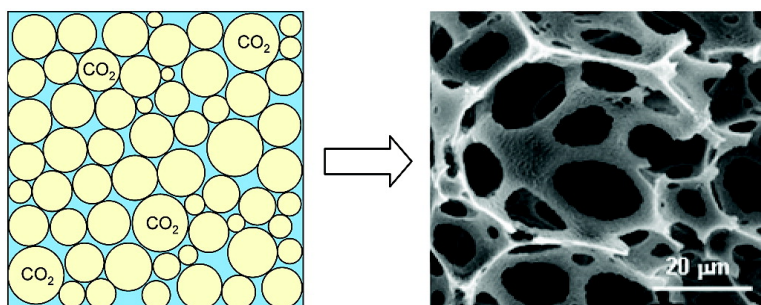


## Synthesis of Porous Emulsion-Templated Polymers Using High Internal Phase CO<sub>2</sub>-in-Water Emulsions

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## Synthesis of Porous Emulsion-Templated Polymers Using High Internal Phase CO<sub>2</sub>-in-Water Emulsions

R. Butler,<sup>†</sup> I. Hopkinson,<sup>§</sup> and A. I. Cooper\*<sup>†</sup>

Contribution from the Donnan and Robert Robinson Laboratories, Department of Chemistry, University of Liverpool, Crown Street, Liverpool L69 3BX, United Kingdom, and Department of Physics, UMIST, PO Box 88, Manchester, M60 1QD, United Kingdom

Received July 28, 2003; E-mail: aicooper@liv.ac.uk

**Abstract:** Highly porous emulsion-templated materials were synthesized by polymerization of concentrated CO<sub>2</sub>-in-water (C/W) emulsions. The method does not use any organic solvents, in either the synthesis or purification steps, and no solvent residues are left in the materials. It was found that the emulsion stability is strongly affected both by the nature of the surfactant and by the viscosity of the aqueous continuous phase. By optimizing these parameters, it was possible to generate a highly porous, low-density polyacrylamide material with a pore volume of 5.22 cm<sup>3</sup>/g, an average pore diameter of 9.72 μm, and a bulk density of 0.14 g/cm<sup>3</sup>. We have broadened the scope of this approach significantly by identifying inexpensive hydrocarbon surfactants to stabilize the C/W emulsions (e.g., Tween 40) and by developing redox initiation routes that allow the synthesis to be carried out at modest temperatures and pressures (20 °C, 65 bar). We have also extended the method to the polymerization of monomers such as hydroxyethyl acrylate, which suggests that it is possible to prepare a range of solvent-free biomaterials by this route.

### Introduction

Emulsion templating is a versatile method for the preparation of highly porous organic polymers,<sup>1–4</sup> inorganic materials,<sup>5–9</sup> and inorganic–organic composites.<sup>10</sup> 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 provides a direct synthetic route to a variety of 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.<sup>5–9</sup> 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. Recently, we developed new methods for the preparation of monodisperse, emulsion-templated cross-linked polyacrylamide (PAM)<sup>11</sup> and silica<sup>12</sup> beads by “oil-in-water-in-oil (O/W/O) sedimentation polymerization”. While it is somewhat easier to remove the internal phase from these beaded products than from monoliths, O/W/O methods still use significant volumes of oil and organic solvent, both for the material synthesis and in purification of the products.<sup>11,12</sup>

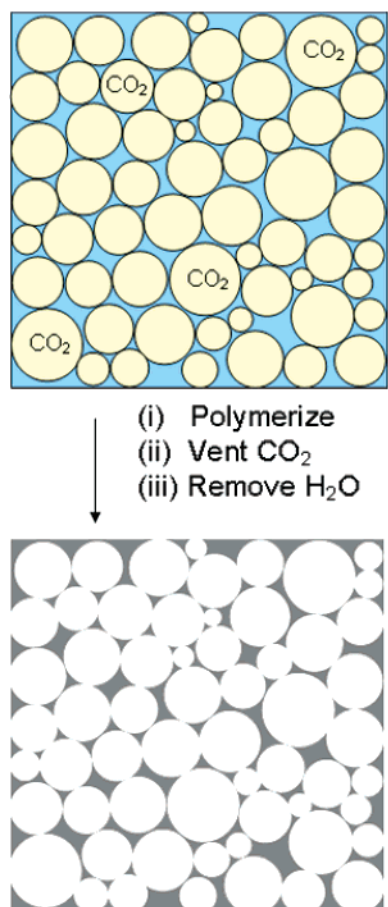
Supercritical carbon dioxide (scCO<sub>2</sub>) has been promoted recently as a sustainable solvent because it is nontoxic, nonflammable, and naturally abundant.<sup>13</sup> In particular, scCO<sub>2</sub> has been shown to be a versatile solvent for polymer synthesis and processing.<sup>14–16</sup> Carbon dioxide has been exploited quite widely for the preparation of porous materials:<sup>17</sup> for example,

<sup>†</sup> University of Liverpool.

<sup>§</sup> UMIST.

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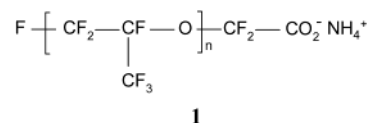


**Figure 1.** Schematic representation of the C/W emulsion templating process. Materials are formed by polymerization occurring in the aqueous, continuous phase.

scCO<sub>2</sub> has been used for the production of microcellular polymer foams,<sup>18,19</sup> biodegradable composite materials,<sup>20</sup> macroporous polyacrylates,<sup>21–23</sup> and fluorinated microcellular materials.<sup>24</sup>

We recently developed a new approach to the synthesis of porous materials which involves the polymerization of high internal phase CO<sub>2</sub>-in-water emulsions (C/W HIPEs).<sup>25</sup> The basic procedure is summarized in Figure 1. 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<sub>2</sub>. Removal of the droplet phase is simple because the CO<sub>2</sub> 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 bisacrylamide (MBAM). We employed a perfluoropolyether (PFPE) ammonium carboxylate surfactant (**1**) since it is known that this surfactant can form both W/C and C/W

macroemulsions<sup>26</sup> and microemulsions<sup>27,28</sup> and that the macroemulsions<sup>26</sup> can exhibit kinetic stability.



We showed that the C/W emulsions could be kinetically stabilized by the addition of poly(vinyl alcohol) (PVA) to the aqueous phase before polymerization (10% w/v relative to H<sub>2</sub>O). In the presence of PVA, open-cell, porous materials were produced which conformed closely to the interior of the reaction vessel.<sup>25</sup>

Our new method allows the formation of highly porous, C/W emulsion-templated hydrophilic polymers without the use of any organic solvents. However, there are four key limitations associated with our initial approach,<sup>25</sup> particularly with respect to the potential for synthesizing biomaterials. First, the method involves a fluorinated surfactant, **1**, that is expensive and nonbiodegradable. Second, acrylamide is toxic, and PAM materials are not in general biocompatible. Third, the method involves high pressures (>300 bar), which contribute to energy consumption and increase the capital equipment costs. Finally, the polymerization is initiated by thermal methods (50–60 °C); in general, elevated temperatures would not be desirable for the incorporation of thermally sensitive biological species such as proteins or enzymes.<sup>20</sup>

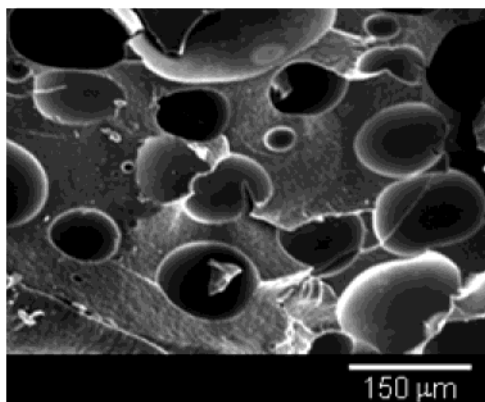
In this study, we investigate the factors affecting the C/W emulsion stability in more detail, and then utilize the more stable emulsions to generate materials with significantly increased levels of porosity. We also present a solution to each of the problems outlined above and show that it is possible to synthesize C/W emulsion-templated materials by redox initiation at much lower temperatures and pressures (20 °C, < 70 bar) from monomers other than acrylamide using inexpensive hydrocarbon surfactants such as Tween 40.

## Results and Discussion

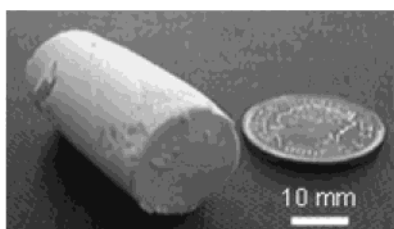
**Formation of Stable C/W Emulsions.** Low molecular weight (<600 g/mol) PFPE ammonium carboxylate surfactants such as **1** are substantially water-soluble and are known to form concentrated, kinetically stable C/W macroemulsions.<sup>26</sup> However, we have shown that these C/W emulsions were strongly destabilized by the addition of monomers such as AM and MBAM.<sup>25</sup> In the absence of stirring, rapid phase separation occurs over a period of a few minutes leading to two distinct phases: an upper, transparent phase (CO<sub>2</sub>) and a milky-white lower phase (H<sub>2</sub>O with a small amount of emulsified CO<sub>2</sub>). This instability becomes even more pronounced as the mixture is heated to 60°C, and materials formed by free-radical polymerization of these partial emulsions occupy somewhat less than 50% of the reactor volume, suggesting that only a small quantity of CO<sub>2</sub> has been “templated”. Electron microscopy confirms that the emulsion-templated “cells” are isolated and exclusively

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**Figure 2.** Electron micrograph of a cross-linked polyacrylamide material formed by polymerization of a C/W emulsion (surfactant **1**) in the absence of poly(vinyl alcohol). The resulting emulsion is unstable and only a small amount of CO<sub>2</sub> is emulsified, leading to isolated, closed-cell pores in the material.



**Figure 3.** Photograph of a low-density, C/W emulsion-templated polyacrylamide (Sample 4) prepared using 2% w/v PVA (10 000 g/mol) as a costabilizer. The material conforms to the cylindrical interior of the reaction vessel.

closed-cell in nature (Figure 2). Mercury intrusion porosimetry analysis shows that the degree of porosity is low (0.2–0.5 cm<sup>3</sup>/g), although this may be an underestimate due to the exclusively closed-cell nature of the material.

It is possible that the monomers act as de-emulsifiers by adsorbing at the water–CO<sub>2</sub> interface, thus reducing interfacial tension gradients and, hence, droplet stability.<sup>26</sup> Another possibility is that the monomers affect the solution properties of the surfactant in the aqueous phase, that is, the surfactant becomes more soluble in the aqueous phase and is shifted away from the C/W interface. We have found that this destabilization can be counteracted by the addition of PVA to the aqueous phase prior to polymerization (10% w/v relative to H<sub>2</sub>O).<sup>25</sup> In the presence of PVA, the emulsions are sufficiently stable for templating to occur and for open-cell porous materials to be produced. The materials conform closely to the interior of the reaction vessel and no significant shrinkage is observed upon venting the CO<sub>2</sub> (Figure 3).

Our tentative explanation<sup>25</sup> for this large increase in emulsion stability is that PVA causes an increase in the interfacial viscosity and the monolayer bending elasticity, thus inhibiting tangential interfacial flow in the thin aqueous film between the CO<sub>2</sub> droplets.<sup>26,29</sup> Previously, Ruckenstein has shown that an increase in the viscosity of the aqueous phase appears to enhance the stability of concentrated *n*-butyl methacrylate emulsions in water, using methyl cellulose as a water-soluble viscosity modifier.<sup>2</sup>

To test this hypothesis further, we have investigated the effect of both PVA concentration and PVA molecular weight on the structure of the emulsion-templated materials.

**Table 1.** Effect of PVA Concentration and  $M_w$  on Porous Properties of C/W Emulsion-Templated Polymers<sup>a</sup>

	PVA (w/v)	PVA $M_w$ (g/mol)	$V_{\text{pore}}$ (cm <sup>3</sup> /g) <sup>b</sup>	median pore diam (μm) <sup>b</sup>	av cell size (μm) <sup>c</sup>	bulk density (g/cm <sup>3</sup> ) <sup>b</sup>
1	0.1	10 000	2.85	8.1	25.0	0.17
2	0.5	10 000	3.49	10.9	25.9	0.18
3	1	10 000	3.69	9.5	24.2	0.23
4	2	10 000	4.37	5.5	20.9	0.18
5	5	10 000	3.40	4.3	13.6	0.23
6	7	10 000	3.52	4.7	13.8	0.20
7	10	10 000	3.23	7.8	12.1	0.24
8	20	10 000	2.90	11.7	23.5	0.25
9	1	16 000	4.68	10.7	17.2	0.18
10	1	22 000	3.52	5.6	14.2	0.23
11	1	40 000	3.62	6.9	17.2	0.16
12	1	88 000	3.58	4.3	13.7	0.21
13	1	95 000	1.18	5.2	66.8	0.55
14 <sup>d</sup>	2	10 000	5.22	9.72	32.0	0.14

<sup>a</sup> Reaction conditions: AM + MBAM (40% w/v in H<sub>2</sub>O, AM/MBAM = 8:2 w/w), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2% w/v), CO<sub>2</sub>/H<sub>2</sub>O = 8:2 v/v, 1% w/v surfactant **1**, PVA ( $M_w$  = 10 000 g/mol, 80% hydrolyzed), 60 °C, 250–290 bar, 12 h.<sup>b</sup> Measured by mercury intrusion porosimetry over the range 7 nm–100 μm. <sup>c</sup> Calculated from confocal microscope images. <sup>d</sup> 1.3% w/v surfactant **1**.

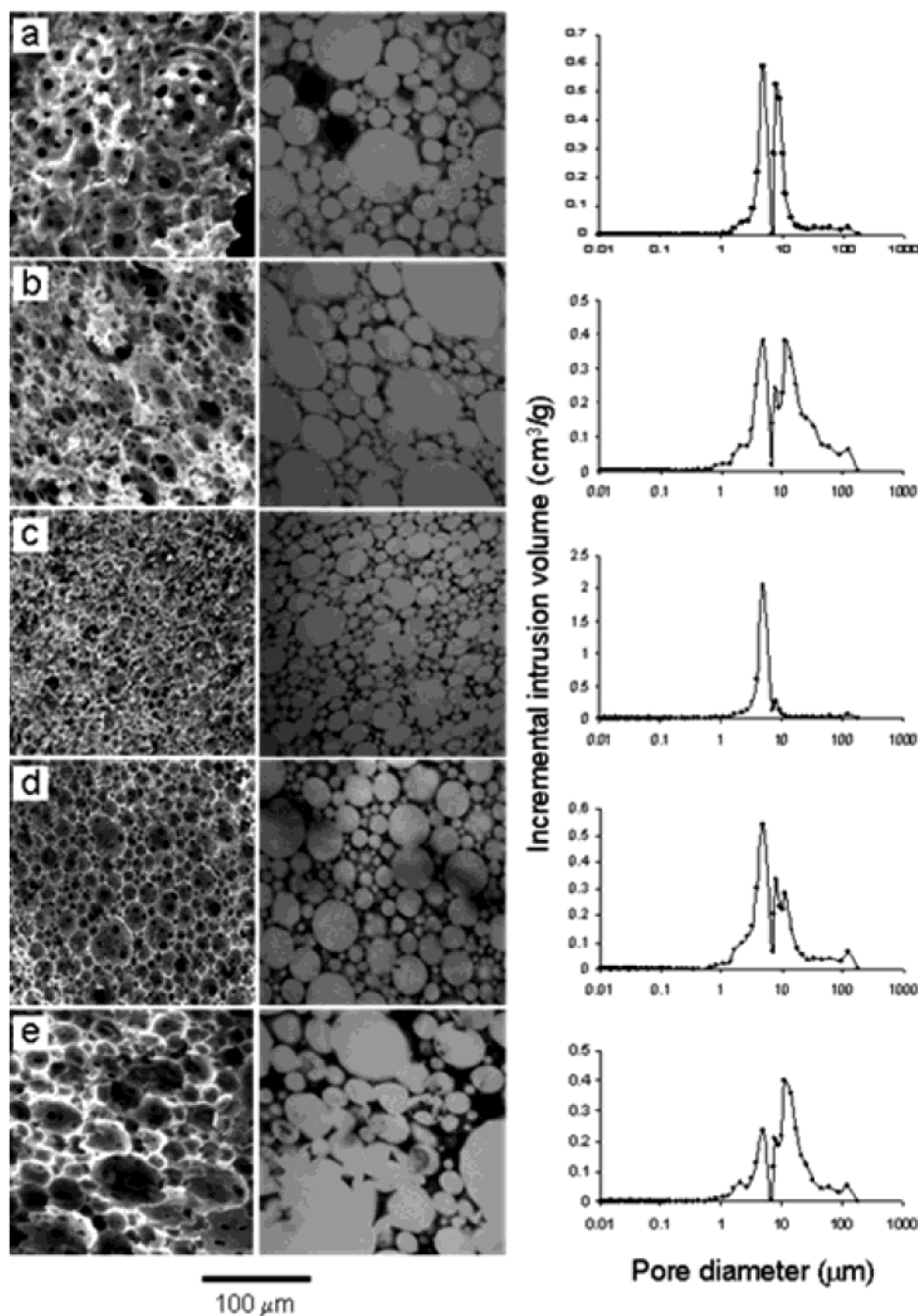
**Effect of PVA Concentration.** A series of emulsion-templated, cross-linked PAM materials was synthesized over a wide range of PVA concentrations (0.1–20% w/v based on the aqueous phase). All other variables such as monomer concentration, initiator concentration, concentration of surfactant **1**, CO<sub>2</sub> volume, CO<sub>2</sub> pressure, stirring speed, and temperature were kept constant. The weight-average molecular weight of the PVA sample,  $M_w$ , was 10 000 g/mol (80% hydrolyzed). The results of these experiments are summarized in Table 1 (samples 1–8). In all cases, uniform, white C/W emulsions were observed that filled the entire reaction vessel and were sufficiently stable to form emulsion-templated polymers which conformed to the internal dimensions of the reaction vessel. This was true even at the lowest PVA concentration (0.1% w/v), although previous studies have shown that stable emulsions were *not* formed under these conditions in the absence of PVA (see Figure 2).<sup>25</sup> Figure 4 shows a series of electron micrographs, confocal micrographs, and mercury intrusion porosimetry plots for PAM materials synthesized at increasing PVA concentrations. The effect of PVA concentration on the intrusion volume (i.e., pore volume), the average cell diameter, and the median pore diameter is summarized in Figure 5. The average cell diameter was measured from a number of confocal images, and we infer that this corresponds, approximately, to the average diameter of the CO<sub>2</sub> emulsion droplets immediately prior to chemical gelation of the system.<sup>30</sup> The median pore diameter was measured by mercury intrusion porosimetry and corresponds to the average size of the pores that connect the emulsion-templated cells. It should be noted that the discontinuity that can be observed at around 7.5 μm in many of the porosimetry plots (e.g., Figure 4a) is an artifact that arises from switching the analysis from the lower-pressure port (large pores) to the high-pressure port (small pores).

The total pore volume in these materials showed a maximum of approximately 4.4 cm<sup>3</sup>/g at a PVA concentration of around 2% w/v (Figure 5a). A sharp increase in pore volume was observed when the PVA concentration was raised from 0.1%

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(30) Not allowing for any shrinkage in the materials during drying.





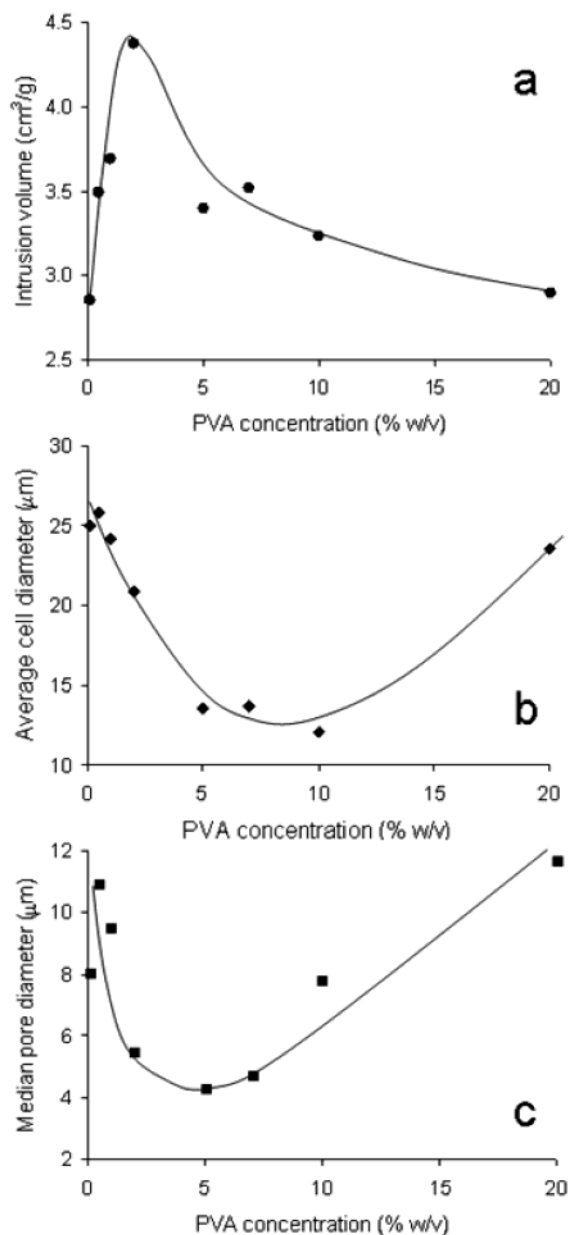
**Figure 4.** Variation in sample morphology for C/W emulsion-templated polyacrylamide materials synthesized using varying concentrations of PVA ( $M_w = 10\,000$  g/mol) as characterized by electron microscopy (left), confocal scanning microscopy (center), and mercury intrusion porosimetry (right). (a) Sample 1, 0.1% w/v PVA. (b) Sample 2, 0.5% w/v PVA. (c) Sample 4, 2.0% w/v PVA. (d) Sample 7, 10% w/v PVA. (e) Sample 8, 20% w/v PVA.

w/v to 2% w/v, while materials synthesized at higher PVA concentrations (5–20% w/v) showed a decreasing trend in pore volume.

The average cell diameter in the materials showed a minimum of approximately  $12\ \mu\text{m}$  at a PVA concentration of around 8% w/v (Figure 5b). The marked decrease in the average cell size over the PVA concentration range 0.1–2% w/v can be observed clearly by comparison of the electron micrographs and confocal micrographs in Figure 4a–c. The sample produced using 20% w/v PVA exhibited a significantly larger average cell diameter, as shown in Figure 4e.

It is common for emulsion-templated polymers to show a relationship between the average cell size and the average pore

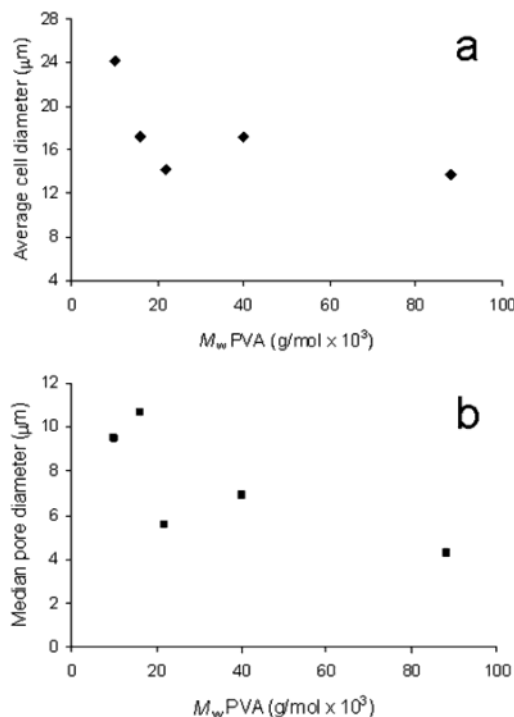
size: typically, the average pore size is of the order of 10–50% of the average cell diameter.<sup>1</sup> This series of materials follows that trend, and the plot of median pore diameter versus PVA concentration (Figure 5c) exhibits a similar shape to the equivalent plot of average cell diameter (Figure 5b), although the minimum in median pore diameter occurs at a slightly lower PVA concentration ( $\sim 5\%$  w/v). In general, the average pore diameter was found to be in the range 30–45% of the average cell diameter for this series of materials. The median pore diameter varies more abruptly than the average cell diameter over the PVA concentration range 0.1–2% w/v. This may reflect the fact that the pores in materials of this type are believed to form by “tearing” of the thin interfacial film during the



**Figure 5.** Variation in polymer properties for C/W emulsion-templated polyacrylamide materials (samples 1–8) synthesized using varying concentrations of PVA ( $M_w = 10\,000$  g/mol). (a) Intrusion volume (i.e., pore volume) as characterized by mercury intrusion porosimetry ( $\text{cm}^3/\text{g}$ ). (b) Average cell diameter ( $\mu\text{m}$ ), as measured from confocal scanning micrographs. (c) Median pore diameter ( $\mu\text{m}$ ), as characterized by mercury intrusion porosimetry.

volumetric contraction that accompanies polymerization.<sup>1</sup> As such, one might expect that size of the pore “windows” could be strongly affected by the viscosity of the aqueous phase.

The above observations are consistent with the emulsions being stabilized by an increase in the aqueous solution viscosity which inhibits tangential interfacial flow. The average cell size (and, inferentially, the average  $\text{CO}_2$  emulsion droplet size) becomes significantly smaller over the PVA concentration range 0.1–2% w/v. The cell size distribution also becomes narrower (Figure 4a–c) over this concentration range. We propose a mechanism whereby small  $\text{CO}_2$  droplets (approximately 10–15  $\mu\text{m}$ ) are formed during shear. These droplets are then mostly “locked” into the form of templated cells in materials produced from the more stable emulsions (i.e., PVA concentration  $\sim 2\%$



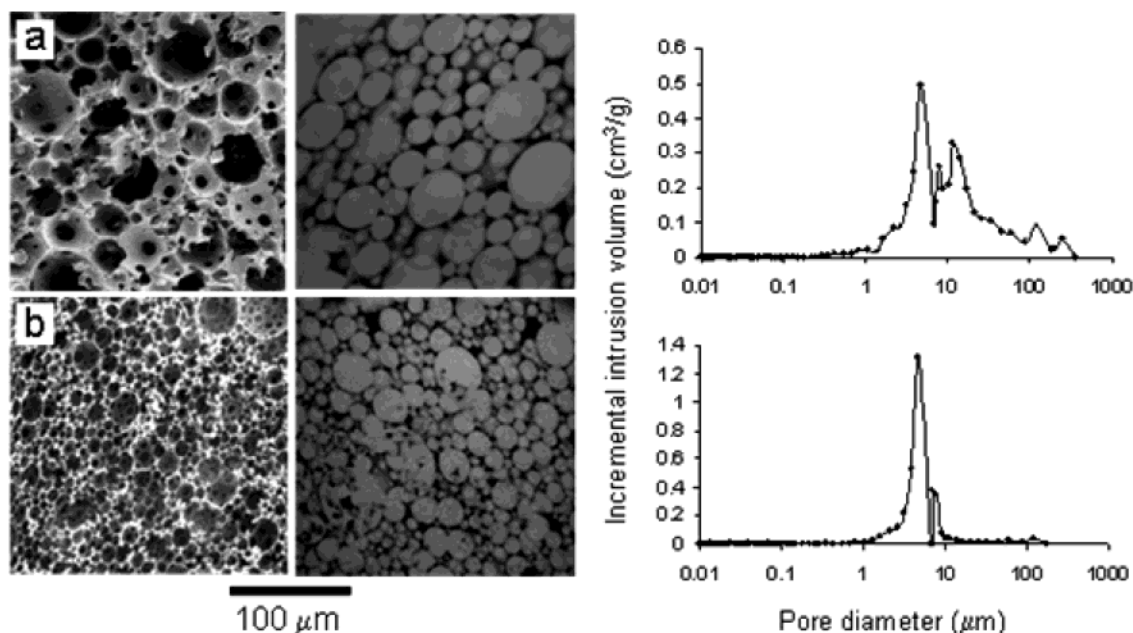
**Figure 6.** Variation in polymer properties for C/W emulsion-templated polyacrylamide materials (samples 3, 9–13) synthesized using PVA (1% w/v) with varying molecular weights. (a) Average cell diameter ( $\mu\text{m}$ ), as measured from confocal scanning micrographs. (b) Median pore diameter ( $\mu\text{m}$ ), as characterized by electron microscopy.

w/v). By contrast, the emulsions formed at lower PVA concentrations (0.1–1% w/v) are less stable, and the average  $\text{CO}_2$  droplet size increases due to partial droplet coalescence. The  $\text{CO}_2$  droplet size distribution is also broadened, and both effects are reflected in the distribution of cell sizes in the materials (see Figure 4a–c).

We rationalize the significant increase in average cell diameter and pore diameter at higher PVA concentrations (20% w/v) by the fact that the aqueous phase becomes so viscous that it is difficult to form smaller emulsions droplets, particularly given the limited shear (magnetic stir bar) that is applied to the system (see Figure 5e). Ruckenstein has reported similar viscosity effects for *n*-butyl methacrylate emulsions in water using high concentrations of methyl cellulose as the water-soluble “thickener”.<sup>2</sup>

**Effect of PVA Molecular Weight.** If the above arguments are correct, then the PVA molecular weight should also affect the structure of the materials at a constant PVA concentration, since polymer solution viscosity is strongly dependent on molecular weight. A series of emulsion-templated materials was synthesized at a PVA concentration of 1% w/v with a range of PVA molecular weights ( $M_w = 10\,000$ – $95\,000$  g/mol; Table 1, samples 3 and 9–13). For PVA molecular weights in the range 10 000–88 000 g/mol (samples 3 and 9–12), both the average cell diameter and the median pore diameter were observed to decrease with increasing  $M_w$  (Figure 6).<sup>31</sup> This is again consistent with an increase in viscosity stabilizing the C/W emulsion and leading to smaller, more kinetically stable  $\text{CO}_2$  emulsion droplets which are then translated into smaller cells

(31) The scatter in these data might be explained in part by the fact that these PVA samples had differing degrees of hydrolysis (see Supporting Information).



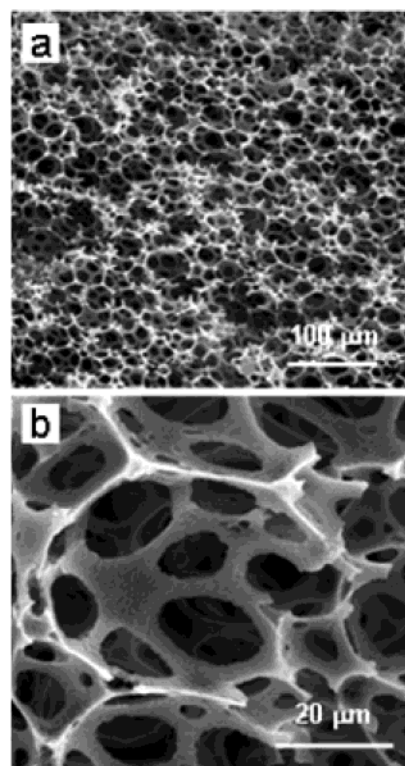
**Figure 7.** Effect of PVA molecular weight on sample morphology for C/W emulsion-templated polyacrylamide materials as characterized by electron microscopy (left), confocal scanning microscopy (center), and mercury intrusion porosimetry (right). (a) Sample 3, PVA = 10 000 g/mol. (b) Sample 11, PVA = 40 000 g/mol.

and pores in the cross-linked PAM material. Figure 7 compares the structures of samples 3 and 11, prepared using 1% w/v 10 000 g/mol PVA and 1% w/v 40 000 g/mol PVA, respectively. It is clear that sample 11, prepared using the higher  $M_w$  PVA, exhibits smaller cells and a narrower pore size distribution than the sample prepared using the lower  $M_w$  PVA (sample 3). The total pore volumes for these two samples, however, are similar (3.69 vs 3.62 g/cm<sup>3</sup>); this suggests that partial droplet coalescence affects the cell size and pore size distribution in these materials, but does not proceed to the formation of two separate phases, thus compromising the total pore volume or reducing the pore connectivity.

Sample 13 (not plotted in Figure 6) does not fit with the above trend. In this experiment, it was observed that the two phases (water and CO<sub>2</sub>) did not fully emulsify on stirring, most likely because the viscosity of the aqueous phase was too high to allow mixing under modest shear.<sup>2</sup> As a result, a relatively high bulk-density material (0.55 g/cm<sup>3</sup>) was obtained with a much lower pore volume (1.18 g/cm<sup>3</sup>) than observed for samples 1–12.

In summary, these results support our hypothesis that the C/W emulsions are kinetically stabilized against coalescence primarily by an increase in the aqueous phase viscosity. The effect of PVA molecular weight at constant PVA concentration fits this interpretation, although this does not preclude the possibility that a change in the interfacial tension also plays a role in stabilizing the emulsions (i.e., the PVA acts as “cosurfactant”). At higher PVA concentrations (>20% w/v, 10 000 g/mol) or at high molecular weights ( $M_w > 95\,000$  g/mol, 1% w/v), the increase in viscosity has a negative effect and prevents full emulsification of the two phases, at least when relatively low-shear mixing (i.e., a magnetic stir bar) is employed.

**Low-Density C/W Emulsion-Templated PAM Materials.** Having investigated the factors affecting the emulsion-templated pore morphology, we attempted to maximize the pore volume in the materials. Figure 8 shows two electron micrographs for a cross-linked PAM material (sample 14) produced under



**Figure 8.** Low-density polyacrylamide material synthesized by C/W emulsion templating under “optimized” conditions (sample 14, surfactant **1** = 1.3% w/v; PVA = 2% w/v, 10 000 g/mol). Pore volume = 5.22 cm<sup>3</sup>/g; bulk density = 0.142 g/cm<sup>3</sup>; average pore diameter = 9.72 μm.

“optimized” conditions (surfactant **1** = 1.3% w/v; PVA = 2% w/v, 10 000 g/mol). The pore structure for this sample is highly interconnected, and the pore volume was found to be 5.22 cm<sup>3</sup>/g (bulk density = 0.142 g/cm<sup>3</sup>; average pore diameter = 9.72 μm). This pore volume is comparable with that achieved in more conventional PolyHIPE materials produced from water-in-styrene/divinylbenzene HIPEs,<sup>1,32</sup> and demonstrates that our new



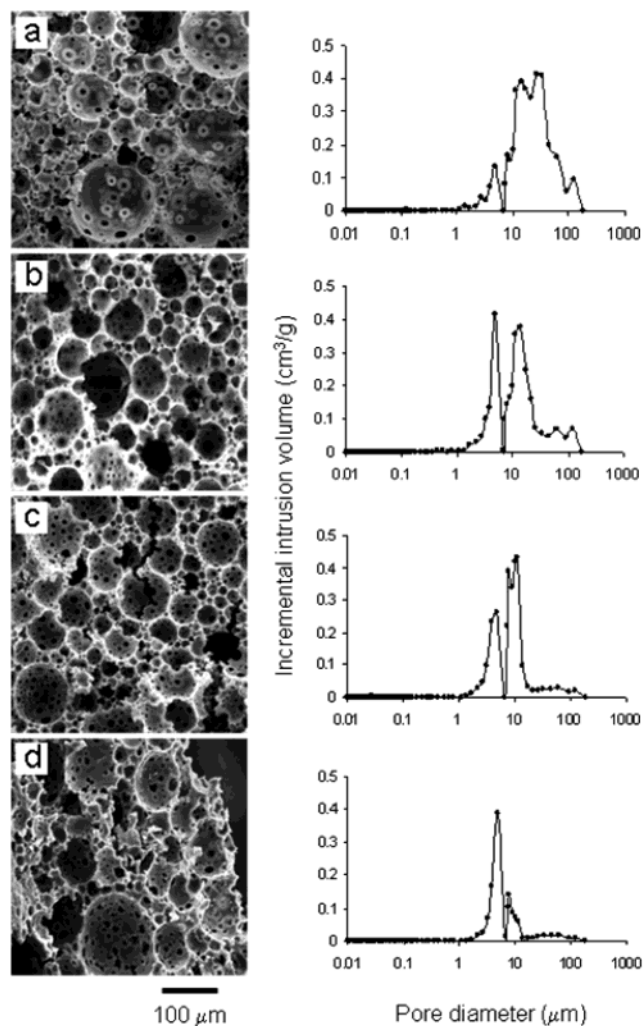
**Table 2.** Synthesis of C/W Emulsion-Templated Polymers by Using Hydrocarbon Surfactants<sup>a</sup>

	surfactant <sup>b</sup>	HLB <sup>c</sup>	$V_{\text{pore}}$ (cm <sup>3</sup> /g) <sup>d</sup>	median pore diameter ( $\mu\text{m}$ ) <sup>d</sup>	bulk density (g/cm <sup>3</sup> ) <sup>d</sup>
15	Span 40	6.7	<i>e</i>	<i>e</i>	<i>e</i>
16	PFPE (1)	8.0	5.89	10.2	0.14
17	CTAB	10.0	2.58	8.4	0.23
18	Triton X-100	13.5	1.26	6.3	0.43
19	Tween 60	14.9	1.14	18.0	0.29
20	Tween 40	15.5	2.79	9.3	0.23
21	Tween 20	16.6	2.90	11.7	0.20
22	Triton X-405	17.9	<i>e</i>	<i>e</i>	<i>e</i>
23	SDBS	36.7	3.70	19.3	0.18
24	SDS	40.0	3.37	14.6	0.20

<sup>a</sup> General reaction conditions as for Table 1, 10% w/v surfactant based on aqueous phase. <sup>b</sup> Span 40 = sorbitan monopalmitate, CTAB = cetyltrimethylammonium bromide, Triton X-100 = polyoxyethylene(10) isooctylphenyl ether, Tween 60 = polyoxyethylene(20) sorbitan monostearate, Tween 40 = polyoxyethylene(20) sorbitan monopalmitate, Tween 20 = polyoxyethylene(20) sorbitan monolaurate, Triton X-405 = polyoxyethylene(40) isooctylphenyl ether, SDBS = sodium dodecylbenzene sulfonate, and SDS = sodium dodecyl sulfonate. <sup>c</sup> Hydrophilic–lipophilic balance, taken from ref 34. <sup>d</sup> Measured by mercury intrusion porosimetry over the range 7 nm–100  $\mu\text{m}$ . <sup>e</sup> No stable emulsion formed.

SCF-based method can be used to generate highly porous structures, once the factors that affect the stability of these multicomponent emulsions are understood.

**C/W Emulsion Templating Using Hydrocarbon Surfactants.** While our new templating procedure completely eliminates organic solvent residues in the resulting porous materials, the examples provided so far have involved the use of a highly fluorinated PFPE surfactant, **1**. This species is too expensive and insufficiently degradable for many applications. Johnston and co-workers have shown recently that it is possible to form concentrated, kinetically stable C/W macroemulsions using much less expensive hydrocarbon surfactants such as poly-(ethylene oxide)-*b*-poly(butylene oxide) (EO<sub>15</sub>-*b*-BO<sub>12</sub>).<sup>33</sup> We have screened a range of ionic and nonionic hydrocarbon surfactants for the preparation of C/W emulsion-templated PAM materials, as summarized in Table 2. The surfactants are arranged in order of increasing hydrophilic–lipophilic balance (HLB) values<sup>34</sup> (i.e., *not* hydrophilic-to-CO<sub>2</sub>-philic balance, or “HCB”<sup>35</sup>). Of the surfactants tested, a number were found to form relatively stable, milky-white C/W HIPEs (CO<sub>2</sub>:H<sub>2</sub>O = 8:2 v/v) even in the presence of the acrylic monomers. In each case, PVA (2% w/v, 10 000 g/mol) was added to the aqueous phase to increase the emulsion stability. Under these conditions, it was possible to produce porous PAM materials with emulsion-templated pore structures that replicated the original C/W emulsion (Figure 9). The exact pore volume depended on the hydrocarbon surfactant that was used, with the highest pore volume (3.70 cm<sup>3</sup>/g) and the lowest bulk density (0.18 g/cm<sup>3</sup>) being attributed to the polymer prepared using 10% w/v sodium dodecylbenzene sulfonate (SDBS) (sample 23, Figure 9a). None of the hydrocarbon surfactants gave rise to pore volumes as high as that obtained for sample 16 using the PFPE surfactant, although it should be noted that these experiments were carried out under conditions that had been optimized for surfactant **1**



**Figure 9.** Polyacrylamide materials synthesized by C/W emulsion templating using hydrocarbon surfactants as characterized by electron microscopy (left) and mercury intrusion porosimetry (right). (a) Sample 23, 10% w/v SDBS. (b) Sample 21, 10% w/v Tween 20. (c) Sample 20, 10% w/v Tween 40. (d) Sample 19, 10% w/v Tween 60.

but not optimized for the hydrocarbon surfactants. No overall correlation was observed between the HLB values for the surfactants and the properties of the PAM materials, although the materials with the highest pore volumes and the lowest bulk densities (samples 23 and 24) were formed with two highly water-soluble ionic surfactants (SDBS and SDS) which had the highest HLB values (36.7 and 40.0, respectively). It was also observed that the intrusion volume increased (while the bulk density decreased) for materials synthesized using a family of Tween surfactants with increasing HLB values (samples 19–21).

These results demonstrate 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 surfactant **1**.

**C/W Emulsion Templating Using Redox Initiation.** Having tackled the issue of surfactant cost and biodegradability, we next focused on reducing both the reaction temperature and the reaction pressure. The reactions described above were carried out at 60 °C and pressures in the range 250–290 bar. In general, elevated reaction temperatures may be incompatible with the production of thermally sensitive materials or with the incor-

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**Table 3.** Synthesis of C/W Emulsion-Templated Polymers by Redox Initiation Using TMEDA as a Redox Coinitiator at 20 °C and  $P < 70$  Bar

	surfactant	surfactant (w/v)	TMEDA (cm <sup>3</sup> )	$P$ (bar)	$V_{\text{pore}}$ (cm <sup>3</sup> /g) <sup>b</sup>	median pore diam ( $\mu\text{m}$ ) <sup>b</sup>	bulk density (g/cm <sup>3</sup> ) <sup>b</sup>
25	PFPE	1	0.01	59	4.12	4.7	0.16
26	PFPE	1	0.1	69	3.41	8.4	0.14
27	Tween 40	10	0.1	62	3.41	10.5	0.17
28	Tween 40	10	0.1	69	3.30	29.1	0.17

<sup>a</sup> Reaction conditions: AM + MBAM (40% w/v in H<sub>2</sub>O, AM/MBAM = 8:2 w/w), (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2% w/v), CO<sub>2</sub>/H<sub>2</sub>O = 8:2 v/v, PVA (2% w/v,  $M_w = 10\,000$  g/mol, 80% hydrolyzed), 20 °C, 1.5 h. Reactor volume = 10 cm<sup>3</sup>. <sup>b</sup> Measured by mercury intrusion porosimetry over the range 7 nm–100  $\mu\text{m}$ .

**Table 4.** Synthesis of C/W Emulsion-Templated Polymers from Various Acrylic Monomers Using Redox Initiation (20 °C,  $P < 70$  bar)<sup>a</sup>

	monomer	cross-linker	surfactant	surfactant (w/v)	$V_{\text{pore}}$ (cm <sup>3</sup> /g) <sup>b</sup>	median pore diam ( $\mu\text{m}$ ) <sup>b</sup>	bulk density (g/cm <sup>3</sup> ) <sup>b</sup>
29	HEA	MBAM	CTAB	10	1.27	11.81	0.29
30	HEA	MBAM	Tween 60	10	1.14	18.01	0.29
31	HEA	MBAM	Tween 40	10	0.34	9.34	0.61
32	HEA	MBAM	Tween 40	20	0.52	7.33	0.51
33	HEMA	MBAM	Tween 40	10	<i>c</i>	<i>c</i>	<i>c</i>
34	HEA	PEG-DA	Tween 80	10	<i>c,d</i>	<i>c,d</i>	<i>c,d</i>
35	HEA	PEG-DA	Tween 40 <sup>e</sup>	10	0.14	13.09	0.84

<sup>a</sup> Reaction conditions: Total monomer concentration = 40% w/v in H<sub>2</sub>O, monomer: cross-linker = 8:2 w/w, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2% w/v), TMEDA (5% v/v based on H<sub>2</sub>O), CO<sub>2</sub>/H<sub>2</sub>O = 8:2 v/v, PVA (2% w/v,  $M_w = 10\,000$  g/mol, 80% hydrolyzed), 20 °C, 1.5 h. <sup>b</sup> Measured by mercury intrusion porosimetry over the range 7 nm–100  $\mu\text{m}$ . <sup>c</sup> No stable emulsion formed. <sup>d</sup> In addition, no stable emulsion was formed in this system with any of the following surfactants: SDS, Brij 56, Triton X-100. <sup>e</sup> Partially stable emulsion.

poration of thermally sensitive species such as proteins, enzymes, or live cells.<sup>20</sup> Elevated temperatures also give rise to elevated reaction pressures, which will increase both energy costs and capital equipment costs significantly.

We used a catalytic amount of a redox co-initiator, tetramethylethylenediamine (TMEDA),<sup>11,36</sup> to initiate these polymerization reactions at a temperature of 20 °C. It was thus possible to perform the reactions using liquid CO<sub>2</sub> at much lower reaction pressures (~65 bar versus ~300 bar). The results of a number of redox-initiated polymerizations are summarized in Table 3 (samples 25–29).<sup>37</sup> 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. For example, samples 27 and 28 were formed by redox initiation using Tween 40 as the surfactant under near-identical conditions and had pore volumes of 3.41 and 3.30 cm<sup>3</sup>/g, respectively, and a bulk density of 0.17 g/cm<sup>3</sup>. The equivalent material synthesized by thermal initiation at 60 °C (sample 20) had a lower pore volume (2.79 cm<sup>3</sup>/g) and a higher bulk density (0.23 g/cm<sup>3</sup>). Our previous studies suggested that these concentrated C/W emulsions are considerably more stable at lower temperatures,<sup>25</sup> although these observations were not made at constant CO<sub>2</sub> density, that is, the reduction in emulsion stability could be a consequence of a sudden decrease in the CO<sub>2</sub> density when the system is heated above the critical temperature (31.1 °C). Johnston and co-workers have shown that an increase in temperature decreases the stability of concentrated C/W emulsions stabilized by 1% w/v EO<sub>15</sub>-*b*-BO<sub>12</sub> when the aqueous phase was a 2 M KBr solution.<sup>33</sup> By contrast, no difference in emulsion stability as a function of temperature was observed in the *absence* of added salt.<sup>38</sup>

Other than avoiding the addition of TMEDA (which is in any case used in very small amounts), it seems that there is no clear advantage in our system to using CO<sub>2</sub> at higher temperatures in the supercritical state.

**Synthesis of Potential Biomaterials by C/W Emulsion Templating.** All of the examples described so far have involved

acrylamide as the monomer. Cross-linked PAM has been used in applications such as enzyme immobilization,<sup>39</sup> but is less useful, for example, in the production of biocomposites. We have therefore investigated the polymerization of other acrylic monomers via this route such as hydroxyethyl acrylate (HEA) and hydroxyethyl methacrylate (HEMA). HEA and HEMA have been investigated previously as monomers for the production of bone scaffolds,<sup>40</sup> nerve guides,<sup>41</sup> and surface patterned hydrogels for biomedical applications.<sup>42</sup> Table 4 summarizes the properties of a number of materials synthesized by C/W emulsion templating using either HEA or HEMA as the monomer and either MBAM or a poly(ethylene glycol) diacrylate (PEG-DA) as the cross-linker. Redox initiation was used in all cases to limit both the temperature and the reaction pressure. In general, it proved somewhat more difficult to form highly porous materials using HEA or HEMA (samples 29–33) as the monomer, even though relatively stable C/W emulsions could be formed by the correct choice of surfactant. A similar trend was observed in our studies on O/W/O sedimentation polymerization using conventional organic solvents.<sup>11</sup> We ascribe this partly to the fact that HEA polymerizes more slowly than AM under these conditions<sup>11</sup> and that it is therefore necessary to form highly stable emulsions. It was also noted that the HEA- and HEMA-based materials showed much greater shrinkage upon removal of the water than did the PAM materials, further reducing the pore volume. Nonetheless, it was possible to form porous C/W emulsion-templated monoliths

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(37) See Supporting Information for electron micrographs.

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from these monomers, particularly when a relatively high concentration of Tween 40 was used as the surfactant (sample 32).<sup>37</sup> We believe that it will prove possible, with further optimization, to produce HEA- and HEMA-based materials with equivalent porosity to that found in the PAM materials described above. The high degree of shrinkage in the materials might be avoided, for example, by using SCF-drying instead of air-drying.<sup>17,43</sup>

An alternative cross-linker, PEG-DA, was also investigated since such species have been used previously for the synthesis of selectively permeable hydrogel membranes<sup>44</sup> and injectable scaffolds or cell carriers in tissue engineering.<sup>45</sup> With these cross-linkers, it proved very difficult to form stable C/W HIPEs, and the materials so produced showed a low level of porosity and only partial templating of the emulsion structure (sample 35). Furthermore, unlike all other materials, sample 35 showed significant shrinkage when the CO<sub>2</sub> phase was vented, suggesting that either the level of cross-linking or the flexible nature of the PEG “spacer” led to a material with much lower mechanical rigidity.

## Conclusions

We have demonstrated that it is possible to synthesize highly porous emulsion-templated materials by polymerization of C/W HIPEs. No organic solvents are used in the process, and no solvent residues are left in the resulting materials. However, a

number of limitations were apparent in our initial approach,<sup>25</sup> namely that the PFPE surfactant was expensive and nondegradable, reaction pressures were high (250–290 bar), and reaction temperatures were elevated (50–60 °C). In this study, we have shown that all of these problems can be overcome and that it is possible to synthesize C/W emulsion-templated polymers at relatively modest pressures (60–70 bar) and low temperatures (20 °C) using inexpensive and readily available hydrocarbon surfactants. Moreover, we have shown that this technique can in principle be extended to the synthesis of emulsion-templated HEA and HEMA hydrogels that may be useful, for example, in biomedical applications.<sup>40–42</sup>

Detailed studies on the PAM/PFPE system suggest that the viscosity of the aqueous phase is the key factor in the stabilization of the C/W HIPEs and that the differences in emulsion stability are reflected in the templated pore structures. We plan to use this knowledge in future studies to develop highly porous materials for a number of applications, particularly those in which organic solvent residues pose a problem.

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**Supporting Information Available:** Experimental section and figures of polyacrylamide materials and porous polymers synthesized by C/W emulsion templating (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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