates a flexible and robust synthetic methodology to produce well-defined architectures for specific applications. For the specific application of C/W emulsion formation it is not necessary to produce materials which are highly CO_2-soluble—indeed, water solubility is key. Even here, though, there are considerable advantages in developing a platform technology whereby biodegradable hydrocarbon surfactants can be produced which may be tuned to be water-soluble, CO_2-soluble, or of intermediate solubility behavior.

Recently, we have used end-functionalized poly(vinyl acetate) oligomers (OVAc) as CO_2-philic building blocks.[36] Poly(vinyl acetate) (OVAc) is an inexpensive, high-tonnage bulk commodity polymer which, unlike most vinyl polymers, is moderately biodegradable and has been used in pharmaceutical excipient formulations.[37] OVAc has also been shown to exhibit anomalously high solubility in CO_2 with respect to other vinyl hydrocarbon polymers,[38] although the polymer is soluble only at relatively low molecular weights under conditions of practical relevance ($P < 300$ bar, $T < 100$ °C).

In a preliminary communication,[36] we demonstrated a simple and generic method for producing inexpensive, functional hydrocarbon CO_2-philes for solubilization, emulsification, and related applications. In the detailed study reported here, a range of H_2O-soluble diblock and triblock surfactant architectures was produced and it was found that both types of structure could stabilize highly concentrated C/W emulsions. We investigate here in detail the factors affecting the C/W emulsion stability and utilize these optimized emulsions to generate materials with significantly increased levels of porosity.

Experimental Section

Materials. Vinyl acetate (VAc, Aldrich, 99+ %) was freed from inhibitor by passing through an alumina column. 2,2′-Azobis(isobutyronitrile) (AIBN, Fisher, 97%) was recrystallized twice from methanol and dried under vacuum before use. 2-Isopropoxyethanol (IPE, Aldrich, 99%), acrylamide (AM, 99+ %, Aldrich), *N,N′*-methylene bis(acrylamide) (MBAM, 99%, Aldrich), potassium persulfate (99+ %, Aldrich), ammonium persulfate (98%, Aldrich), poly(vinyl alcohol) (PVA, Aldrich, $M_w = 9000-10\,000$ g/mol, 80% hydrolyzed), poly(ethylene glycol)monomethylether, (Aldrich, $M_w = 750$ g/mol), poly(ethylene glycol)monomethylether (Aldrich, $M_w = 2000$ g/mol), triethylene glycol monomethyl ether (95%, Aldrich, $M_w = 164$ g/mol), poly(ethylene glycol) diol (PEG, Aldrich, $M_w = 2000$ g/mol), 1,1′-carbonyldiimidazole (CDI, Aldrich), sodium sulfate, anhydrous tetrahydrofuran (THF), and dichloromethane were all used as received. Deionized water was used throughout. High purity carbon dioxide (SFC grade, 99.9999%) was purchased from BOC Gases.

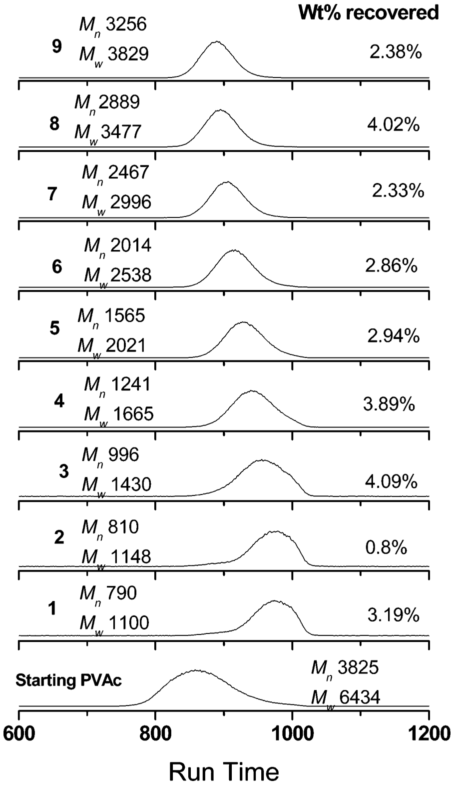


Figure 1. Representative series of nine OVAc fractions collected by supercritical fluid extraction of OVAc−OH. Figures on the right refer to the weight percentage of the total original sample represented by that fraction.

Synthesis of PVAc—OH. The synthesis of PVAc−OH was based on methods described previously (see ref 39 and references therein). Briefly, VAc (64.07 g, 0.745 mol) was added to IPE (480 mL, 4.16 mol) containing AIBN (9.61 g, 15% w/w based upon monomer). The resulting solution was heated to 65 °C with stirring for 12 h. The solvent was removed under reduced pressure and the polymer was reprecipitated into cold *n*-hexane. The product was then dissolved in acetone and was reprecipitated in cold *n*-hexane again. This was repeated two more times followed by drying under vacuum at 30 °C to afford the product as a colorless viscous liquid (59.5 g, 93%). M_n (GPC) = 3830 g/mol, M_w = 6430 g/mol.

NMR data (400 MHz, $CDCl_3$): δ 4.87−5.25, 50H; δ 4.02−4.18, 2H; δ 3.59−3.73, 2H; δ 3.34−3.52, 2H; δ 1.94−2.23, 150H; δ 1.54−1.94, 100H; δ 1.10−1.29,6H.

SCF Fractionation of PVAc—OH. About 100 g of PVAc−OH (M_n = 3830 g/mol, M_w = 6430 g/mol) was weighed accurately into a vertically mounted 500 cm^3 stainless steel extraction vessel (Thar Designs). Compressed CO_2 was flowed into the bottom of the vessel at a predetermined pressure and constant flow rate (CO_2 flow rate = 5 mL/min for all pressures) as controlled by a syringe pump. The extraction pressure was varied over the range 70−300 bar. The lower molecular weight OVAc fractions were extracted using pure CO_2. In order to collect higher molecular weight fractions, a modifier, MeOH, was coinjected into system (MeOH is a good solvent for PVAc). Extracts were collected after predetermined time intervals, thus producing a series of PVAc fractions with different molecular weights (Figure 1).

The low molecular weight PVAc materials were found to have high solubility in CO_2 (cloud point pressure = 90−100 bar, see Supporting Information).

Synthesis of OVAc—Imidazole Carboxylic Ester. The general procedure for the synthesis of the imidazole carboxylic esters was as follows: anhydrous THF (30 mL) was added to a 100 mL round-bottom flask fitted with a dry N_2 inlet and magnetic stirrer. 1,1′-Carbonyldiimidazole (CDI, 1.62 g, 10.0 mmol) and KOH (0.056

Table 1. Variation Reaction Conditions on M_w of PVAc

								mol wt [a]		
	VAc (mmol)	IPE (mmol)	temp (°C)	AIBN (wt %)	time (min)	heating method	yield (%)	M_n (g/mol)	M_w (g/mol)	PDI
1	100	260	65	0.22	600	C[d]	41.0	8020	12 180	1.52
2	100	260	65	0.88	600	C[d]	86.0	5650	9580	1.69
3	100	260	65	1.76	600	C[d]	90.8	6100	9970	1.63
4	100	260	65	3.52	600	C[d]	94.1	5740	9930	1.73
5	100	260	65	7.04	600	C[d]	93.8	4540	8290	1.82
6	11	860	90	0.2	1440	C[d]	[c]	2550	3990	1.57
7	23	860	90	1.0	1440	C[d]	[c]	3450	5830	1.69
8	11	860	90	1.0	1440	C[d]	[c]	2270	3570	1.57
9	11	860	90	1.0[b]	1440	C[d]	[c]	2530	3980	1.57
10	11	30	65	3.52	5	M[e]	60.7	6730	9510	1.41
11	11	30	65	3.52	10	M[e]	60.1	6200	8670	1.40
12	11	30	65	3.52	30	M[e]	89.0	4920	7440	1.51
13	11	30	90	3.52	10	M[e]	64.5	3180	4500	1.41

[a] Determined by GPC. [b] Low temperature initiator V65. [c] Not determined. [d] C = conventional oil bath heating. [e] M = microwave heating. Microwave heating was carried out with a Discover LabMate (CEM Corporation) at 150 W.

Table 2. OVAc−Imidazole Ester Synthesis

	mol wt (g/mol)			
	M_n	M_w	PDI	yield (%)
OVAc−OH	1070	1520	1.42	
OVAc−Im	1300	1700	1.31	98.9

Table 3. OVAc-*b*-PEG Diblock Synthesis

	mol wt (g/mol)				
	M_n	M_w	PDI	weight (g)	yield (%)
OVAc−Im	1300	1700	1.31	0.5569	
OVAc-*b*-PEG	3020	3300	1.09	1.2601	97.4

g, 1.0 mmol) were added to the flask followed by the dropwise addition over the period of 60 min of a solution of OVAc−OH (3.00 g, M_n (GPC) = 1070 g/mol, M_w = 1520 g/mol, 2.8 mmol) dissolved in THF (20 mL). The mixture was then heated at 65 °C with stirring for 10 h. The clear, pale-yellow solution that was formed was allowed to cool and then concentrated under vacuum. The crude product was dissolved in dichloromethane (50 mL) and washed three times with water (3 × 100 mL). The organic layer was then dried over anhydrous Na_2SO_4 and the solvent removed under vacuum to obtain the end-functionalized polymer as a pale yellow solid (3.59 g, M_n (GPC) = 1300 g/mol, M_w = 1700 g/mol, 98.9%) (Table 2).

^{1}H NMR data (400 MHz, $CDCl_3$): δ 8.09−8.25; δ 7.40−7.51; δ 7.00−7.15; δ 4.72−5.23; δ 4.43−4.56; δ 4.02−4.23; δ 3.37−3.76; δ 1.94−2.23; δ 1.57−1.93; δ 1.05−1.27.

Synthesis of OVAc-*b*-PEG and OVAc-*b*-PEG-*b*-OVAc Diblock and Triblock Copolymers. (i) OVAc-*b*-PEG Diblock Copolymer. The general procedure for coupling the OVAc−imidazole carboxylic ester with HO−PEG−OMe to produce a diblock copolymer was as follows: dry THF (30 mL) was added to a 100 mL round-bottom flask fitted with a dry N_2 inlet and a magnetic stirrer. OVAc carboxylic ester (M_n(GPC) = 1300 g/mol, M_w = 1700 g/mol, 0.557 g, 4.3 mmol) was added followed by PEG-monomethyl ether (HO−PEG-OMe, (M_n = 2000 g/mol, 0.86 g, 4.3 mmol) and KOH (0.0224, 0.4 mmol). The mixture was stirred at 65 °C for 10 h. The clear, pale-yellow solution that was formed was allowed to cool and then concentrated under vacuum before was reprecipitating into cold *n*-hexane. The resulting polymer was dissolved in acetone and reprecipitated again. This was repeated two more times followed by drying under vacuum at 30 °C to produce the diblock copolymer as a clear, colorless viscous liquid (1.260 g, M_n(GPC) = 3000 g/mol, M_w = 3300 g/mol; 97.4%). (See Table 3 and Figure 3 for details.)

^{1}H NMR data (400 MHz, $CDCl_3$): δ 4.74−5.23; δ 4.20−4.39; δ 4.01−4.12; δ 3.76−3.90; δ 3.57−3.69; δ 3.33−3.44; δ 1.97−2.12; δ 1.63−1.96; δ 1.03−1.29.

(ii) OVAc-*b*-PEG-*b*-OVAc Triblock Copolymer. Triblock copolymers were synthesized using an analogous procedure to that described above by coupling OVAc−imidazole carboxylic esters with PEG−diols (M_n = 2000 g/mol). (See Table 4 and Figure 3 for details.)

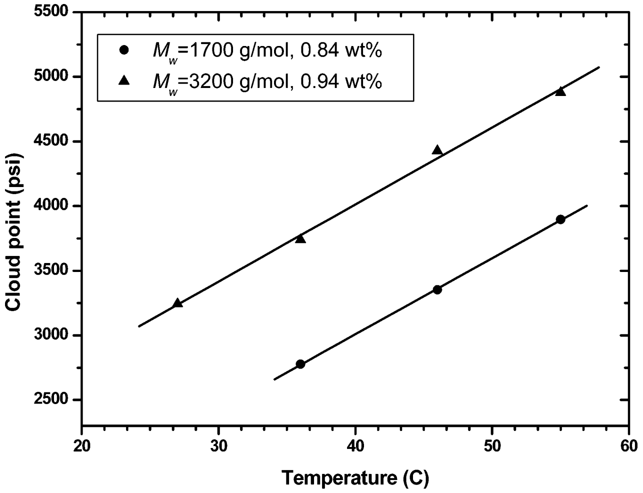
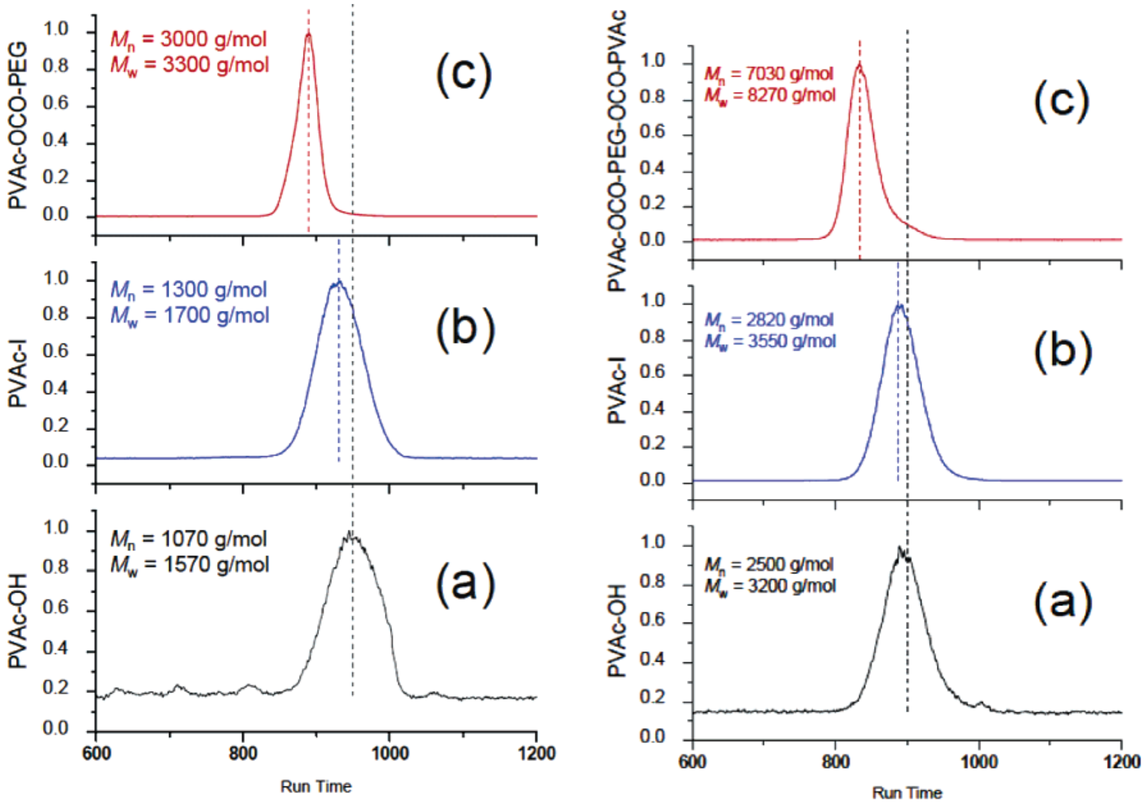


Figure 2. Cloud point curves for OVAc fractions as a function of molecular weight.

Polymerization of C/W Emulsions. In a typical polymerization,[24] a 10 cm^3 stainless steel view cell reactor was charged with an aqueous solution of monomers (40% w/v), $(NH_4)_2S_2O_8$ initiator (2% w/v based on monomer), surfactant, and a “cosurfactant” (PVA)[24] before purging with a slow flow of CO_2 for 5 min to remove any oxygen. The reactor was then pressurized with liquid CO_2 (20 °C, 100 ± 5 bar) and stirring was commenced (magnetic stir bar, 600 rpm) to form a milky white C/W emulsion. When a stable emulsion had been formed, a controlled volume of tetramethylethylenediamine (TMEDA, 0.1 cm^3) was added to the vessel at a rate of 1 cm^3 min^{-1}) using an HPLC pump. Stirring was ceased 5 min after the TMEDA addition. The CO_2 was vented 90 min after the addition of the TMEDA. The product was recovered as a continuous, white monolithic sample that conformed to the internal dimensions of the reactor (Figure 5). The material was dried either by air drying or by freeze drying using a Heto Lyolab 3000 freeze-dryer.

Polymer Characterization. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker Analytic GmbH 400 MHz spectrometer using tetramethylsilane (TMS) as an internal reference. ^{13}C NMR spectra were recorded at 400 MHz in $CDCl_3$ solution on a Bruker Analytic GmbH 400 MHz spectrometer using solvent carbon signal as standard. Gel permeation chromatography (GPC) was performed using a Polymer Laboratories system equipped with a PL-ELS 1000 evaporative light scattering detector and a series of PL$_{gel}$ columns 5 μm MIXED C and D. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. Calibration was carried out using



OVAc-*b*-PEG

OVAc-*b*-PEG-*b*-OVAc

Figure 3. GPC elution curves for (a) OVAc−OH, (b) OVAc-imidazolide, and (c, left side) OVAc(1070)-*b*-PEG(2000) diblock copolymer (polymer **1** of Scheme 3) and (c, right side) OVAc-*b*-PEG-*b*-OVAc triblock copolymer (polymer **2** of Scheme 3). The shift in molecular weight as recorded by GPC is consistent with the theoretical increase in molar mass for each reaction step.

Table 4. Synthesis of OVAc-*b*-PEG-*b*-OVAc Triblock Copolymer

	mol wt (g/mol)			
	M_n	M_w	PDI	yield (%)
OVAc−OH	2500	3200	1.28	
OVAc−Im	2820	3550	1.26	
OVAc-*b*-PEG-*b*-OVAc	7030	8270	1.18	80.0

EasiCal polystyrene standards (Polymer Laboratories). For porosity analysis, the continuous monolithic polymer samples were fractured into millimeter-sized pieces with a scalpel before loading into the glass penetrometer. Pore size distributions were recorded by mercury intrusion porosimetry using a Micromeritics Autopore IV 9500 porosimeter. Samples were subjected to a pressure cycle starting at approximately 0.5 psia, increasing to 60 000 psia in predefined steps to give pore size/ pore volume information. Polymer morphologies were investigated with a Hitachi S-2460N scanning electron microscope (SEM). Samples were mounted on aluminum studs using adhesive graphite tape and sputter-coated with approximately 10 nm of gold before analysis.

Results and Discussion

Synthesis of PVAc−OH. The synthetic strategy presented here is based on the preparation of monohydroxyl functionalized PVAc (Scheme 1) by free-radical polymerization in the presence of a chain-transfer agent, 2-isopropoxyethanol (IPE).[39]

Although PVAc is one of the most CO_2-soluble hydrocarbon polymers discovered so far, the extent of solubility of PVAc−OH in CO_2 has a close relationship with molecular weight. PVAc has relatively high solubility in CO_2 only when its molecular weight is lower than 3000 g/mol (see Figure 2). We studied a number of reaction variables (reaction temperature, IPE concentration and initiator concentration) in order to obtain lower molar mass PVAc−OH.

Our results showed that the number-average molecule weight of PVAc−OH decreased from 8020 to 4540 g/mol when the initiator concentration [I] was increased from 0.22 to 7.04 wt % (see Table 1). Microwave-assisted PVAc synthesis led, in general, to somewhat lower molecular weights and narrower PDIs, but it was still not possible to obtain molecular weights of less than 2000 g/mol in this way.

The PVAc−OH structures were characterized by NMR (see Supporting Information). It was found that the molecular weight calculated by NMR compared very well with the M_n determined by GPC. Since it proved difficult to synthesize oligomeric PVAc−OH of sufficiently low M_n in one step, we investigated SCF fractionation of the bulk samples.

SCF Fractionation of PVAc—OH. From the literature[38] and our experience, only oligomeric PVAc−OH has high solubility in CO_2 at modest pressures. The bulk PVAc−OH material was therefore fractionated by supercritical fluid extraction (CO_2 pressure 70−300 bar) to produce a series of end-functionalized PVAc−OH materials with number-average molecular weights, M_n, ranging from 800−4000 g/mol (see Figure 1). The fractionated PVAc−OH samples exhibited relatively narrow molecular weight distributions (M_w/M_n) in the range 1.14−1.40. It was found that fractionation with pure CO_2 was rather slow and inefficient. Methanol is a good solvent for PVAc−OH and was therefore used as a modifier. During the fractionation process, the CO_2 flow-rate was kept constant (10 mL/min) while the MeOH flow-rate was increased from 0 to 1.0 mL/min. By using this method, the fractionation efficiency was dramatically improved.

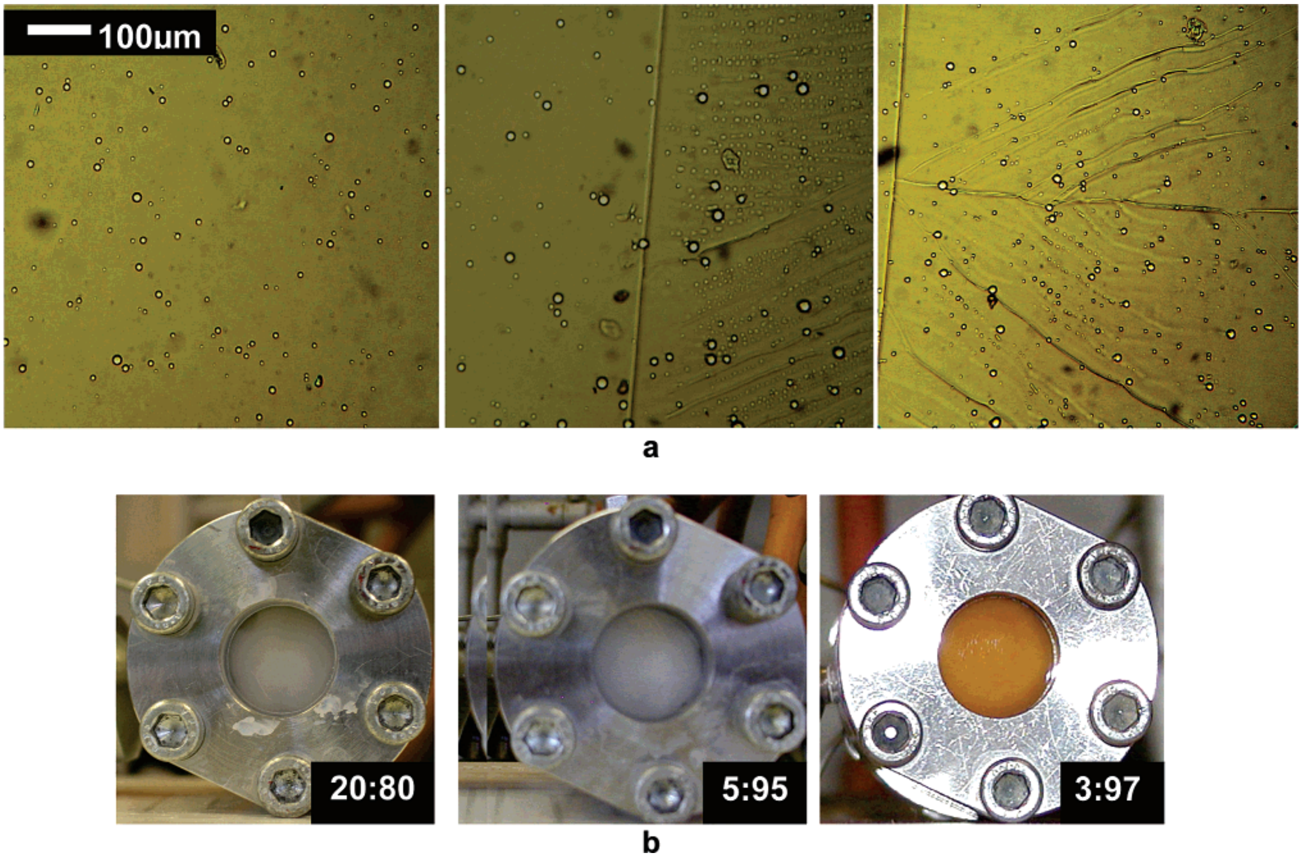


Figure 4. (a) Optical micrographs of hexane in water emulsions; (b) Optical image of C/W using OVAC(1070)-*b*-PEG(2000) surfactants at varying CO_2 : H_2O volume ratios.

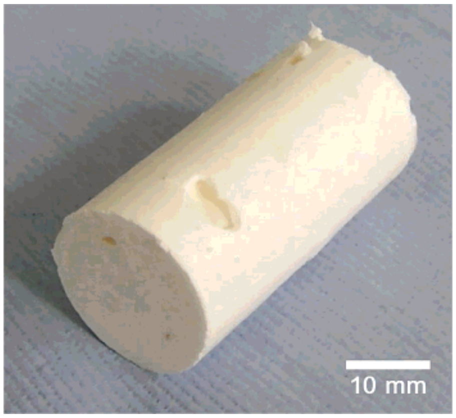
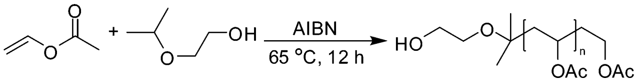


Figure 5. Photograph of monolithic cross-linked poly(acrylamide) material (PAM-3) formed by polymerization of a concentrated C/W emulsion (80% v/v CO_2) stabilized by a OVAc(2650)-*b*-PEG(2000)-*b*-OVAc(2650) triblock copolymer surfactant. Preparation conditions listed in Table 7.

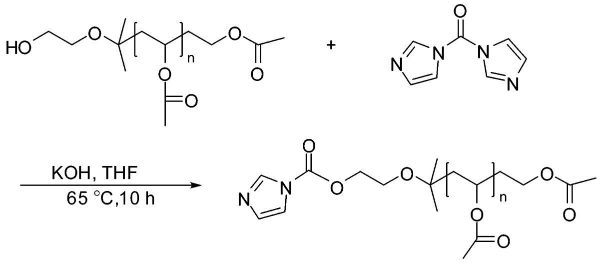
Scheme 1



The oligomeric fractions were soluble in CO_2 up to significant concentrations—for example, a PVAc−OH fraction with M_n of 840 g/mol and M_w of 1048 g/mol was soluble at 10% w/v in liquid CO_2 (25 °C) at a pressure of 100 bar. A “high throughput” solubility screen also confirmed that the PVAc−OH solubility in CO_2 was strongly dependent on molecular weight.[40]

Synthesis of OVAc—Imidazole Carboxylic Ester. The monohydroxyl end groups of the PVAc−OH species may be modified readily by a number of synthetic routes. We have utilized carbonyldiimidazole (CDI) coupling, as exploited previously for the synthesis of dendrimers and hyperbranched polymers[41−43] (Scheme 2), in order to form functional CO_2-philic architectures. This route has a number of advantages. First, the OVAc−imidazolide intermediate can be isolated, purified, and then coupled with a wide range of alcohols (or amines) to produce a variety of structures. Second, the route introduces a carbonate linkage that may further enhance CO_2 solubility[31,44−46] and could also improve the biodegradability of the resulting materials.

Scheme 2



Synthesis of OVAc-*b*-PEG and OVAc-*b*-PEG-*b*-OVAc Diblock and Triblock Copolymers. The CDI route (Scheme 3) was used to couple OVAc−OH with poly(ethylene glycol) monomethyl ethers (HO−PEG−OMe) and poly(ethylene glycol) diols (PEG) to produce diblock (**1**) and triblock (**2**) copolymers, respectively.

Figure 3 shows the shift in molecular weight as measured by GPC to be broadly consistent with the theoretical increase in molar mass for each reaction step. All products gave rise to unimodal molecular weight distributions. There is no evidence for the presence of any unreacted OVAc−OH in the diblock copolymer sample (Figure 3). Elution curve “c” (right, Figure

Scheme 3

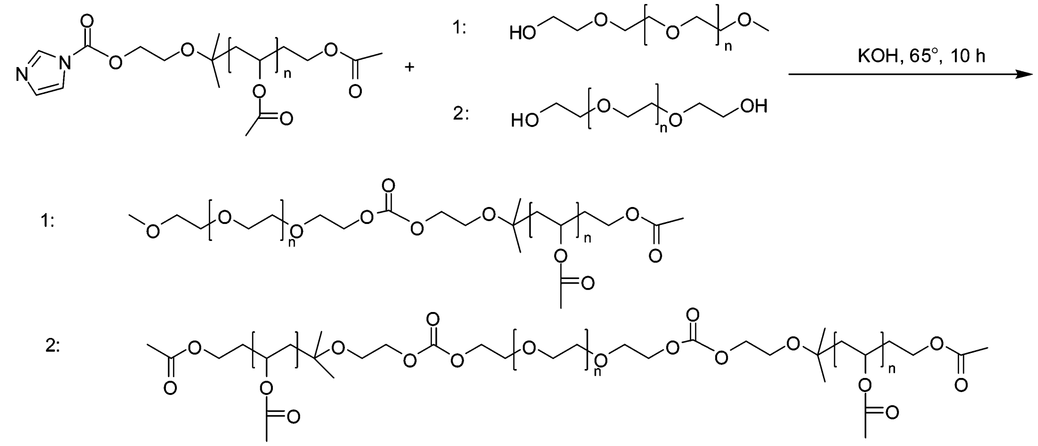


Table 5. Molecular Weight of Hydrocarbon Stabilizers Prepared

	OVAc (M_n)	PEG (M_n)	mol wt (g/mol)		
			M_n	M_w	PDI
1[a]	1000	164	1130	1540	1.37
2[a]	1000	750	1460	1740	1.19
3[a],[b]	2 × 1070	400	1580	1950	1.23
5	2 × 1070	2000	4240	4700	1.11
7	1070	2000	3000	3300	1.10
8[b]	2 × 2010	2000	2910	3620	1.25
9	2650	2000	4350	5310	1.22
10[b]	2 × 2650	2000	7030	8270	1.18
11	3600	2000	5380	6670	1.24
12	7180	2000	10 600	13 500	1.28
13	7180	164	7100	11 900	1.67

[a] CO_2-soluble (300 bar, 1% w/v). [b] OVAc-*b*-PEG-*b*-PEG.

3) suggests that the product is predominantly the triblock copolymer, perhaps with a small quantity of partially reacted OVAc-*b*-PEG−OH diblock material as an impurity.

The solubility behavior of these materials can be controlled by varying the overall molecular weight and the molar ratio of OVAc to PEG. It was found that both CO_2-soluble and H_2O-soluble structures could be synthesized in this way. Table 5 lists the molecular weights of all the stabilizers prepared along with the solubility characteristics (H_2O- or CO_2-soluble).

Emulsion Stability. First, we studied the emulsification of pure water and CO_2 (temperature = 25 °C, CO_2 pressure = 60−300 bar, volume fraction of CO_2 = 70−97%, surfactant concentration = 10% w/v based on H_2O). Table 6 shows summaries the results obtained by using the different stabilizers. No polyvinylalcohol (PVA) was added to these systems, although PVA was used in subsequent emulsion-templating experiments in order to counter the destabilizing effects of the vinyl monomers.

Neither PEG, OVAc−OH, nor a 1:2 w/w mixture of these two materials (NB1−NB3, Table 6) formed stable C/W emulsions at equivalent concentrations. This demonstrates the requirement for the amphiphilic block copolymer structure. Not all OVAc-*b*-PEG block copolymers lead to stable emulsions, as detailed in Table 6.

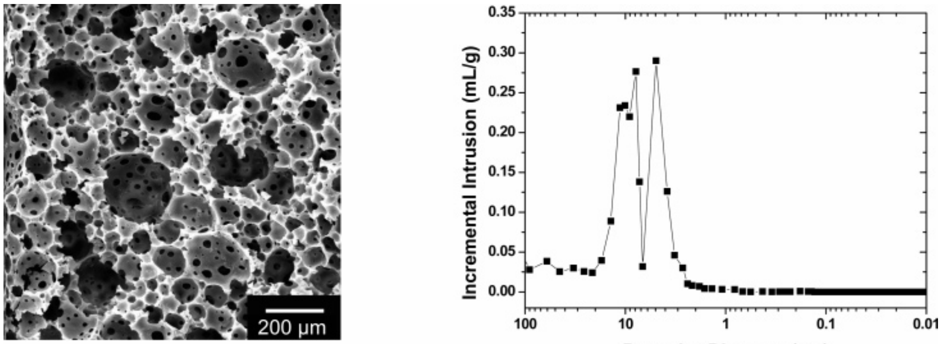
It was found that the ratio of OVAc to PEG was a very important factor. If the OVAc block had too high molecular weight, this led to poor CO_2 miscibility (**11**−**13**, Table 6), and/or an unsuitable hydrophilic −lipophilic balance. On the other hand, highly CO_2-soluble OVAc with a short PEG chain (3−4, Table 6) was also found to make a poor stabilizer for C/W emulsions, in keeping with Bancroft's rule. Achieving an appropriate hydrophilic-CO_2-philic balance for surfactants is a key factor for C/W emulsion stability[47] and this synthetic method allows a fine degree of control over this balance.

OVAc-*b*-PEG-*b*-OVAc (**5**, **8**, and **10**, Table 6) and OVAc-*b*-PEG (**1**, **2**, **6**, **7**, and **9**, Table 6) surfactants with a suitable ratio of OVAc to PEG blocks led to milky-white C/W emulsions which filled the entire reaction vessel. Depending on the precise conditions, the emulsions were stable for periods ranging from

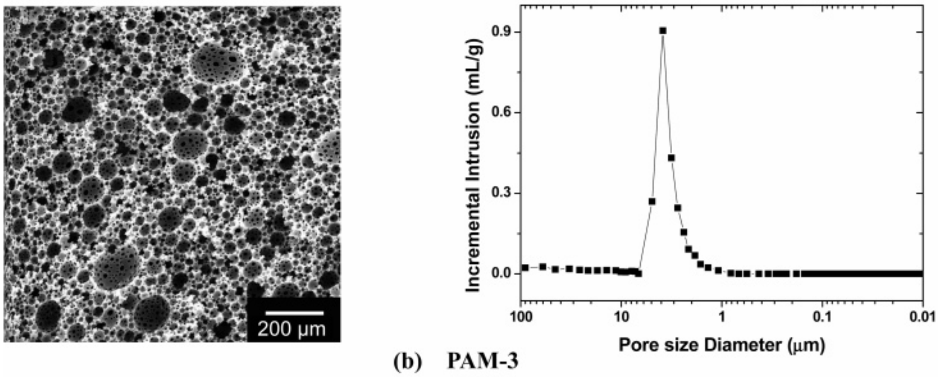
Table 6. Stability of Emulsion Prepared Using OVAc-*b*-PEG Block Copolymers

	OVAc−PEG				
	OVAc (g/mol)	PEG (g/mol)	H_2O/CO_2 (v/v)	(w/v) (%)	note
NB-1	1070		2.0/8.0	1.0	no emulsion formed
NB-2		2000	2.0/8.0	1.0	no emulsion formed
NB-3[a]	1070	2000	2.0/8.0	1.0	no emulsion formed
1[b]	1000	164	0.3/9.7	2.3	stable emulsion at 100 bar, >24 h
2[b]	1000	750	0.3/9.7	2.2	stable emulsion at 200 bar, >24 h
3[b, c]	2 × 1070	400	2.0/8.0	1.0	partial emulsion, 100−300 bar
4	1070	750	2.0/8.0	1.0	partial emulsion, 100−300 bar
5	2 × 1070	2000	2.0/8.0	1.0	stable emulsion at 60 bar, >24 h
6	1070	2000	2.0/8.0	1.0	stable emulsion at 100 bar, >48 h
7	1070	2000	0.5/9.5	1.0	stable emulsion at 200 bar, >24 h
8[c]	2 × 2010	2000	2.0/8.0	1.0	stable emulsion at 100 bar, >48 h
9	2650	2000	2.0/8.0	1.0	stable emulsion at 200 bar, >24 h
10[c]	2 × 2650	2000	2.0/8.0	1.0	stable emulsion at 100 bar, >48 h
11	3600	2000	2.0/8.0	1.0	partial emulsion, 100−300 bar
12	7180	2000	2.0/8.0	1.0	no emulsion, 100−300 bar
13	7180	164	2.0/8.0	1.0	no emulsion, 100−300 bar

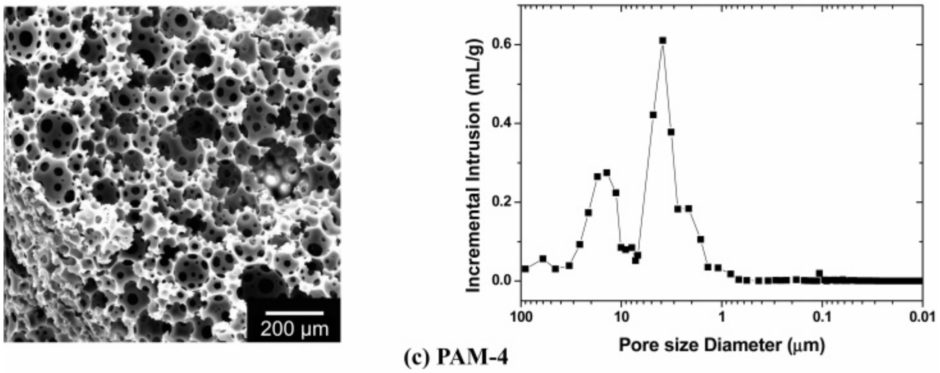
[a] Physical mixture of PEG and OVAc, not block copolymer. [b] CO_2-soluble. [c] OVAc-*b*-PEG-*b*-OVAc triblock copolymer.



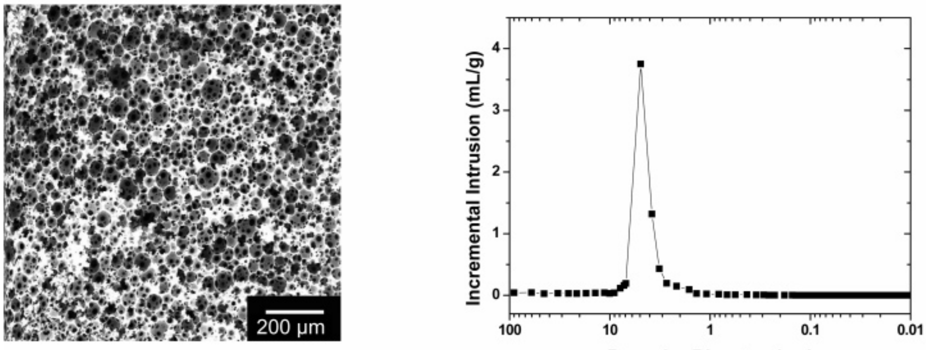
(a) PAM-2



(b) PAM-3



(c) PAM-4



(d) PAM-6

Figure 6. Variation in sample morphology for C/W emulsion-templated polyacrylamide materials synthesized using varying conditions as characterized by electron microscopy (left), and mercury intrusion porosimetry (right). Preparation conditions listed in Table 7.

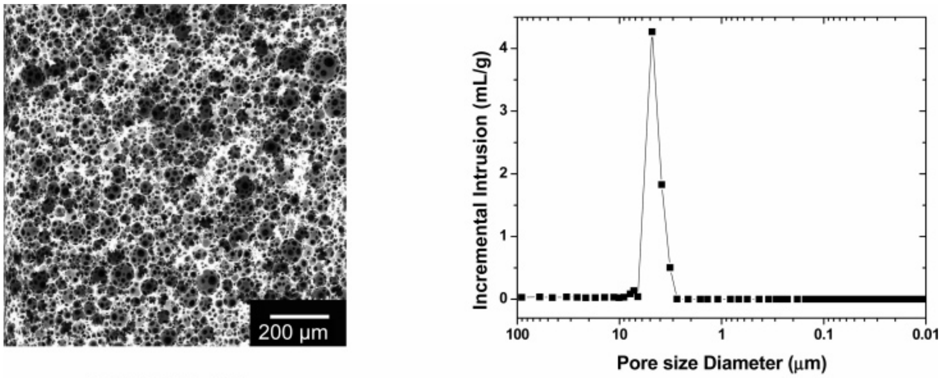
several seconds to several hours in the absence of stirring. Some degree of settling usually occurred after extended periods (i.e., more than 48 h).

Johnston and co-workers reported the stability of concentrated C/W emulsions that were prepared by using amphiphiles containing alkylene oxide-, siloxane-, and fluorocarbon-based tails as a function of temperature and salinity.[47] Poly(ethylene oxide)-*b*-poly(butylene oxide) (EO_{15}-*b*-BO_{12}) was found to emulsify up to 70% CO_2 with droplet sizes from 2 to 4 μm in diameter, as determined by video-enhanced microscopy.[47] In comparison with EO_{15}-*b*-BO_{12}, the results in Table 6 indicate the remarkable emulsification properties of these PVAc-based surfactants. An OVAc-*b*-PEG-*b*-OVAc triblock surfactant (type **2**, $m \sim 60$, $n \sim 30$) was found to emulsify up to 97% v/v CO_2 in water and to form a uniform, opaque emulsion which was stable for at least 48 h (see Figure 4b). By increasing the OVAc

Table 7. Synthesis of C/W Emulsion-Templated Polymers Using OVAc-Based Surfactants[a]

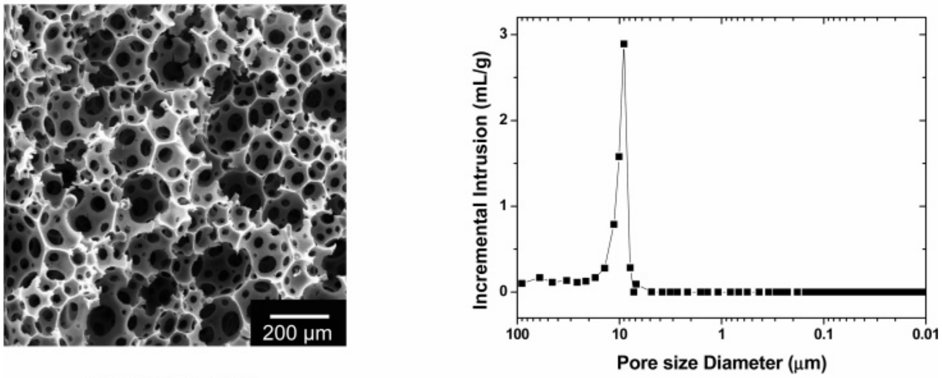
	stabilizer	CO_2/H_2O (v/v)	median pore diameter (μm)[b]	total intrusion vol (cm^3/g)[b]	bulk density (g/cm^3)[b]	drying method
PAM-1[c]	OVAc(1070)-*b*-PEG(2000)	8:2				air
PAM-2	OVAc(1070)-*b*-PEG(2000)	8:2	9.46	2.15	0.32	air
			4.18	2.58	0.30	air
PAM-3	OVAc(2650)-*b*-PEG(2000)-*b*-OVAc(2650)	8:2				
			5.37	7.98	0.06	freeze
			6.95	4.12	0.14	air
PAM-4	OVAc(1070)-*b*-PEG(2000)	9:1				
			10.85	8.68	0.06	freeze
PAM-5	OVAc(2110)-*b*-PEG(2000)-*b*-OVAc(2110)	9:1	12.50	7.50	0.07	freeze
PAM-6	OVAc(2110)-*b*-PEG(2000)-*b*-OVAc(2110	8:2	5.55	7.51	0.09	freeze

[a] Reaction conditions: AM + MBAM (40% w/v in H_2O, AM/MBAM) 8:2 w/w), $(NH_4)_2S_2O_8$ (2% w/v), 0.1 g of surfactant, PVA ($M_w \sim$ 10 000 g/mol, 80% hydrolyzed), 25 °C, 100 bar, and 10 h. [b] Measured by mercury intrusion porosimetry over the range 7 nm to 100 μm. [c] No PVA added.



PAM-3F (×300)

PAM-3F



PAM-4F (×300)

PAM-4F

Figure 7. Sample morphology for C/W emulsion-templated polyacrylamide materials dried using freeze drying method as characterized by electron microscopy (left), and mercury intrusion porosimetry (right). Preparation conditions are listed in Table 7.

solubility by using a shorter OVAc block, one could form stable emulsions formed at pressures lower than 70 bar.

For emulsions prepared in high pressure autoclaves it is not always trivial to judge the emulsion type (W/C or C/W). By using electric conductivity methods,[48] we confirmed that these systems were indeed C/W emulsions (see Supporting Information). In fact, it is difficult to prepare W/C emulsion by using OVAc surfactants of this type since the materials tend to partition into the water phase.

These results suggested that the systems are promising for emulsion templating approaches because the free-radical polymerization chemistry would be expected to occur before the emulsion became destabilized. Previous studies[23,24] have shown that the presence of organic monomers such as acrylamide tends to have a destabilizing effect on C/W emulsions: as such, very efficient surfactants are a requirement.

We also showed that more conventional O/W emulsions could be prepared using these block copolymer surfactants. For example, 0.03 g of OVAc(1070)-*b*-PEG(2000) was used as a surfactant to prepare an emulsion of hexane (0.6 mL) and H_2O (3.0 mL). After 60 s stirring at 300 rpm, a stable emulsion was formed. The emulsion type was verified by optical microscopy and hexane droplets with a size of about 1−10 μm (see Figure 4a) were observed. We also determined critical micelle concentration (cmc) of this surfactant and found that OVAc(2010)-*b*-PEG(2000)-*b*-OVAc(2010) had a lower cmc (0.023 mM) than that of OVAc(2650)-*b*-PEG(2000) (0.047 mM) in pure deionized water.

Polymerization of C/W Emulsions. Although our C/W templating procedure completely eliminates organic solvent residues in the resulting porous materials, the examples provided so far[23,24,28] have involved the use of a highly fluorinated PFPE surfactant. In order to find a viable replacement for these fluorinated surfactants, several commercial hydrocarbon materials were screened as stabilizers to prepare C/W emulsions.[24] Although it was possible to produce C/W emulsion-templated

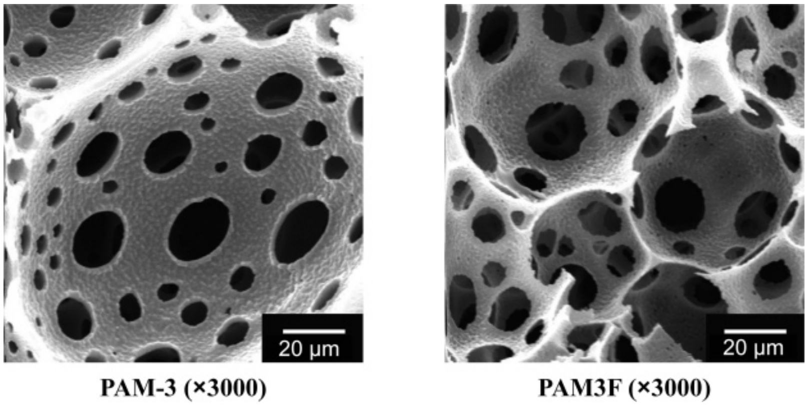


Figure 8. Sample morphology for C/W emulsion-templated polyacrylamide materials dried using air drying (left) and freeze drying (right).

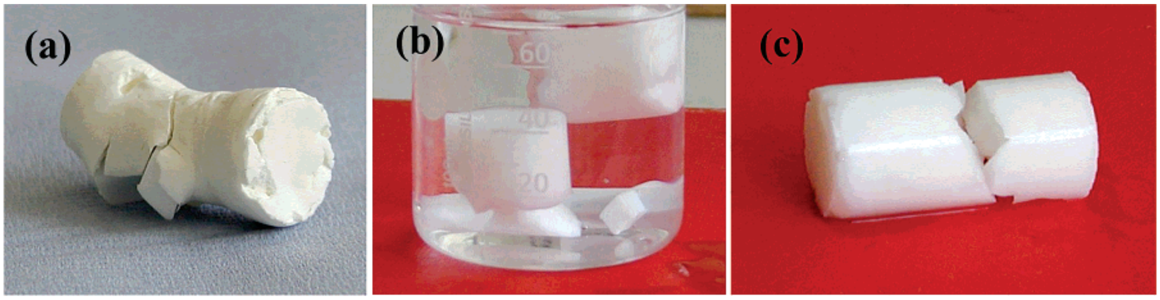


Figure 9. Shape memory effect in C/W emulsion-templated polyacrylamide materials: (a) dried sample; (b) sample upon addition to water; (c) hydrated material with recovery of original shape.

structures using a range of commercial ionic and nonionic hydrocarbon surfactants, the structures were in general less porous and less well-defined than when a PFPE surfactant was used.[24]

In this study, we employed diblock and triblock OVAc surfactants in a similar procedure. We used a catalytic amount of a redox co-initiator, tetramethylethylenediamine (TMEDA),[24,49,50] to initiate the polymerizations at a reaction temperature of 20 °C. It was therefore possible to carry out the reactions using liquid CO_2 at much lower reaction pressures. In general, the materials produced using redox initiation gave rise to materials that were at least as porous (and often more porous) than the equivalent samples produced using thermal initiation at 60 °C.

The remarkable stability of the C/W emulsions was further demonstrated by polymerization of the continuous aqueous phase to give porous, cross-linked poly(acrylamide) (PAM) materials, as produced previously from C/W emulsions stabilized with perfluoropolyether (PFPE) ammonium carboxylate surfactants.[23,24] Both OVAc-*b*-PEG diblock and OVAc-*b*-PEG-*b*-OVAc surfactants formed stable milky emulsions with these monomers present. In comparison with the equivalent pure water system, the stability of the emulsions appeared to be similar.

The emulsion-templated polymers were recovered as uniform monolith with a smooth, defect-free surface which conformed to the cylindrical interior of the reaction vessel (Figure 6). Table 7 summarizes the porous properties of emulsion-templated polymers synthesized using OVAc−PEG surfactants under a variety of conditions. The presence of PVA played an important role in the emulsion templating process, as reported previously.[24]

The precise pore volume did not depend very strongly on the particular OVAc surfactant that was used but was dependent on the CO_2/H_2O ratio. For example, PAM-4 was stabilized by a diblock copolymer and PAM-5 was stabilized by a triblock copolymer, both at a C/W ratio of 9:1. The two materials had pore volumes of 8.68 and 7.50 cm^3/g, respectively, suggesting that the diblock copolymer was a somewhat more effective surfactant. By contrast, PAM-4 (C/W = 9:1) had a pore volume which was almost twice that of PAM-2 (C/W = 8:2).

The highest pore volume (8.68 cm^3/g) and the lowest bulk density (0.06 g/cm^3) arose in PAM-4 which was prepared using 1% w/v OVAc(1070)-*b*-PEG(2000). The median pore diameter in this material was found to be 10.85 μm. This material was more porous than any produced using PFPE surfactants[24]—indeed, it was not possible to generate stable 90% v/v C/W emulsions using PFPE in the presence of the acrylamide monomer.

Similar results were obtained with water-soluble OVAc-*b*-PEG-*b*-OVAc triblocks. This suggests that OVAc-based diblock and triblock surfactants are functionally superior to perfluorinated materials for this application, in addition to being potentially less expensive and biodegradable.

Figure 7 shows an electron micrograph of such a material formed from a 90% v/v C/W emulsion stabilized using an OVAc-*b*-PEG diblock copolymer surfactant, **2**. The structure demonstrates unambiguously that the emulsion was C/W as opposed to W/C.

From SEM images, it was apparent that the triblock polymer formed smaller macropores than the diblock stabilizer. PAM-3 and PAM-6, which used triblock copolymers as stabilizers, had smaller pore sizes and mercury porosimetry showed monomodal pore size distributions. PAM-2 and PAM-4 exhibited larger macropores. In our previous study, we found that C/W emulsion droplets were not monodisperse, as evident from the distribution of cell sizes observed in the electron micrographs.[24] The material shown in Figure 6d is significantly more homogeneous and it follows that more stable, monodisperse C/W emulsions were formed by using triblock OVAc(2110)-*b*-PEG-*b*-OVAc(2110).

Effect of Drying Method on Pore Structure. For the emulsion-templated PAM samples, two drying methods were investigated: air drying and freeze drying. For the freeze drying method, the monolith was recovered from the reaction cell and immersed in liquid nitrogen before freeze drying. Results showed that the freeze drying method led to increased pore sizes and pore volumes. After freeze drying, the monolith retained its original shape; only its size was reduced. By contrast, for samples which were dried in air, the overall shrinkage of the monolith was more noticeable. At the same time, lower pore volumes and the higher densities were obtained. This tendency can also be observed by SEM imaging (Figure 6−8).

It was found that these porous polymers exhibited a shape memory effect. After drying, shrinkage occurred (Figure 9a) and the monolith lost its original shape. When the monolith was placed into water, its shape recovered completely in a few seconds (Figure 9b) and the monolith diameter returned to its original size (Figure 9c). This kind of property may be useful for cell culture scaffolds and tissue engineering applications.

Conclusions

In conclusion, we present here a simple and generic method for producing inexpensive and biodegradable polymer surfactants for the generation of C/W emulsions. The synthetic methodology also allows fine-tuning of the hydrophilic-CO_2-philic balance to suit different applications. We have shown that these surfactants can out-perform perfluorinated analogs in the preparation of C/W emulsions and in emulsion-templated polymer synthesis.[23,24] Surfactants of this type may find a range of additional uses in emulsion technology, particularly where biodegradability of the hydrophobic segment is required.

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Supporting Information Available: Figures showing ^{1}H NMR, details of extraction equipment, GPC data, phase behavior data, and surface tension data and a table of molecular weight data. This material is available free of charge via the Internet at http://pubs.acs.org.

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