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Synthesis of highly porous matrices by CO_2-in-water emulsion polymerization stabilized with new glycosurfactants

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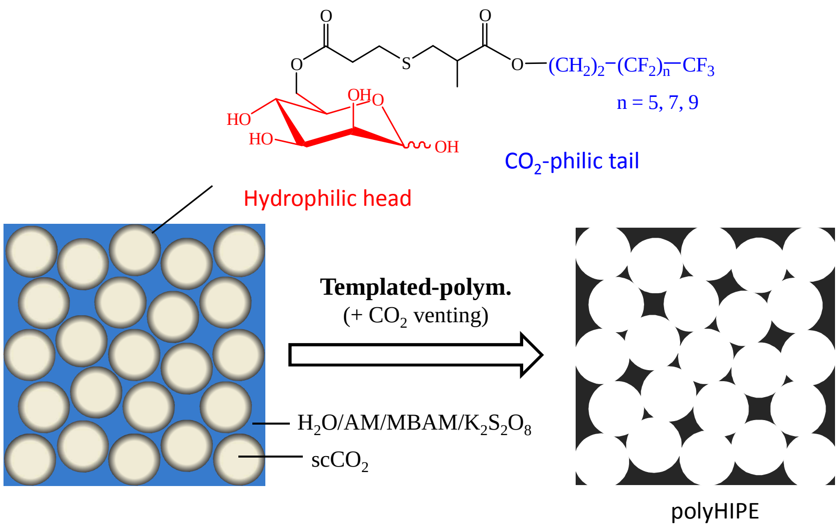
Porous polymer structures can be prepared by high internal phase emulsion (HIPE) polymerization. Typically, the internal droplets phase of the emulsion exceeds 74% of the total volume and the monomer is located in the continuous phase. After polymerization, the removal of the internal phase creates cavities in the polymer matrix (scheme 1). The resulting materials, called polyHIPEs, exhibit highly interconnected voids and sustain a variety of applications such as scaffolds for tissue engineering, support for catalyst, immobilization of proteins, etc.[1] Interestingly, Cooper *et al.* reported the possible use of supercritical carbon dioxide ($scCO_2$) as an alternative to the traditional organic solvents for the synthesis of polyHIPE.[2] In addition to be an inexpensive, non-toxic, non-flammable and environmentally friendlier medium, CO_2 is readily removed at the end of the process since it reverts to gaseous phase upon depressurization.



Scheme 1. Synthesis of polyHIPE by $scCO_2$-in-water emulsion polymerization.

In this work, we designed novel non-ionic fluorinated carbohydrates by enzymatic modification of mannose[3, 4] and we used it as surfactants for the synthesis of polyHIPEs in $scCO_2$ (scheme 1). The hydrophilic head of the surfactant consists in a sugar moiety whereas the fluorinated tail has a strong affinity for the $scCO_2$ phase. The stabilization of the $scCO_2$-water interface by these glycosurfactants was demonstrated by tensiometry measurements[5] and the resulting acrylamide polyHIPEs were characterized by scanning electron microscopy (Figure 1A), pycnometry and porosimetry.[6] The effect of the nature and the concentration of the surfactant on the porous polymer structure will be discussed. Finally, the properties of the resulting polymer scaffolds were tuned by performing dispersion polymerizations within their cavities filled with supercritical CO_2 leading to microsphere-loaded porous polymers[6] (Figure 1B).

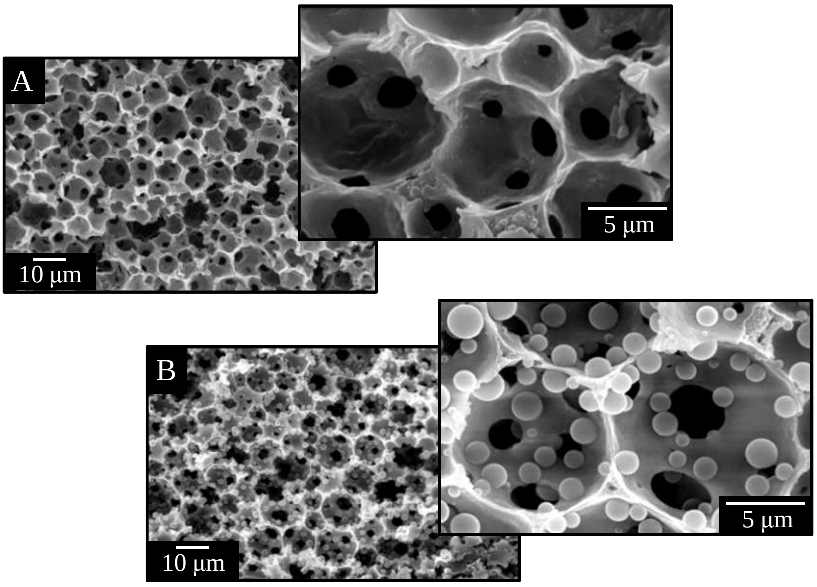


Figure 1. Scanning electron microscopy images of a polyacrylamide polyHIPE before (A) and after (B) methyl methacrylate dispersion polymerization within the cavities.

References

1. Kimmins S. D., Cameron N. R. *Adv. Funct. Mater.*, **2011**, 21, 211-225.
2. Butler R., Davies C. M., Cooper A. I., *Adv. Mater.*, **2001**, 13, 1459-1463.
3. Favrelle A., Boyère C., Laurent P., Broze G., Blecker C., Paquot M., Jérôme C., Debuigne A., *Carbohydr. Res.*, **2011**, 346, 1161-1164.
4. Boyère C., Favrelle A., Broze G., Laurent P., Nott K., Paquot M., Blecker C., Jérôme C., Debuigne A., *Carbohydr. Res.*, **2011**, 346, 2121-2125.
5. Favrelle A., Boyère C., Tran M. K., Clavignac B, Paquot M., Boury F., Jérôme C., Debuigne A. *J. Colloid Int. Sci*., **2012,** submitted.
6. Boyère C., Léonard A. F., Grignard B., Favrelle A., Pirard J.-P., Paquot M., Jérôme C., Debuigne A., *Chem. Commun.* **2012**, 48, 8356-8358.

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