

Preparation of Ultra-Low-Density Microcellular Materials

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ABSTRACT: Microcellular polymeric materials can be obtained by the polymerization of a high-internal-phase emulsion. These materials are good candidates as targets toward inertial confinement fusion. This application requires severe specifications, including a very low density and a small cell size. In this study, we examined the influence of parameters such as emulsification conditions, surfactant nature, and the presence of a porogen on the obtainment of those require-

ments. It was possible to obtain microcellular polymeric foams with apparent densities as low as 0.0126 g/cm³. However, it was difficult to obtain very low material density and still maintain a small average pore size. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 2053–2063, 2005

Key words: foams; emulsion polymerization; macroporous polymers; density

INTRODUCTION

Low-density microcellular materials (LDMMs) are a particular class of porous materials used as deuterium and tritium sponges in direct-drive target designs (inertial confinement fusion experiments).¹ The material is composed of only low-atomic-weight atoms (in this case, carbon and hydrogen) and has to meet severe target designer's specifications with respect to cell size (<2–3 μm), density (<0.020 g/cm³), density uniformity, machinability, radiation stability, and thermal contraction. Initial efforts were attempted with phase-separated polyethylene.² Those efforts were abandoned after it was found that liquid deuterium/tritium did not wet the material. A more promising approach was to adapt a process patented by Unilever toward the production of interconnected microcellular foams made of polystyrene.³

Basically, an inverse emulsion is made from the association of water, a mixture of styrene (S) and divinylbenzene (DVB), and a suitable surfactant. In this emulsion, the water is the internal phase and occupies 90–95% of the total volume. With a water-soluble radical initiator previously added to the water, the polymerization of the S/DVB film that surrounds the water droplets can be thermally initiated. In this way, the structure of the oil phase is effectively frozen as a solid polymer. The water can then be removed by drying, resulting in a low-density foam material.

The conditions of obtaining and stabilizing a high-internal-phase emulsion (HIPE) have been thoroughly investigated.⁴ The properties and applications of high-internal-phase-emulsion-derived microcellular foams (polyHIPE) have been reviewed.⁵ With this approach, foams with densities as low as 0.040 g/cm³ and a cell size as low as 4–5 μm have been obtained.⁶

The objectives of this study were to reinvestigate the preparation of LDMMs via the emulsion templating approach to improve the material morphology with two objectives: to obtain (1) very low-density foams (ca. 0.010 g/cm³) and (2) a cell size as small as possible (preferably around 1 μm) with a reduced dispersion and a good homogeneity of the structure at medium range. Both requirements were studied separately, as they probably did not involve the same emulsification parameters.

EXPERIMENTAL

Materials

S (Aldrich), DVB (80% DVB, technology grade, Aldrich), diethylbenzene (Aldrich), Span 80 (sorbitan monooleate, Aldrich), potassium persulfate (Aldrich), and 2,2' azobis(2-methylpropanamide) dihydrochloride (V50, Aldrich) were used as supplied.

HIPE preparation and polymerization

Progressive addition of water method and overhead stirring

In a typical experiment, a mixture of 50/50 w/w S/DVB (4 g) and Span 80 (1 g) was placed in a 250-mL, round-bottom glass reactor and mixed with a D-

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TABLE I
Preparation of Microcellular Foams with the Progressive Water Addition Method and Overhead Stirring

| Ratio of aqueous phase (% w/w) | Stable emulsion | Stable foam | Foam | ρ (g/cm ³) | BET S_m (m ² /g) | d (μ m) |
|--------------------------------|-----------------|-------------|----------------|-----------------------------|-------------------------------|----------------|
| 93 | Y | Y | P ₁ | 0.0557 | 18.2 | 4.0 |
| 95 | Y | Y | P ₂ | 0.0429 | 15.5 | 6.0 |
| 96 | Y | Y | P ₃ | 0.0337 | 12.8 | 9.3 |
| 97 | N | — | — | — | — | — |
| 97 ^a | N | — | — | — | — | — |

Y = yes; N = no. The surfactant was Span 80 (20% w/w of the organic phase), and the polymerization was thermally initiated by potassium persulfate (0.15% w/w of the aqueous phase).

^a With 25% w/w of Span 80.

shaped polytetrafluoroethane (PTFE) paddle at 300 rpm. After complete homogenization, the aqueous phase (NaCl, 1.42 g, 1.5% w/w; K₂S₂O₈, 0.14 g, 0.15% w/w; and water, 93.4 g) was added under stirring with a syringe pump at a 2-mL/min addition rate. After total addition, the resulting thick white opaque cream was stirred for an additional 30 min. We chose to call the resulting material a HIPE of 95% internal phase volume. The surfactant was accounted in the organic phase, where it was, by far, more soluble. The emulsion was then poured into cylindrical PTFE-coated molds (internal size $\approx 10 \times 20$ mm) and polymerized at 60°C for 12 h. After their removal from the molds, the cylindrical monoliths were exhaustively extracted with a 1/1 H₂O/ethanol mixture (24 h) then ethanol (24 h) in a Soxhlet apparatus and then dried in a vacuum oven at 60°C to a constant weight.

Progressive addition of water method and vortexer mixing

Basically, the monomer phase (0.23 g) was made up of a 50/50 w/w S/DVB mixture and placed in a 50-mL test tube. PGE was added (0.025 g), and the tube was sealed with a septum. It was then fixed on the vortexer (Glas-Col Multipulse vortexer, Terre Haute, IN) and vibrated at 2400 rpm. The aqueous phase, prepared as previously described (12.0 g), was then slowly added dropwise with a syringe; a thick white emulsion was immediately obtained. We called this HIPE a 98% aqueous phase emulsion. The tube containing the emulsion was then placed in a thermostated bath and polymerized at 60°C for 12 h. After the tube was broken, the monolith was extracted as previously described. The resulting very low-density foam was carefully dried under a gentle airflow at room temperature.

Multiple-emulsion method and overhead stirring

All of the emulsion components, the monomers, surfactant, and aqueous phase, were added simultaneously into the reactor with proportions to obtain

about 100 g of a 98.5% w/w aqueous phase ratio emulsion. This mixture was stirred at 300 rpm with a D-shaped PTFE paddle until a thick white opaque concentrated emulsion was obtained (30–60 min). The emulsion was then poured into cylindrical PTFE-coated molds (internal size $\approx 10 \times 20$ mm) and polymerized at 60°C for 12 h. After their removal from the molds, the resulting cylindrical very low-density foams were carefully dried under a gentle airflow at room temperature.

Characterization of the microcellular foams

Physical parameters

Surface area. The specific surface area (S_m) values were calculated from N₂ adsorption data with the Brunauer-Emmett-Teller model. Adsorption data were obtained with a Micromeritics ASAP 2010.

Apparent densities. Apparent density (ρ) values were obtained with a Micromeritic autoPore IV mercury penetrometer.

Microcellular morphology analysis. The ultrastructure of the microcellular foams was investigated with scanning electron microscopy (SEM). Foams, extracted and dried, were carefully broken into pieces (1 \times 2 \times 2 mm), which were mounted on stubs with the fresh face uppermost in each case. Samples were sputter-coated with a gold/platinum electrode. SEM pictures were obtained with a Jeol JSM-5200 at 1000 \times and 5000 \times .

Average cell size determination. At first glance, the accurate texture characterization of an open-connected microcellular material is not an easy task. Traditional methods for characterizing the cells include mercury porosimetry, nitrogen adsorption, and SEM. To interpret the first of these measurements, one must make a morphological assumption. Usually, the assumption is that the morphology is cylindrical. Hence, although this technique can be a good candidate in providing comparative information, direct morphological information cannot be obtained from this characterization method. Furthermore, in the case of very low-density

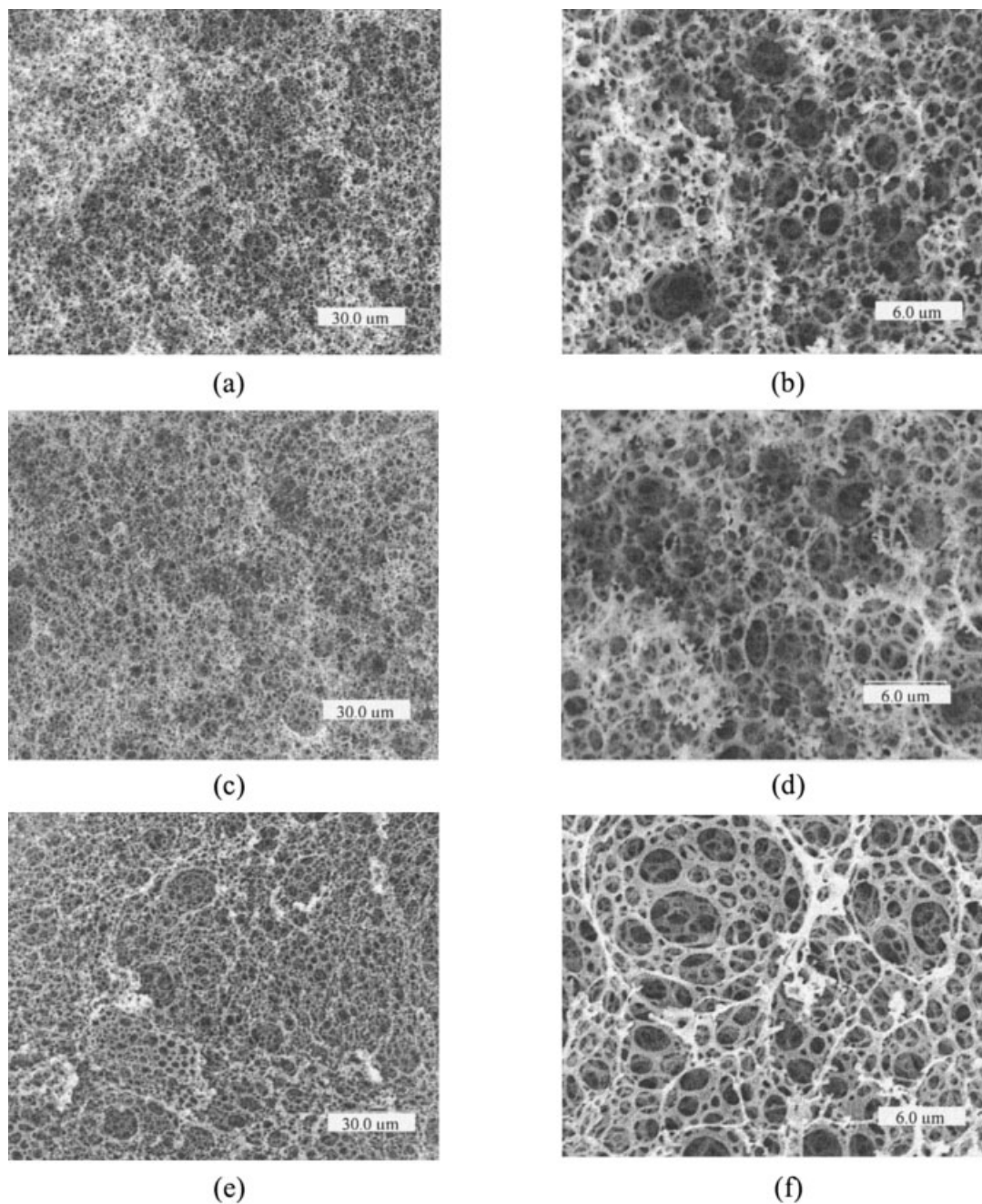


Figure 1 SEM micrographs of (a) P₁ (1000×), (b) P₁ (5000×), (c) P₂ (1000×), (d) P₂ (5000×), (e) P₃ (1000×), and (f) P₃ (5000×).

materials such the ones described in this study, the foam usually collapses under high mercury pressure. S_{mv} again, obtained through the BET treatment of nitrogen adsorption data, does not give any direct morphological information. SEM is a very useful tool for analyzing the morphology of low-density microcellular foams. A close examination of the micrographs allows the estimation of an average cell size at high magnification, whereas at lower magnification, the medium-range homogeneity of the structure can be appreciated with some accuracy. For all of this study, SEM micrographs of the obtained foams were recorded at two different magnifications (1000× and

5000×) to facilitate textural comparisons. The limitations of this approach included the fact that SEM samples represented only a small area of the total foam. We suffered also from the fundamental limitation of having only a two-dimensional image of a three-dimensional foam. It would be very useful to characterize the microcellular morphology by a simple and reproducible value estimated from the three-dimensional morphology of the foam. Stereological relationships exist between average two-dimensional morphology properties and the three-dimensional properties desired.⁷ If the thickness of the polymeric phase is negligible behind the average width of the

TABLE II
Preparation of Microcellular Foams with Diethylbenzene as a Porogen

| Ratio of aqueous phase (% w/w) | Porogen (%) ^a | Stable emulsion | Stable foam | Foam | ρ (g/cm ³) | BET S_m (m ² /g) |
|--------------------------------|--------------------------|-----------------|----------------|----------------|-----------------------------|-------------------------------|
| 95 | 25 | Y | Y | P ₄ | 0.0237 | 183.5 |
| 95 | 50 | Y | N ^b | — | — | — |
| 96 | 37 | Y | N ^b | — | — | — |

Y = yes; N = no. The surfactant was Span 80 (20% w/w of the organic phase), and the polymerization was thermally initiated by potassium persulfate (0.15% w/w of the aqueous phase).

^a Weight percentage of the oil phase.

^b Polymerization was effective, but the structure collapsed during drying.

porosity, the microcellular morphology can be considered as a continuous surface ribbon. With this assumption, a stereological relationship between the average distance that separates adjacent walls of the foam (d) and the surface area per unit volume (S_v) can be written:

$$d = 4/S_v \quad (1)$$

The d value can be thought of a generalized cell size. Hence, by knowing the value of d for various foams, one can objectively compare their morphology. This average d value is the ratio of the third moment to the second moment, which does indeed over-weight the large cells very heavily. It is, therefore, possible to relate the d value (μm) with the S_m (m²/g) and ρ (g/cm³) values of the foam:

$$d = 4/(S_m\rho) \quad (2)$$

For the microcellular foams, constituted of cells interconnected by pores, or windows, of smaller size, the d value could be explained as an average size with the cell sizes considered before pore sizes.

RESULTS AND DISCUSSION

Toward very low-density microcellular foams

Preliminary experiments

Creating a concentrated inverse emulsion involves mixing a small amount of an oil-based component with a much larger amount of water-based component in the presence of a suitable surfactant so that an inverse emulsion is obtained (one in which the oil phase is the continuous phase). To obtain such an emulsion, the choice of the surfactant is crucial. Williams carried out an extensive study of surfactants and cosurfactants for this system.⁸ It turns out that when the oil phase is composed of a S/DVB mixture, sorbitan monooleate (Span 80) is the best surfactant tested with respect to the achievement of small cell size morphology. He also found that the S/DVB ratio had relatively little effect on the emulsion structure.

Therefore, we chose to make all emulsions with a 50/50 S/DVB ratio. The method of adding the water phase to the oil one is also important. Following our previous studies on polyHIPE synthesis,⁹ we decided, in the first step, to slowly add the water to the stirred mixture of the oil phase and surfactant. The amount of Span 80 was fixed at 20% w/w of the oil phase, as recommended by Williams et al., to obtain an open cellular structure.¹⁰

With this system, the maximum water ratio inserted within the emulsion described in the literature was around 95%. Our first objective was to explore the limitations of this system in terms of amount of water insertion possible while obtaining a stable HIPE. The main results of this preliminary study are reported in Table I.

The results described in Table I indicate that with the experimental conditions usually reported in the literature, stable emulsions containing 93, 95, and 96 wt % water ratios were easily made, and the corresponding microcellular materials (P₁, P₂, and P₃, respectively) were obtained after polymerization at 60°C. The S_m 's were in agreement with the literature.¹¹

SEM micrographs of foams P₁–P₃ are reported in Figure 1. The structure of the foams was similar than described in the literature for similar emulsion compositions.¹² Rather spherical cells were interconnected by smaller window or pores cut into the continuous polymer film. The d values increased regularly from P₁ (4.0 μm) to P₂ (6.1 μm) to P₃ (9.3 μm). This means that the characteristic distance between solid phases increased with the water ratio inserted into the emulsion. The structure of the 96% sample (P₃) was particularly characteristic, with rather large cells associated with a large number of pores ($\emptyset = 2\text{--}3 \mu\text{m}$). Examination of the low-magnification micrograph indicated that the homogeneity of the structure at medium range (dimensions of the square = 150 \times 120 μm) was rather poor for each sample.

It was not possible to obtain a stable emulsion above 96% aqueous phase corresponding to ρ for the final foam of 0.0337 g/cm³. This result met, roughly, the lower density described in the literature for emulsion-

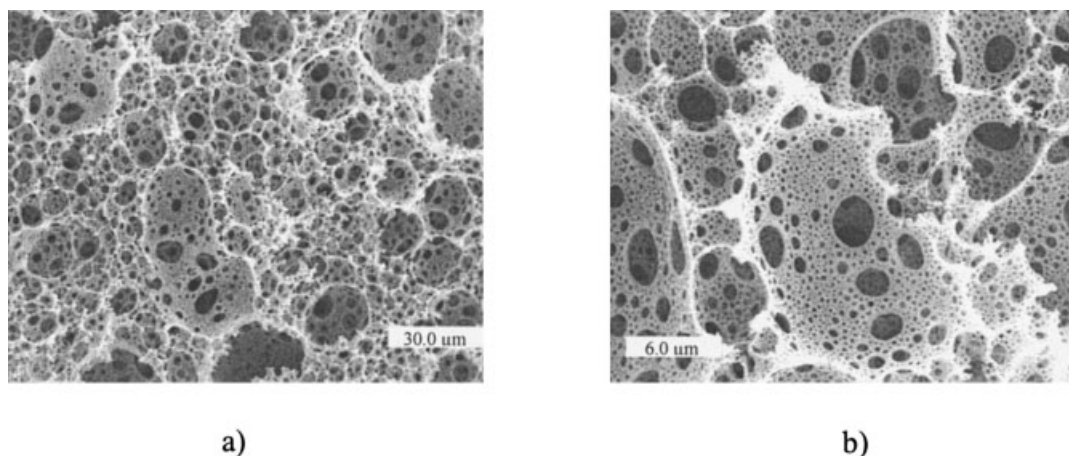


Figure 2 SEM micrographs of P₅: (a) 1000× and (b) 5000×.

derived microcellular foams.¹⁰ To decrease this density, several approaches are possible, one of them includes the use of a porogen.

Attempts to lower the density with a porogen

The formation and stability of a high-internal-phase-ratio emulsion seems to depend primarily on the relative amount of oil, water, and surfactant and, to a lesser extent, on the specific composition of the oil phase as far as its components remain sufficiently hydrophobic. This allows the replacement of a part of the S/DVB by a nonpolymerizing solvent, a porogen, and makes a good emulsion yet. The selection of the specific porogen was imposed by an effort to mimic the monomer molecules. Williams¹³ looked at a number of possible porogens whose structures differed from those of the S and DVB monomers and found that they were segregated somewhat, leading to a final polymerized structure showing reduced strength. Our objective was to “fool” the emulsion and the polymerizing structure as long as possible so that the polymerization would lock in the emulsion structure. Clearly, the porogen was excluded during the polymerization as part of the phase separation process, but with diethylbenzene, we delayed the process until the structure was set.

Table II reports the experiments performed with diethylbenzene as the porogen.

From these results, we concluded that diethylbenzene levels as high as 50% w/w of the oil phase did not destabilize the emulsion. However, despite the polymerization, the resulting materials were so brittle that they collapsed during the drying process. Therefore, it appeared that the higher amount of porogen compatible still with a reasonably rigid final material was 25% w/w, leading to a ρ of 0.0237 g/cm³ (P₄). However, even in this case, the foam was very fragile. A d value could not be calculated when the porogen was used because the porosity was bimodal with a microcellular porosity and a microporosity and mesoporosity.¹⁴

In summary, the use of a porogen to reduce the final density of the material did not seem to be a good route. The positive gain in term of density was more than negatively counterbalanced by the fact that the porogen introduced, by a porogenic effect, some porosity in the walls of the structure, which greatly reduced its mechanical strength.

Influence of the emulsification mode

In view of the previous results, we had to modify other parameters involved in the emulsification pro-

TABLE III
Preparation of Microcellular Foams with the Progressive Water Addition Method and a Vortex Apparatus

| PGE ^a | Stable emulsion | Stable foam | Foam | ρ (g/cm ³) | BET S_m (m ² /g) | d (μ m) |
|------------------|-----------------|-------------|----------------|-----------------------------|-------------------------------|----------------|
| 10 | Y | Y | P ₆ | 0.0191 | 38.0 | 5.5 |
| 8 | Y | Y | P ₇ | 0.0214 | 32.2 | 5.8 |
| 4 | N | — | — | — | — | — |

Y = yes; N = no. The surfactant was PGE, and the polymerization was thermally initiated by potassium persulfate (0.15% w/w of the aqueous phase).

^a Weight percentage of the oil phase

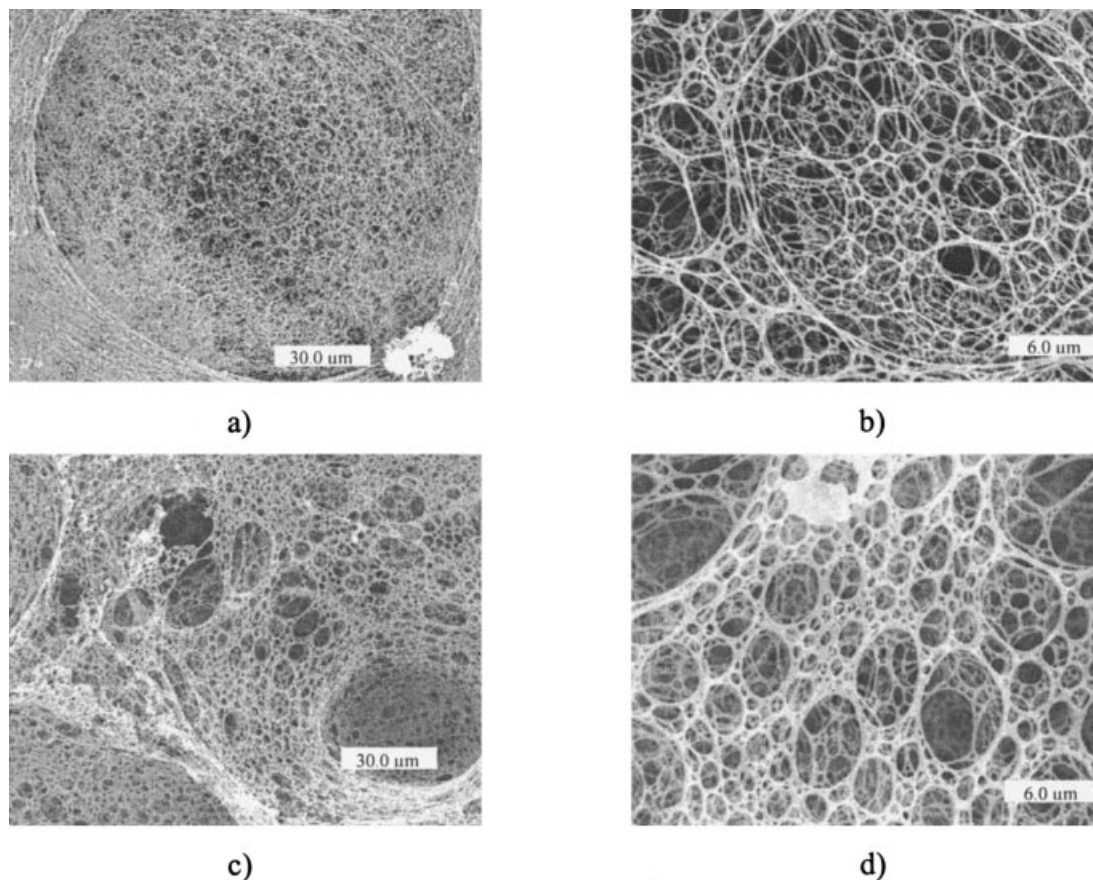


Figure 3 SEM micrographs of (a) P_6 (1000 \times), (b) P_6 (5000 \times), (c) P_7 (1000 \times), and (d) P_7 (5000 \times).

cess to increase the amount of water inserted into the emulsion. One of them was the nature of the mixing method used during the emulsion preparation.

Up to this point, we performed our emulsifications by a gentle stirring at 300 rpm with an overhead stirrer and a D-shaped PTFE paddle. As the insertion of water in the emulsion was more and more difficult as its volume ratio increased, we expected that a more vigorous mixing, such as with a laboratory vortex could improve this insertion at high water ratios.¹⁵ With this device, it was possible to insert 97% of the

water phase on a 50/50 w/w S/DVB oil phase containing 20% w/w Span 80. The corresponding foam was successfully obtained after polymerization and showed a good rigidity (P_5). However, it was not possible by this method to insert any more water under these conditions.

The SEM micrographs of sample P_5 showed a structure of deformed large cells (average cell size = 7 μm) with little connections of rather small size (1 μm ; Fig. 2). The d value was estimated to be 6.8 μm . The low-magnification micrograph analysis indicated a

TABLE IV
Preparation of Microcellular Foams with the Multiple-Emulsion Method and Overhead Stirring

| Ratio of aqueous phase (% w/w) | PGE ^a | Stable emulsion | Stable foam | Foam | ρ (g/cm ³) | BET S_m (m ² /g ¹) | d (μm) |
|--------------------------------|------------------|-----------------|----------------|-------|-----------------------------|---|-----------------------|
| 8 | 10 | Y | Y | P_8 | 0.019 | 43.9 | 4.8 |
| 98.5 | 10 | N | — | — | — | — | — |
| 98.5 | 15 | N | — | — | — | — | — |
| 98.5 | 20 | Y | Y | P_9 | 0.0126 | 40.7 | 7.7 |
| 99 | 20 | N | — | — | — | — | — |
| 99 | 25 | Y | N ² | — | — | — | — |

Y = yes; N = no. Polymerization was thermally initiated by potassium persulfate (0.15% w/w of the aqueous phase).

^a Weight percentage of the oil phase.

^b Polymerization was effective, but the structure collapsed during drying.

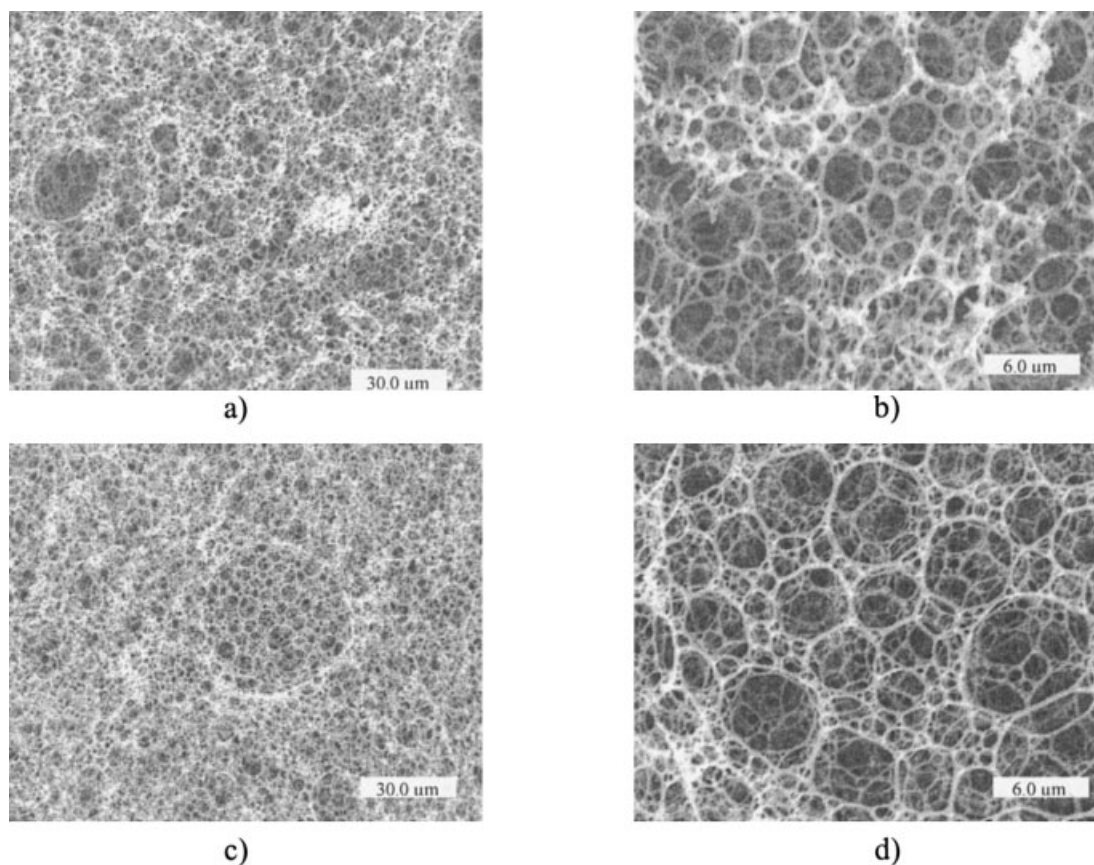


Figure 4 SEM micrographs of (a) P_8 (1000 \times), (b) P_8 (5000 \times), (c) P_9 (1000 \times), and (d) P_9 (5000 \times).

poor homogeneity of the texture with a lot of droplet coalescence and probably the template of air bubbles inserted during the emulsification step.

Influence of the surfactant

At this point in the study, we decided to reinvestigate the influence of the more important parameter of the system: the surfactant. A recent patent disclosed the high efficiency of polyglycerol aliphatic esters for the preparation of HIPEs.¹⁶ According to this study, polyglycerol aliphatic esters characterized by a high

level of linear (i.e., acyclic) diglycerol monoaliphatic esters (i.e., the esters comprising high levels of diglycerol moieties with one aliphatic group) were surprisingly efficient in stabilizing a HIPE constituted of S/DVB as the oil phase. Therefore, we decided to substitute, in our preparations, Span 80 with a commercially available poly(glycerol ester) (PGE) of fatty acid mainly constituted of diglycerol monooleate (Grinsted PGE O 80 was kindly supplied by Danisco, Denmark).

Table III discloses the principal experiments conducted with PGE as the emulsifier, with the stirring device being the vortexer at 2400 rpm. In all cases, the aqueous phase ratio was 98 wt %.

According to these results, PGE was a very efficient emulsifier for stabilizing HIPE with a water ratio as high as 98 wt %. The amount of emulsifier required could be lowered to 8% of the oil phase, which gave access to the corresponding microcellular foams (P_6 and P_7). The apparent densities of the obtained foams were around 0.020 g/cm³.

The structures of those foams derived from 98 wt % water content concentrated emulsions were quite different from the ones described so far (Fig. 3). They seemed more closely related with porous polyolefin foams obtained by thermally induced phase separation.¹⁷ It was difficult at this point to distinguish be-

TABLE V
Preparation of Microcellular Foams with the Progressive Water Addition Method and a High-Speed Emulsification Device

| Ratio of aqueous phase (% w/w) | Stable emulsion | Stable foam | Foam |
|--------------------------------|-----------------|-------------|----------|
| 70 | Y | Y | P_{10} |
| 80 | Y | Y | P_{11} |
| 90 | Y | Y | P_{12} |
| 95 | N | — | — |

Y = yes; N = no. The surfactant was Span 80 (20% w/w of the organic phase), and the polymerization was thermally induced by potassium persulfate (0.15% w/w of the aqueous phase).

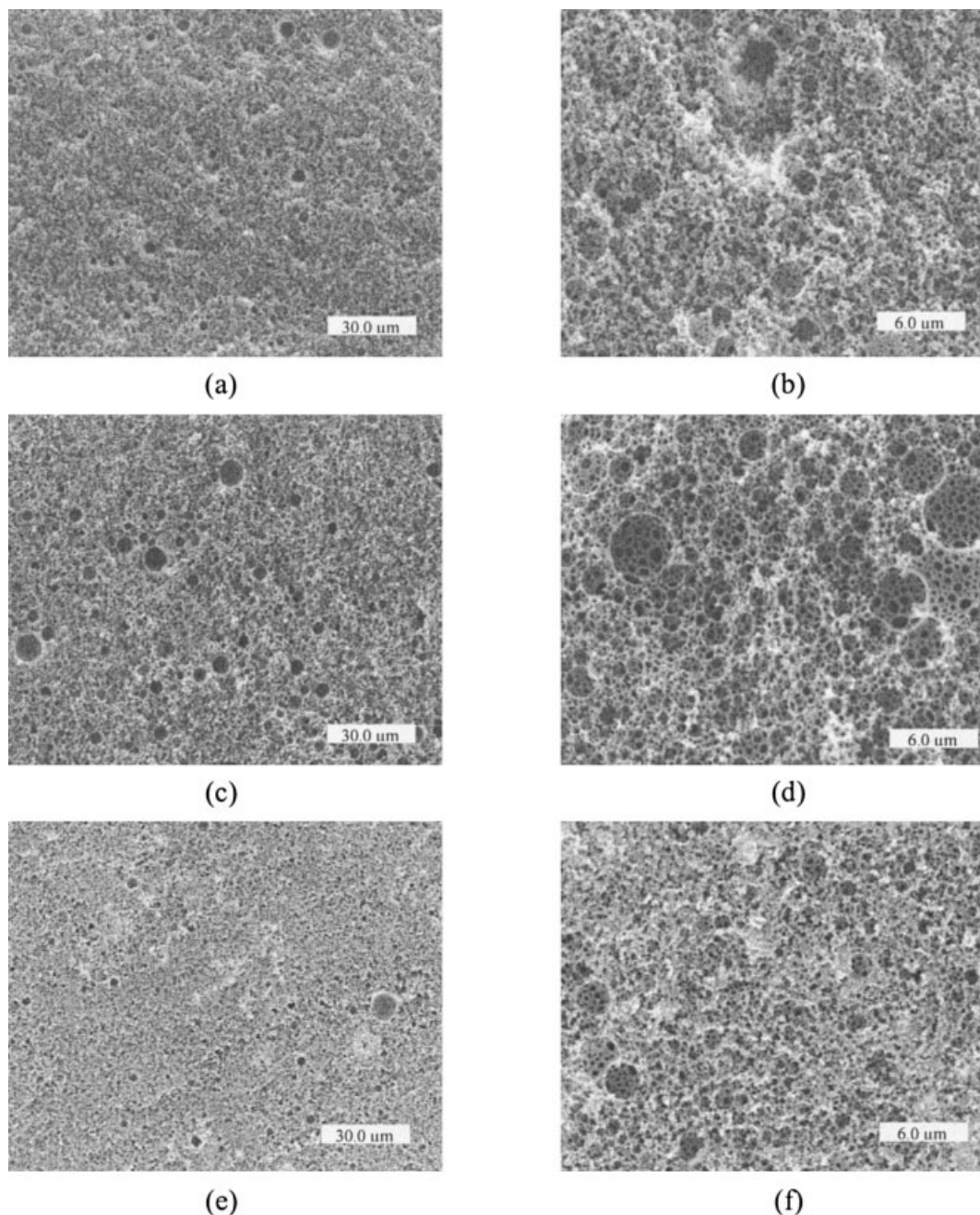


Figure 5 SEM micrographs of (a) P_{10} (1000 \times), (b) P_{10} (5000 \times), (c) P_{11} (1000 \times), (d) P_{11} (5000 \times), (e) P_{12} (1000 \times), and (f) P_{12} (5000 \times).

tween cells and pores. With the structure being rather more fibrous, the d value corresponded really to an average distance between struts. In both samples studied (P_6 and P_7), the d values were very close.

Attempts to overincrease the amount of water inserted in the HIPE with this method were fruitless.

Influence of the emulsification method

Different methods of emulsification other than the slow addition of the aqueous phase have been de-

scribed for the preparation of very high-internal-phase-ratio emulsions.¹⁸

One of them is called the multiple-emulsion method. In this approach, the various components, oil, water, and surfactant, are mixed together at the appropriate ratio. The system is then stirred until the HIPE forms. The evolution of the system is complex. At first, the composition consists of oil droplets dispersed in water. Later on, the oil droplets coalesce and grow due to the incorporation of water droplets. A water/oil/water emulsion is formed. Continuous ag-

TABLE VI
Preparation of Microcellular Foams with the Progressive Water Addition Method and an Overhead Stirring Motor

| Ratio of aqueous phase (% w/w) | Polymerisation type ^a | Stable emulsion | Stable foam | Foam | ρ (g/cm ³) | BET S_m (m ² /g) | d (μ m) |
|--------------------------------|----------------------------------|-----------------|-------------|-----------------|-----------------------------|-------------------------------|----------------|
| 90 | Thermal (50) | Y | Y | P ₁₃ | 0.0919 | 10.1 | 4.3 |
| 90 | Thermal (40) | Y | Y | P ₁₄ | 0.0921 | 11.1 | 3.9 |
| 90 | Photochemical (20) | Y | Y | P ₁₅ | 0.0935 | 26.7 | 1.6 |

Y = yes; N = no. The surfactant was PGE (10% w/w), and the polymerization was thermally initiated by potassium persulfate (0.15% w/w of the aqueous phase).

^a The temperature (°C) is given in parentheses.

itation finally produces the HIPE. We decided to use this method to increase the amount of water inserted in the emulsion. The results are reported in Table IV.

Insertion of 98% water with 10% PGE led to a fairly stable HIPE, which gave after polymerization, a fragile but self-standing material (P₈). Attempts to reach the 98.5% water ratio were successful only after the surfactant level was increased up to 20% w/w. In that case, again it was possible to obtain a satisfactory material (P₉) with a ρ as low as 0.0126 g/cm³. Finally, an emulsion with a 99 wt % water ratio level was obtained with 25% w/w of PGE. This emulsion could be correctly polymerized, but the resulting ultra-low-density material (expected ρ below 0.010 g/cm³) collapsed even under very gentle drying. The foam structure was rather similar to those obtained with 98% aqueous water content with the progressive water addition. However, the d values were larger and were estimated to be 4.8 μ m for P₈ and 7.8 μ m for P₉ (Fig. 4). The medium-range homogeneity appeared to be better with fewer air-bubble prints.

Optimization of the cell size

In the previous section, we showed that it was possible to obtain microcellular foams with densities as low as 0.0126 g/cm³. However, the resulting materials had an average cell sizes much greater than those expected. In this part, we discuss the investigation of methods to significantly reduce the average foam cell size.

In the first part, we showed that a high stirring rate during the emulsification process strongly reduced the average cell size of the emulsions. To increase this effect, we synthesized rather high-density foams (i.e., from emulsions with a comparatively low water ratios), substituting a vortex mixing (2400 rpm) with a high-speed emulsification device (10,000 rpm; Ultraturax). In our first attempt, the surfactant used was Span 80 at 20% w/w of the continuous phase, and the water phase was added progressively as described previously. The more significant results obtained are reported in Table V.

Foams with ratios of inserted water of 70, 80, and 90% w/w, respectively, were successfully obtained.

However, it was not possible to obtain a stable HIPE containing 95% inserted water.

SEM micrographs showed improved medium-range homogeneity for the three structures. The average cells could be estimated at 2 μ m or maybe smaller in all of the samples (Fig. 5). The d values were not calculated for these samples.

Despite the efficiency of this approach to reduce the average size of the cells of the foams, its inability to form very high-internal-phase-ratio emulsions caused us to abandon this route.

Influence of the polymerization temperature

The influence of the polymerization temperature on the average cell size of the resulting foams seemed to have not been investigated yet in the literature. The average cell size of a foam can be expected to decrease significantly with a decrease in the temperature of polymerization, as the coalescence rate of the droplets of the dispersed phase in the emulsion is reduced.

All of the previous polymerization experiments were performed at 60°C with potassium persulfate as a water-soluble radical initiator. We decided to change the temperature for 2,2' azobis(2-methylpropionamide) dihydrochloride (V50), a water-soluble azo initiator known to have a lower half-life temperature (the half-life time at 60°C of sodium persulfate and V50 were about 17 and 5 h, respectively, according to the brochure *Azo Polymerization Initiator* by Wako, Ltd., 1999).

Table VI reports the first experiments conducted with V50 as initiator on a 90 wt % aqueous phase ratio emulsion prepared by the progressive water addition method and overhead stirring.

Foams were satisfactorily generated by thermal polymerization at 50°C (P₁₃) and 40°C (P₁₄). Furthermore, we succeeded in polymerizing a 90 wt % aqueous phase content emulsion by ultraviolet irradiation (365 nm) at room temperature (P₁₅).

The SEM micrographs of the foams derived from the 90 wt % aqueous phase content emulsions polymerized at 50°C (P₁₃) and 40°C (P₁₄) looked very similar (Fig. 6).

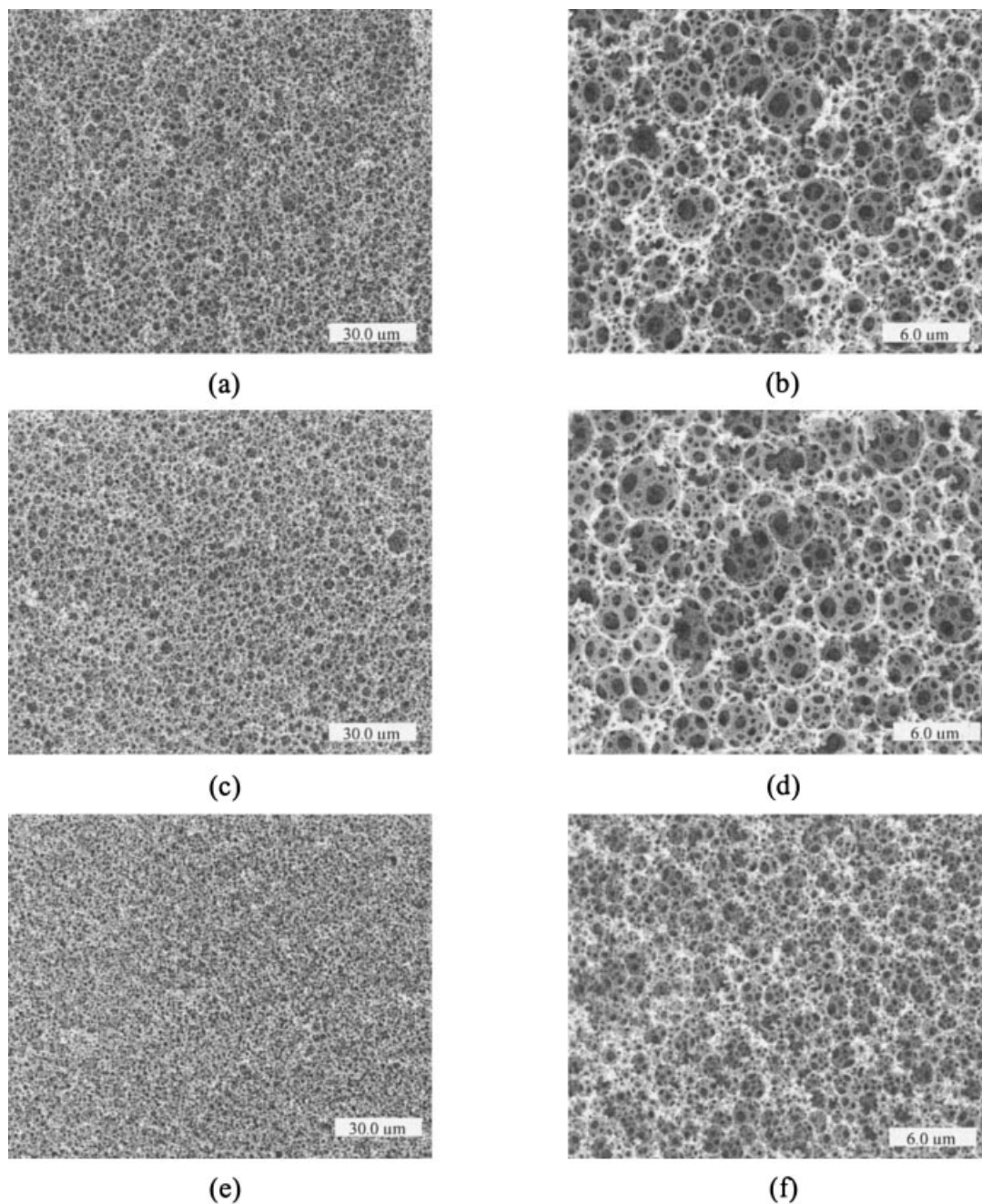


Figure 6 SEM micrographs of (a) P₁₃ (1000 \times), (b) P₁₃ (5000 \times), (c) P₁₄ (1000 \times), (d) P₁₄ (5000 \times), (e) P₁₅ (1000 \times), and (f) P₁₅ (5000 \times).

The low magnification indicated a good homogeneity of the structure in both cases. The d values were almost the same, around 4 μm . The morphology analysis of the foam photopolymerized at room temperature (P₁₅) showed a d value of 1.6 μm , and the foam appeared very homogeneous at low magnification. A close examination of the higher magnification micrographs allowed an average cell size estimation of 2 μm with an average pore diameter below 0.5 μm .

Finally, a 95% HIPE was obtained in the same conditions (P₁₆) with the multiple-emulsification method. The micrographs of sample P₁₆ polymerized photo-

chemically at room temperature showed good homogeneity at medium-range distance, but the d value appeared to be greater than those of its 90% equivalents (6.2 μm ; Fig. 7).

The average cell size was estimated to be 7 μm with an average pore diameter of about 2 μm . S_m was 40.3 m^2/g .

CONCLUSIONS

In this study, we clearly demonstrated that it was possible to prepare microcellular polymeric foams derived

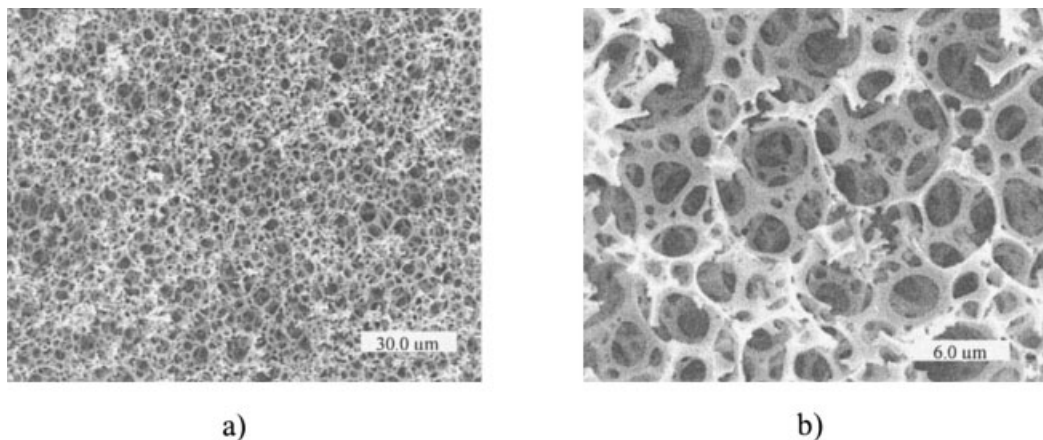


Figure 7 SEM micrographs of P₁₆: (a) 1000× and (b) 5000×.

from high-internal-phase-ratio emulsions with a ρ , in the dry state, as low as 0.0126 g/cm³ and an average distance between struts of around 8 μm . To reach this result, stable high internal phase ratio emulsion were prepared by the insertion of more than 98.5 wt % aqueous phase ratio. Those very highly concentrated emulsions were obtained with a PGE of fatty acid as the emulsifier and by the improvement of the emulsification conditions. Beyond, it was possible to obtain stable emulsions with 99 wt % water ratios, but the resulting polymerized microcellular structures collapses on drying under an airflow. It would be worth it to try a supercritical CO₂ drying process to reduce the stress experienced by the structure during drying. We established that the average cell size increased with increasing porosity of the foam. The difference in size between the cells and pores decreased accordingly. Above a 98% aqueous phase ratio, it was not possible any more to distinguish both kinds of structure, and the material looked fibrous. The d value could be reduced below 2 μm with a 90% aqueous phase ratio emulsion with a room-temperature photochemical polymerization. However, in the case of the 95 wt % aqueous phase content HIPE, the use of the multiple-emulsion method combined with a room-temperature photochemical polymerization allowed us to only obtain a foam with an average cell size of about 6 μm . Therefore, it was difficult with the emulsification methods described in this study to simultaneously obtain a very low-density material and a small average characteristic porosity size. We are now focusing our research efforts toward other emulsification methods, such as spontaneous gelification above the phase-inversion temperature, to meet these requirements.

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