Oil–in–Alcohol Highly Concentrated Emulsions as Templates for the Preparation of Macroporous Materials

5 AUTHORS, INCLUDING:

Susana Vílchez Maldonado
Instituto de Química Avanzada

21 PUBLICATIONS **138** CITATIONS

SEE PROFILE

Lourdes A Pérez-Carrillo
University of Guadalajara

16 PUBLICATIONS **72** CITATIONS

SEE PROFILE

Jonathan Miras
Spanish National Research Council

**12** PUBLICATIONS **33** CITATIONS

SEE PROFILE

Oil-in-Alcohol Highly Concentrated Emulsions as Templates for the Preparation of Macroporous Materials

Susana Vílchez, Lourdes A. Pérez-Carrillo,[†] Jonathan Miras, Conxita Solans, and Jordi Esquena*

Institute for Advanced Chemistry of Catalonia, Consejo Superior de Investigaciones Científicas (IQAC-CSIC) and CIBER de Bioingeniería, Biomateriales y Nanomedicina (CIBER-BBN), Jordi Girona, 18-26, 08034 Barcelona, Spain

S *Supporting Information*

ABSTRACT: New oil-in-alcohol highly concentrated emulsions were formulated and were used as a templates to obtain macroporous poly(furfuryl alcohol) monoliths by a one-step method. The oil-in-alcohol highly concentrated emulsions were prepared by stepwise addition of the oil phase to the surfactant-alcohol solution and were characterized by optical microscopy and by laser diffraction. The typical structure of highly concentrated emulsions, with close-packed polyhedral droplets, has been observed. Poly(furfuryl alcohol) monoliths were obtained by polymerizing in the external phase of these emulsions. These materials are mainly macroporous and retain the size distribution and morphology from the highly concentrated emulsions. The internal structure of the monoliths was observed by scanning electron microscopy. The images showed an interconnected network with pore size similar to the droplet size of the highly concentrated emulsions used as templates.

Decane-in-furfuryl alcohol highly concentrated emulsion → Poly(furfuryl alcohol) macroporous monolith
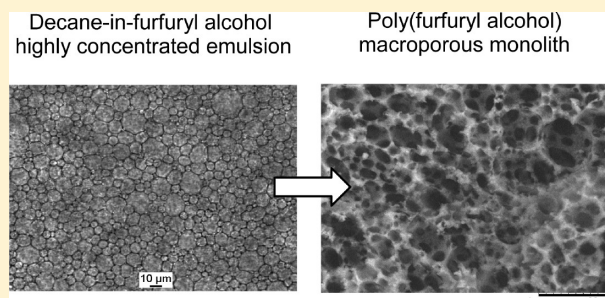
INTRODUCTION

Highly concentrated emulsions, also referred to in the literature as high-internal-phase ratio emulsions (HIPRE or HIPE), have received a great deal of attention during several decades due to their theoretical interest and technological applications.[1−6] Highly concentrated emulsions are characterized by a volume fraction of the disperse phase greater than 0.74, which is the critical volume of the most compact arrangement of uniform spherical droplets.[1−3] For this reason, the structure of highly concentrated emulsions generally consists of polyhedral and polydisperse droplets separated by a thin film of continuous phase.[4−6]

One of the most interesting applications of highly concentrated emulsions is their use as templates for the preparation of macroporous solid foams, a method that was first described in a patent by Unilever in 1982,[7] being worth mentioning the early contributions from Williams, Ruckenstein, and co-authors.[8−10] Since then, many different low-density macroporous materials have been obtained by polymerizing in the external phase of emulsions, followed by the removal of the dispersed phase.[11−33] In this context, organic polymer foams with extremely low densities (around 0.02 g mL^{-1}), and consequently very high pore volume, can be obtained by templating in highly concentrated emulsions.[7−21] Many different oil-soluble and water-soluble monomers can be used for the preparation of these organic polymer foams, despite the fact that many works have focused on styrene or acrylates.[10−16]

Porous inorganic materials have also been obtained by templating in concentrated and highly concentrated emulsions. Several authors have described the use of emulsions as

templates, in simple one-step processes, for the preparation of inorganic materials with complex porous structures.[22−33] In this context, Pine and Imhof described a procedure for the preparation of porous materials by carrying out sol−gel processes in the external phase of isooctane-in-formamide emulsions, with a very narrow droplet size distribution.[22] Therefore, these materials possess uniform macropores, with pore walls consisting of mesoporous inorganic oxides. This procedure can be adapted to obtain more complex structures, as shown in a more recent work that describes the formation of materials consisting of particles with controlled inner porosity, prepared by a double templating method that combines emulsion droplets and solid particles as templates.[23]

Backov and his co-authors have also described the formation of porous inorganic oxides and hybrid organo-inorganic, with bimodal pore size distribution, by a one-pot synthesis method consisting in sol−gel processing in the external phase of highly concentrated emulsions.[24,25] The films that separate adjacent droplets are very thin in highly concentrated emulsions, and consequently, the precursor species are located mainly in the emulsion plateau borders, templating the formation of polyhedral macropores that are interconnected though narrow necks. Moreover, it has been described that polymerization starts at the oil/water interface, because the interface facilitates nucleation.[24] In a recent work, the preparation of carbonaceous foams was achieved by pyrolysis of phenolic resin using a dual

template approach, which consists of silica monoliths as hard templates and triblock copolymers as soft templating agents.[26]

In most cases, the emulsions were prepared using surfactants as emulsifiers. However, macroporous foams can also be obtained in highly concentrated emulsions stabilized solely with solid particles (Pickering emulsions), as demonstrated by Binks.[27] Moreover, nanocomposite materials can be obtained by polymerizing an organic monomer in particle-stabilized emulsions, obtaining macroporous organic foams with imbibed inorganic nanoparticles, as shown by Bismarck et al.[21]

The preparation of organic polymer foams with controlled porosity may have great applications in the development of novel materials. In this context, carbonaceous materials, which can be obtained by pyrolization of macroporous organic polymers, are of special interest in many technological applications.[34] Poly(furfuryl alcohol) is widely used in the field of carbonaceous materials, since it is one of the few thermosetting polymers that form carbon with acceptable yield on carbonization.[35−38] However, the preparation of macroporous foams based on furfuryl alcohol is not an easy task. The main difficulty arises from the fact that oil-in-furfuryl alcohol emulsions are required, and such emulsions are usually very unstable due to low surfactant adsorption in oil-alcohol interfaces, resulting in flexible monolayers that are highly prone to coalescence.[39−41] The reason is the high polarity of furfuryl alcohol, which is completely miscible with water (but chemically unstable) and highly insoluble in nonpolar organic solvents.[42] The molecular structure is shown in Scheme 1.

Scheme 1. Molecular Structure of Furfuryl Alcohol
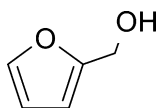
Therefore, furfuryl alcohol behaves similarly to short chain alcohols (i.e., isopropyl alcohol). Emulsions of oil dispersed in short chain alcohols are not stable and consequently oil-in-furfuryl alcohol emulsions have not been reported in the preparation of macroporous foams. In the literature, the preparation of poly(furfuryl alcohol) porous materials has been achieved by using two-step synthesis methods, consisting in acid-catalyzed polycondensation of furfuryl alcohol vapors on porous solids used as scaffolds.[19,43,44] A recent example is the preparation of polystyrene/divinylbenzene−poly(furfuryl alcohol) composites with high macropore volume, by a two-step method.[19]

Consequently, to the best of our knowledge, there are no reports in which a water-soluble alcohol is used as the main component of the emulsion continuous phase for the synthesis of macroporous foams. In the present work, solid foams made of poly(furfuryl alcohol) have been obtained, and therefore, this is the first time that macroporous foams materials have been prepared using oil-in-alcohol highly concentrated emulsions as templates.

■ EXPERIMENTAL SECTION

Materials. Furfuryl Alcohol (99%) was a product from Sigma-Aldrich. The Pluronic surfactants L121, which has the molecular structure denoted as $(EO)_5$-$(PO)_{70}$-$(EO)_5$, P123 described as $(EO)_{20}$-$(PO)_{70}$-$(EO)_{20}$, and F127, $(EO)_{100}$-$(PO)_{70}$-$(EO)_{100}$, have the general structure poly(ethylene oxide)-b-poly(propylene oxide)-b-poly-

(ethylene oxide) triblock copolymer. These surfactants, generically known as poloxamers, were purchased from BASF.

Synperonic A20 $(C_{13−15}(EO)_{20})$ was from Uniquema, and sodium dodecyl sulfate (SDS) was from Sigma. All surfactants were used without further purification. Decane (98 wt %), chosen as a model oil, and concentrated hydrochloric acid, 37 wt %, were from Fluka and Merck, respectively.

Phase Diagram Determination. For the ternary phase diagram, samples were prepared by weighing appropriate amounts of surfactant, decane, and furfuryl alcohol, which were placed in vials and homogenized with a Heidolph Reax vibromixer. The samples were then placed in a water bath at a constant temperature of 25 °C until phase equilibrium was reached. The different phases were assessed by visual inspection of samples. Crossed polarizers were used to identify the possible presence of liquid crystalline phases.

Preparation of Highly Concentrated Emulsions. Oil-in-alcohol highly concentrated emulsions were prepared by the conventional method which consists of stepwise addition with stirring, of disperse phase (decane) to the mixture of furfuryl alcohol and surfactant, at 25 °C. Agitation was applied either with a vibromixer at 300 rpm (for preparation of small volumes) or with an inverted T-shaped paddle made of stainless steel connected to a Heidolph stirrer (for large volumes). In this case, the agitation speed was varied during emulsification, starting from 100 rpm and increasing gradually up to 500 rpm, because viscosity greatly increased during the formation of highly concentrated emulsions.

Different surfactant/alcohol mixing ratios were used, and decane was slowly added to the mixture until reaching either 70 or 80 wt %. A small amount of HCl(aq), 37 wt %, was also added dropwise (between 0.01 and 0.04 weight fraction referred to furfuryl alcohol). After addition of all components, agitation was continued for 10 min, to ensure homogeneous composition in the emulsion. Approximately 2 h afterward, color changes were evident by visual inspection, indicating the progress of polymerization.

Characterization of Highly Concentrated Emulsions. The highly concentrated emulsions were observed using an optical microscope Leica Reichert Polyvar 2. The images were acquired using a CCD camera (Sony CCD-Iris) connected to a digital image processing software (Leica IM500). The droplet size distribution of the highly concentrated emulsions was determined by light diffraction, from emulsions that were diluted using purified water, using a Mastersizer 2000 equipped with a Hydro 2000G dispersion unit, and a He−Ne red light laser. In light diffraction, the particle size distribution is calculated by obtaining the scattering pattern of the sample and fitting the droplet size distribution with the Fraunhofer and Mie diffraction theory, using a mathematical inversion process.

The average droplet diameter in the volume distribution, $(D[4,3])$, eq 1, and polydispersity (span), eq 2, were calculated from the measured droplet diameter (d).

$$D[4, 3] = \frac{\sum d^4}{\sum d^3} \tag{1}$$

$$span = \frac{d(0.9) - d(0.1)}{d(0.5)} \tag{2}$$

where $d(0.1)$, $d(0.5)$, and $d(0.9)$ are the 10th, 50th, and 90th percentiles in the volume distribution, respectively. In the case of a Gaussian distribution, $D[4/3]$ is equal to $d(0.5)$.

Synthesis of Poly(furfuryl alcohol) Monoliths. The monoliths were prepared by polymerizing in the external phase of decane-in-alcohol highly concentrated emulsions, for 48 h at 25 °C, with the addition of a small volume of concentrated HCl, at 0.1 wt % final concentration. After polymerization, oil and surfactant were removed by Soxhlet solvent extraction, washing with ethanol for 12 h. Finally, samples were dried at room temperature, until constant weight was reached.

Characterization of Poly(furfuryl alcohol) Monoliths. The macroporous structure of the materials obtained was characterized by scanning electron microscopy (SEM), using either a Hitachi-2300 or a

Table 1. Formation and Stability of Oil-in-Alcohol (O/A) Emulsions, in the Surfactant/Furfuryl Alcohol/Decane System[a]

surfactant	[surfactant]/wt%	[decane]/wt%	[surfactant]/[alcohol] ratio	emulsion formation	stability time/h
$C_{13-15}(EO)_{20}$ (Synperonic A20)	5	70	1/5	no	
	10	70	1/2	no	
	12	70	1/1.5	yes	~1
	15	70	1/1	yes	~1
	2	80	1/9	no	
	5	80	1/3	no	
	10	80	1/1	no	
$(EO)_{20}(PO)_{70}(EO)_{20}$ (Pluronic P123)	10	70	1/2	yes	~12
	12	70	1/1.5	yes	~12
	15	70	1/1	yes	~12
	10	80	1/1	yes	~12
$(EO)_{100}(PO)_{70}(EO)_{100}$ (Pluronic P127)	5	70	1/5	yes	~1
	10	70	1/2	yes	~12
	12	70	1/1.5	yes	~12
	15	70	1/1	yes	>24
	2	80	1/9	no	
	5	80	1/3	yes	~1
	10	80	1/1	yes	>24

[a]Surfactants and compositions are indicated. The ability to form and stabilize emulsions, containing either 70 or 80 wt % decane dispersed into the alcohol continuous phase, was qualitatively evaluated by visual inspection.

Hitachi TM-1000 instrument. Samples were coated by sputtering with a carbon layer approximately 60 nm in thickness. Observations were carried out at 20 kV acceleration voltage.

The chemical composition of the monoliths was studied by IR spectroscopy using a Fourier transform infrared (FTIR) spectrophotometer Nicolet 510. Spectra were collected at 4 cm^{-1} resolution with 64 averaged scans. For these IR determinations, samples were ground with dried KBr, and pellets were prepared by compression in a mold.

Nitrogen adsorption/desorption isotherms were determined at 77.3 K using a Tristar 3000 apparatus. The specific surface area was calculated by the Brunauer−Emmett−Teller (BET) equation[45] from the adsorption isotherm over the relatively low pressure range (0.1− 0.3 p/p_0). Mesoporosity was analyzed from the desorption branch of the isotherms using the Barrett−Joyner−Halenda (BJH) method.[46] The bulk density was estimated by measuring the volume of monoliths with regular shape.

Pyrolyzation of Poly(furfuryl alcohol) Monoliths. First, the materials were degassed by heating at 200 °C, under vacuum for 2 h. Afterward, carbonization was carried out by pyrolyzing under nitrogen atmosphere. Temperature was slowly increased at a 0.5 °C/min rate, and then samples were kept at constant temperature for 2 h, on three successive treatments, at 200, 250, and 300 °C.

Characterization of Carbonaceous Monoliths. The texture of these materials was observed via SEM, using a Hitachi TM-1000 instrument, at 15 kV acceleration voltage. Samples were not coated by sputtering, since pyrolyzed carbonaceous materials are conductive. Element analysis was carried out in a Flash 1112 Thermo Finnigan microanalyzer.

■ RESULTS AND DISCUSSION

According to the simple and well-known Brancroft rule, the phase in which an emulsifier is more soluble constitutes the continuous phase of any emulsion.[47] Although exceptions are possible, one should consider that, in oil-in-alcohol emulsions (O/A), the surfactant should be preferably soluble in the alcohol continuous phase, and less soluble in the oil. Preliminary solubility experiments were carried out for selecting the most appropriate emulsifier. The solubility in furfuryl alcohol of different surfactants, described before in the Experimental Section, was visually assessed. Sodium dodecyl

sulfate (HLB ≈ 40) and Pluronic L121 (HLB = 4.5) were insoluble in furfuryl alcohol at room temperature. Therefore, highly concentrated emulsions could not be prepared using these surfactants, by addition of decane to surfactant−alcohol mixtures. Simple experiments confirmed that the emulsions could not be formed.

Synperonic A20 (HLB = 16.2), Pluronic P123 (HLB = 9), and Pluronic F127 (HLB = 20) were soluble in furfuryl alcohol. Consequently, it was concluded that this alcohol required a relatively hydrophilic nonionic surfactant, as expected. Highly concentrated emulsions were prepared using these surfactants, and the stability of the resulting emulsions was evaluated by simple visual inspection. Table 1 shows a summary of the results obtained using different surfactants, in which decane was used as oil at either 70 or 80 wt %.

Emulsions containing 70 wt % decane, and requiring more than 10 wt % surfactant, could be prepared using Synperonic A20 as surfactant, in accordance to Brancroft rule. However, the stability was very poor, and almost complete phase separation due to coalescence occurred in approximately 1 h.

In order to prevent coalescence, P123 and F127 nonionic copolymers were also tested (Table 1). Highly concentrated emulsions could be obtained using these surfactants, which are relatively hydrophilic and possess large molecular weights that may increase adsorption and thus enhance steric stabilization. The most stable emulsions were those prepared with F127, with higher hydrophilicity. For this reason, F127 surfactant was selected and the phase behavior of the system composed by furfuryl alcohol/Pluronic F127/decane was studied.

Figure 1 shows a partial ternary phase diagram of this system at 25 °C. Furfuryl alcohol polymerized slowly, even in the absence of HCl, and therefore, phase separation could not be extended over long periods of time (more than 1 month). Consequently, the phase boundaries between different regions in the phase diagram are approximate, and are represented by dotted lines.
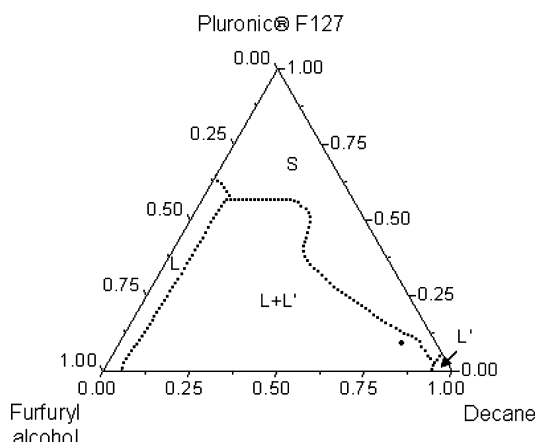
Figure 1. Partial ternary phase diagram of furfuryl alcohol/Pluronic P127/decane system. Two single-phase regions (L) and (L′), and a large immiscibility region (L+L′) are observed. Another large region, in which the surfactant is present as an insoluble solid phase (S), is observed. The filled circle indicates the composition selected for furfuryl alcohol polymerization.

A rather simple phase behavior was obtained, since only two single phase regions (indicated as L and L′) were observed. Moreover, liquid crystalline phases were not present. The phase diagram shows a large two liquid-phase region (L+L′), along the alcohol−oil axis, in which decane-in-alcohol emulsions could be prepared. The F127 surfactant shows higher affinity for furfuryl alcohol than for decane, since the alcohol can dissolve up to ≈35 wt % surfactant, whereas the maximum concentration of F127 surfactant that can be dissolved in decane is around 5 wt %. Therefore, one can conclude that F127 could stabilize oil-in-alcohol highly concentrated emulsions.

The composition 10 wt % surfactant, 10 wt % alcohol, and 80 wt % decane was selected, since stability of this emulsion was higher (Table 1). Optical microscopy images of oil-in-alcohol highly concentrated emulsion, just after preparation and 24 h later, are shown in Figure 2. The emulsions consisted of close-packed polyhedral and polydisperse droplets separated by a thin film of continuous phase. The average droplet size was around 10 μm (Figure 2a) just after preparation, while after 24 h the size had increased to around 25 μm (Figure 2b). The increase in droplet size is clearly observed by comparing the micrographs in Figure 2a and b, in which magnification was the same. It was attributed to coalescence, since generally oil−alcohol interfaces result in low surfactant adsorption, producing flexible monolayers, which are highly prone to coalescence.[39−41] It is also known that polar solvents, such as short-chain alcohols (e.g., ethanol), decrease the cohesive properties of water. This effect produces a significant increase of the critical micelle concentration (CMC) at high alcohol concentrations, in water−alcohol mixtures.[39−41] Consequently, polar solvents inhibit formation of micelles, although submicellar aggregates can be formed. The overall effect is a reduction in surfactant adsorption, and emulsion stability is greatly affected due to coalescence, as observed in oil−alcohol mixtures. In addition, it could be postulated that coalescence may also be favored by a depletion mechanism, because of the high surfactant concentration.

The droplet size distribution, just after preparation, was determined by laser diffraction, and the results are presented in Figure 3. The average droplet size was approximately 19 μm
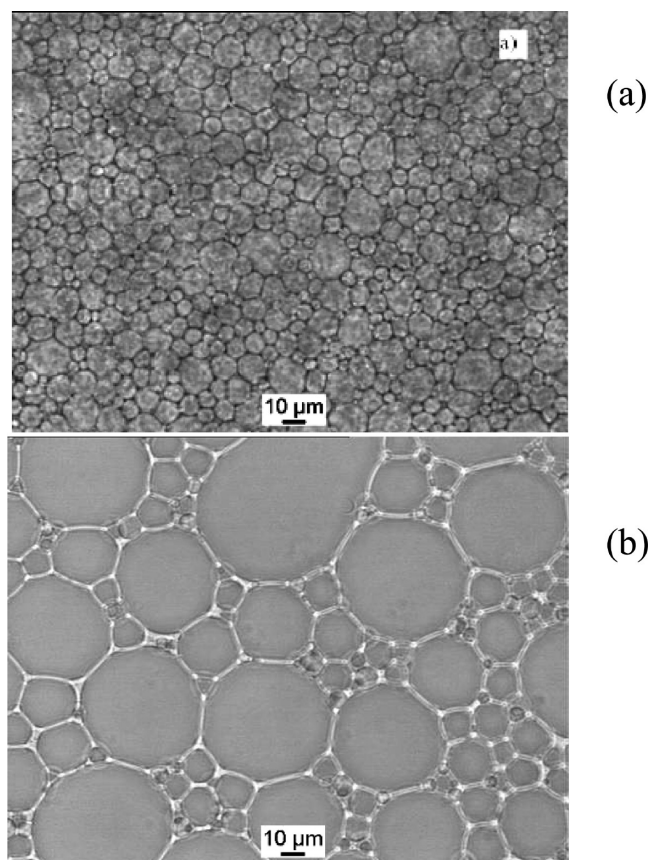

Figure 2. Images of a decane-in-furfuryl alcohol highly concentrated emulsion after preparation (a) and 24 h later (b). A large increase in droplet size can be observed.
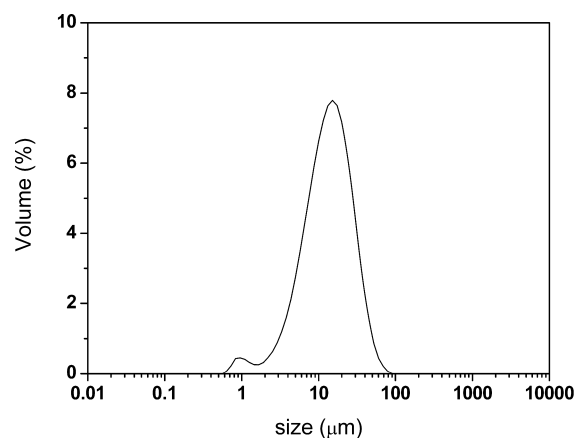

Figure 3. Droplet size distribution of furfuryl alcohol highly concentrated emulsions, determined by light diffraction, in freshly prepared samples.

and the polydispersity (span) was 1.9. The droplet size distribution at 24 h could not be precisely determined by light diffraction, because of inhomogeneous coalescence and droplet segregation.

Although this highly concentrated emulsion was not very stable, it showed enough stability to carry out the polymerization at 25 °C, induced by addition of hydrochloric acid as described in the Experimental Section. As expected, a dark monolith was obtained, since oligomers were formed with an intense beige color, which turned to black as the reaction

reaches its end.[38] After purification and drying, no shrinkage of the monoliths was observed, as can be seen in Figure 4. It
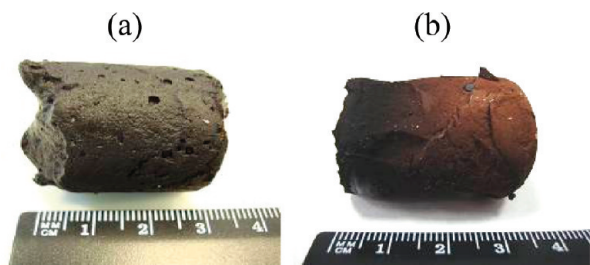
(a)   (b)

Figure 4. Photographs of the poly(furfuryl alcohol) monoliths (a) before purification and (b) after purification and drying.

should be remarked that, to the best of our knowledge, it is the first time that macroprous foams are obtained by using oil-in-alcohol highly concentrated emulsions, since the stability of emulsions with low and medium chain-length alcohols is rather low due to poor surfactant adsorption in such interfaces.[39−41] However, emulsions can have sufficient stability for polymerization, by using hydrophilic block copolymers with high molecular weight that enhance steric stabilization.

The bulk density of the material obtained by this single-pot method was rather low, ≈ 0.11 g mL^{-1}, and the total pore volume was quite large, ≈ 8.2 mL g^{-1}, as calculated from $1/\rho_b - 1/\rho_w$, where ρ_w is the wall density, assumed to be the polymer density ≈ 1.1 g mL^{-1}, and ρ_b is the bulk density. These values of bulk density and total pore volume are similar to other macroporous materials already described in the literature.[7,17]

The scanning electron micrograph (Figure 5) shows that the macroporous structure of the solid foams consists of a pore network with cells interconnected though narrow necks. The cell size seems similar to the droplet size of highly concentrated emulsion used as template (average droplet size = 19 μm). The comparison between emulsions and foams is not straightforward, since mercury intrusion porosimetry cannot be used to obtain precise measurements of cell size, due to damage of pore walls at high mercury pressure. However, from microscopy images, it can be inferred that droplet size did not greatly change during polymerization. Therefore, the solid foam is an approximate replica of the emulsion.

The transmission infrared spectrum of the poly(furfuryl alcohol) monolith (Figure 6) showed two bands at 2921 and 1714 cm^{-1}, attributed to poly(furfuryl alcohol),[37] confirming the formation of this polymer. The band at 2921 cm^{-1} is attributed to C−H stretching of the aliphatic CH$_2$ groups in the polymer, and the band at 1714 cm^{-1} is related to diketone C=O stretching, which is formed by the opening of furan rings.[37]

Information about the porosity of the poly(furfuryl alcohol) monolith was obtained by nitrogen adsorption/desorption isotherms (Figure S1 in the Supporting Information). The purified monolith showed an isotherm typical for a purely macroporous foam, without hysteresis loop, and small adsorption at low pressure, which indicates no presence of micropores and mesopores. The BET analysis showed a very small surface area (S_{BET} = 11.9 ± 0.1 m^2 g^{-1}), and therefore, the material is macroporous, with negligible microporosity and mesoporosity. Consequently, the BJH analysis indicated a very small mesopore volume, which is approximately zero (the calculated value was 0.07 mL g^{-1}). It is likely that almost all pore volume remains in large pores since the total pore volume
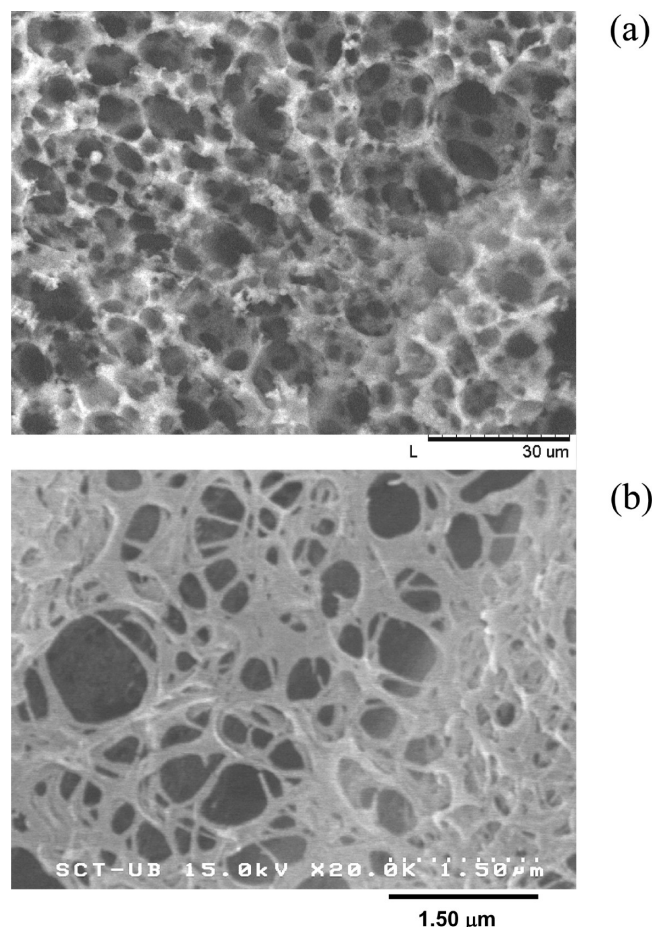

Figure 5. SEM images of poly(furfuryl alcohol) monoliths. (a) Image captured at low magnification (scale bar = 30 μm) and (b) higher magnification (scale bar = 1.5 μm).

is ≈ 8.2 mL g^{-1}, as mentioned before. Big macropores, observed by SEM, and the sharp increase of the adsorbed volume in the nitrogen isotherms also indicate a large macropore volume.

It is known that pyrolization of poly(furfuryl alcohol) leads to carbonization, and this polymer can allow one to obtain carbon materials with an acceptable yield.[36,38,48] The mechanism of carbonization has been described.[48] Poly(purfuryl alcohol) spontaneously decomposes upon heating at 300 °C in the absence of oxygen, and it begins to form a mesoporous solid consisting of polymer remnants and aromatic cores. However, it has also been described that the mesopores collapse by pyrolyzing at higher temperatures. The heteroatoms are driven out by pyrolyzing above 400 °C, and the pores become unstable and collapse, forming a glassy microporous carbon material which is nongraphitizing, with the absence of long-range layering.[48]

A similar trend has been observed for the materials described in the present work. The material mostly decomposed by pyrolyzation at 400 °C under nitrogen atmosphere, leaving only a small residue of nondecomposed material. However, more careful experiments were carried out by degassing the poly(furfuryl alcohol) monoliths, under vacuum at 200 °C, and then heating up to 300 °C, under nitrogen atmosphere. The resulting monoliths had a black color, indicating that carbonization had occurred. Observations by SEM (Figure 7) showed that macropores were preserved.
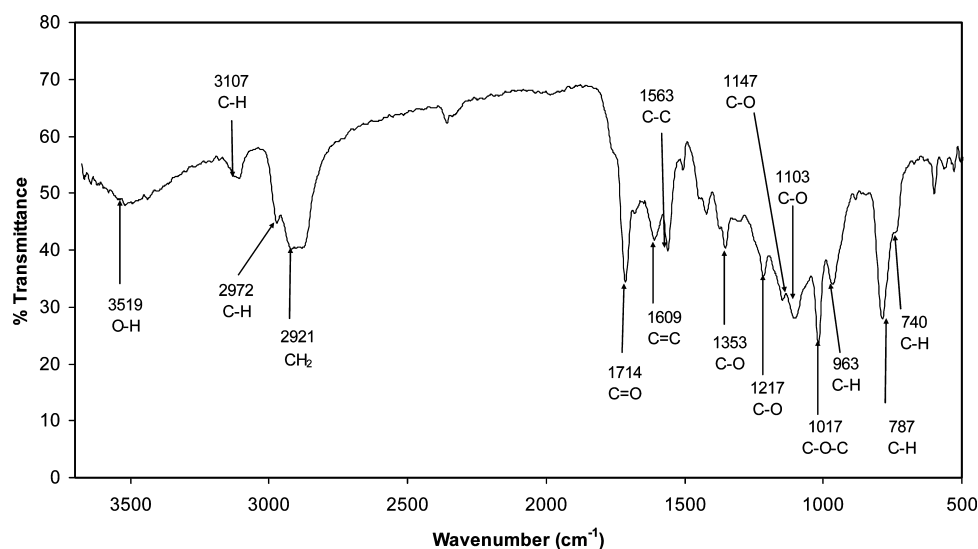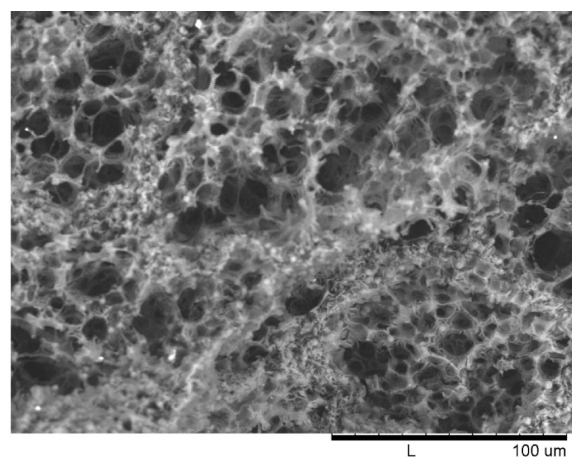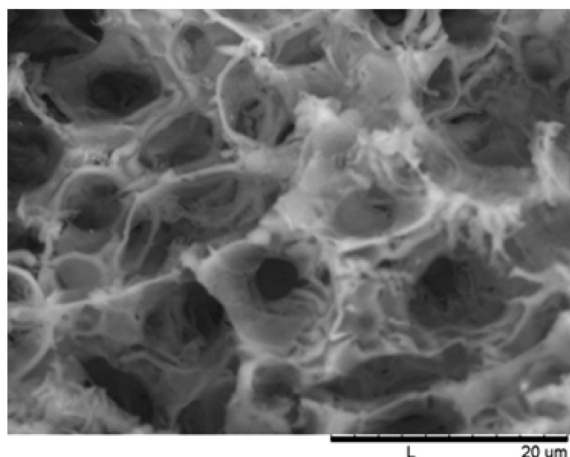
Figure 6. FTIR spectrum of a poly(furfuryl alcohol) porous monolith.

The images shown in Figure 7 indicate that the resulting material is macroporous. However, the pore morphology and surface topography were affected by the thermal treatment, and

(a)

(b)

Figure 7. SEM Images of a carbonaceous monolith treated at 300 °C, under nitrogen atmosphere. (a) Image captured at low magnification (scale bar = 100 μm) and (b) higher magnification (scale bar = 20 μm).

a rough surface can be observed. The material has a rather high carbon content, since determinations by element analysis indicated that the C/H molar ratio was 2.55/1, which is more than twice the theoretical ratio, 1.25/1, for poly(furfuryl alcohol). Consequently, the thermal treatment increased the carbon content, and as a conclusion it could be postulated that these poly(furfuryl alcohol) porous monoliths may have interesting applications as precursors for the preparation of highly porous carbonaceous materials. The preparation of these porous materials will be the subject of future works.

■ **CONCLUSIONS**

Oil-in-furfuryl alcohol highly concentrated emulsions have been prepared, and their stability was sufficient for use as templates. Poly(furfuryl alcohol) solid foams have been obtained using a simple method, by polymerizing furfuryl alcohol in the external phase of the emulsions. The resulting materials are mainly macroporous and retain the size distribution and morphology from the highly concentrated emulsions. The bulk density is low, ≈0.11 g mL^{-1}, the total pore volume is large, ≈8.2 mL g^{-1}, and the porous texture consists of an interconnected open network. These materials could be used as precursors for carbonaceous foams, obtained by thermal treatment under nitrogen atmosphere. Macroporous carbonaceous materials, with a C/H molar ratio equal to 2.55/1, could be prepared.

■ **ASSOCIATED CONTENT**

ⓢ Supporting Information

Nitrogen adsorption/desorption isotherms of a poly(furfuryl alcohol) macroporous foam (Figure S1). The composition of the initial emulsion was 10 wt % F127, 10 wt % furfuryl alcohol, and 80 wt % decane. This material is available free of charge via the Internet at http://pubs.acs.org.

■ **AUTHOR INFORMATION**

Corresponding Author

*E-mail: jordi.esquena@iqac.csic.es. Telephone: 34 93 400 61 78. Fax: 34 93 204 59 04.

■ **REFERENCES**

(1) Lissant, K. J. The geometry of high-internal-phase-ratio emulsions. *J. Colloid Interface Sci.* **1966**, *22*, 462−468.

(2) Lissant, K. J.; Mayhan, K. G. A study of medium and high internal phase ratio water/polymer emulsions. *J. Colloid Interface Sci.* **1973**, *42*, 201−208.

(3) Princen, H. M. Highly concentrated emulsions. I. Cylindrical systems. *J. Colloid Interface Sci.* **1979**, *71*, 55−66.

(4) Kunieda, H.; Fukui, Y.; Uchiyama, H.; Solans, C. Spontaneous formation of highly concentrated water-in-oil emulsions (gel-emulsions). *Langmuir* **1996**, *12*, 2136−2140.

(5) Solans, C.; Pons, R.; Kunieda, H. In *Modern Aspects of Emulsion Science*; Binks, B.P., Ed.; Royal Society of Chemistry: Cambridge, 1998.

(6) Solans, C.; Esquena, J.; Azemar, N.; Rodríguez, C.; Kunieda, H. In *Emulsions: Structure, Stability and Interactions*; Petsev, D.N., Ed.; Elsevier: Amsterdam, 2004.

(7) Barby, D.; Haq, Z. Low density porous cross-linked polymeric materials and their preparation. European patent 0060138, 1982.

(8) Williams, J. M.; Wrobleski, D. A. Spatial distribution of the phases in water-in-oil emulsions. Open and closed microcellular foams form cross-linked polystyrene. *Langmuir* **1988**, *4*, 656−662.

(9) Williams, J. M. Toroidal microstructures from water-in-oil emulsions. *Langmuir* **1988**, *4*, 44−49.

(10) Ruckenstein, E.; Park, J. S. Hydrophilic-hydrophobic polymer composites. *J. Polym. Sci., Polym. Lett.* **1988**, *26*, 529−536.

(11) Hainey, P.; Huxham, I. M.; Rowatt, B.; Sherrington, D. C.; Tetley, L. Synthesis and ultrastructural studies of styrene-divinylbenzene polyHIPE polymers. *Macromolecules* **1991**, *24*, 117−121.

(12) Ruckenstein, E.; Park, J. S. Stable concentrated emulsions as precursors for hydrophilic-hydrophobic polymers composites. *Polymer* **1992**, *33*, 405−417.

(13) Cameron, N. R.; Sherrington, D. C.; Albiston, L.; Gregory, D. P. Study of the formation of the open-cellular morphology of poly(styrene/divinylbenzene) polyHIPE materials by cryo-SEM. *Colloid Polym. Sci.* **1996**, *274*, 592−595.

(14) Cameron, N. R.; Sherrington, D. C. High Internal Phase Emulsions (HIPEs) − Structure, Properties and Use in Polymer Preparation. *Adv. Polym. Sci.* **1996**, *126*, 163−214.

(15) Esquena, J.; Sankar, G. S. R. R.; Solans, C. Highly concentrated W/O emulsions prepared by the PIT method as templates for solid foams. *Langmuir* **2003**, *19*, 2983−2988.

(16) Maekawa, H.; Esquena, J.; Bishop, S.; Solans, C.; Chmelka, B. F. Meso/macroporous inorganic oxide monoliths from polymer foams. *Adv. Mater.* **2003**, *15*, 591−596.

(17) Esquena, J.; Solans, C. In *Emulsions and emulsion stability*; Sjöblom, J., Ed.; Surfactant Science Series; Francis & Taylor: New York, 2006.

(18) Solans, C.; Esquena, J.; Azemar, N. Highly concentrated (gel) emulsions, versatile reaction media. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 156−163.

(19) Lépine, O.; Birot, M.; Deleuze, H. Preparation of a poly(furfuryl alcohol)-coated highly porous polystyrene matrix. *Macromol. Mater. Eng.* **2009**, *294*, 599−604.

(20) Menner, A.; Powell, R.; Bismarck, A. Open porous polymer foams via inverse emulsion polymerization: Should the definition of high phase (ratio) emulsions be extended? *Macromolecules* **2006**, *39*, 2034−2035.

(21) Ikem, V. O.; Menner, A.; Bismarck, A. High internal phase emulsions stabilized solely by functionalized silica particles. *Angew. Chem., Int. Ed.* **2008**, *47*, 8277−8279.

(22) Imhof, A.; Pine, D. J. Ordered macroporous materials by emulsion templating. *Nature* **1997**, *389*, 948−951.

(23) Yi, G. R.; Moon, J. H.; Manoharan, V. N.; Pine, D. J.; Yang, S. M. Packings of uniform microspheres with ordered macroporous fabricated by double templating. *J. Am. Chem. Soc.* **2002**, *124*, 13354−13355.

(24) Carn, F.; Colin, A.; Achard, M. F.; Deleuze, H.; Sellier, E.; Birot, M.; Backov, R. Inorganic monoliths hierarchically textured via concentrated direct emulsion and micellar templates. *J. Mater. Chem.* **2004**, *14*, 1370−1376.

(25) Ungureanu, S.; Birot, M.; Laurent, G.; Deleuze, H.; Babot, O.; Julián-López, B.; Achard, M. F.; Popa, M. I.; Sanchez, C.; Backov, R. One-pot synthesis of the first series of emulsion based hierarchical hybrid organic-inorganic open-cell monolith possessing tunable functionally (organo-Si(HIPE) series). *Chem. Mater.* **2007**, *19*, 5786−5796.

(26) Brun, N.; Prabaharan, S. R. S.; Surcin, C.; Morcrette, M.; Deleuze, H.; Birot, M.; Babot, O.; Achard, M. F.; Backov, R. Design of hierarchical porous carbonaceous foams a dual-template approach and their use as electrochemical capacitor and Li ion battery negative electrodes. *J. Phys. Chem. C* **2012**, *116*, 1408−1421.

(27) Binks, B. P. Macroporous silica from solid-stabilized emulsion templates. *Adv. Mater.* **2002**, *14*, 1824−1827.

(28) Chiu, J. J.; Pine, D. J.; Bishop, S. T.; Chmelka, B. F. Friedel-Crafts alkylation properties of aluminosilica SBA-15 meso/macro-porous monoliths and mesoporous powders. *J. Catal.* **2004**, *221*, 400−412.

(29) Sen, T.; Tiddy, G. J. T.; Casci, J. L.; Anderson, M. W. Meso-cellular silica foams, macro-cellular silica foams and mesoporous solids: A study of emulsion-mediated synthesis. *Microporous Mesoporous Mater.* **2005**, *78*, 255−263.

(30) Blin, J. L.; Bleta, R.; Ghanbaja, J.; Stébé, M. J. Fluorinated emulsions: Templates for the direct preparation of macroporous-mesoporous silica with a highly ordered array of large mesopores. *Microporous Mesoporous Mater.* **2006**, *94*, 74−80.

(31) Sen, T.; Tiddy, G. J. T.; Casci, J. L.; Anderson, M. W. Silica materials with meso- and macropores. WO/2003/064322 Patent Application, 2003.

(32) Hu, Y.; Nareen, M.; Humphries, A.; Christian, P. A novel preparation of macroscopic beads of porous silica. *J. Sol-Gel Sci. Technol.* **2010**, *53*, 300−306.

(33) Fournier, A. C.; McGrath, K. M. Synthesis of porous oxide ceramics using a soft responsive scaffold. *J. Mater. Sci.* **2012**, *47*, 1217−1222.

(34) Franklin, R. E. Crystalline growth in graphitizing and non-graphitizing carbons. *Proc. R. Soc. London* **1951**, *209*, 196−218.

(35) Liu, D.; Lei, J. H.; Guo, L. P.; Qu, D.; Li, Su, B.L. One-pot aqueous route to synthesize highly ordered cubic and hexagonal mesoporous carbons from resorcinol and hexamine. *Carbon* **2012**, *50*, 476−487.

(36) Fitzer, E.; Schaefer, W.; Yamada, S. The formation of glasslike carbon by pyrolysis of polyfurfuryl alcohol and phenolic resin. *Carbon* **1969**, *7*, 643−646.

(37) Zarbin, A. J. G.; Bertholdo, R.; Oliveira, M. A. F. C. Preparation, characterization and pyrolysis of poly(furfuryl alcohol)/porous silica glass nanocomposites: novel route to carbon template. *Carbon* **2002**, *40*, 2413−2422.

(38) Bertarione, S.; Bonino, F.; Cesano, F.; Jain, S.; Zanetti, M.; Scarano, D.; Zecchina, A. Micro-FTIR and micro-raman studies of a

carbon film prepared from furfuryl alcohol polymerization. *J. Phys. Chem. C* **2009**, *113*, 10571−10574.

(39) Shirahama, K.; Kashiwabara, T. The CMC-decreasing effects of some added alcohols on the aqueous sodium dodecyl sulfate solutions. *J. Colloid Interface Sci.* **1971**, *36*, 65−70.

(40) Singh, H. N.; Swarup, S. Effect of monohydroxy alcohols and urea on the cmc of surfactants. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1534−1538.

(41) Zana, R. Aqueous surfactant-alcohol systems: A review. *Adv. Colloid Interface Sci.* **1995**, *57*, 1−64.

(42) The Merck Index: an encyclopedia of chemical drugs, and biologicals, 11th ed.; Budavari, S., Ed; Merck & Co. Inc.: Rahway, NJ, 1989.

(43) Álvarez, S.; Fuertes, A. B.; Esquena, J.; Solans, C. Meso/macroporous carbon monoliths from polymeric foams. *Adv. Mater.* **2004**, *6*, 897−899.

(44) Álvarez, S.; Fuertes, A. B. Synthesis of macro/mesoporous silica and carbon monoliths by using a commercial polyurethane foam as sacrificial template. *Mater. Lett.* **2007**, *61*, 2378−2381.

(45) Brunauer, S.; Emmett, P. H.; Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, *60*, 309−319.

(46) Barrett, E. P.; Joyner, L. G.; Halenda, P. H. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373−380.

(47) Bancroft, W. D. The theory of emulsification, V. *J. Phys. Chem.* **1913**, *17*, 501−519.

(48) Burket, C. L.; Rajagopalan, R.; Marencic, A. P.; Dronvajjala, K.; Foley, H. C. Genesis of porosity in polyfurfuryl alcohol derived nanoporous carbon. *Carbon* **2006**, *44*, 2957.