Cellular Polymer Monoliths Made via Pickering High Internal Phase Emulsions

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Cellular materials have a porous structure, which can consist of closed cells and/or open cells. This feature makes these materials interesting for a wide range of applications, such as supports for catalysts, mechanical scaffolds, for example, for tissue growth, materials for electrical, sound, and heat insulation, three-dimensional batteries, and optical band gap materials.[1]

One way to create cellular materials is to use emulsion droplets as templates.[2] Imhof and Pine showed the preparation of uniform macroporous silica, titania, and poly(acrylamide) which were synthesized around a concentrated dispersion of liquid emulsion droplets with narrow particle size distribution.[3] Binks reported the preparation of macroporous silica using solid-stabilized/Pickering[4] emulsions as templates. These materials had either cellular, bicontinuous, or colloidal gel type morphologies.[5]

Cellular polymers formed by creation of a high internal phase emulsion and subsequent polymerization of the continuous phase are often referred to as poly(HIPE) and were pioneered by Bartl,[6,7] Lissant,[8] and Barby.[9] A high internal phase emulsion, or gel emulsion, has values for its volume fraction of the dispersed phase greater than 0.74, the maximum packing density for monodisperse hard spheres. The porous polymer materials are generally formed via templates of water-in-monomer gel emulsions stabilized with surfactants such as sorbitan monooleate (SPAN 80)[10] or a mixture of nonionic, anionic, and cationic surfactants: sorbitan monolaureate (SPAN 20), dodecylbenzenesulfonic acid sodium salt (DDBSS), and cetyltrimethylammonium bromide (CTAB).[11]

Herein we report for the first time the concept of using particle-stabilized, or Pickering,[4] emulsions as a template to manufacture poly(HIPE)s. The particles used as stabilizers in Pickering emulsions are generally perceived to be irreversibly trapped at the liquid−liquid interface.[12] The energy barrier to re-enter either of the two bulk phases is typically several orders of magnitude larger than the thermal energy, k_BT. Moreover, after an initial limited coalescence process, Pickering emulsions are known to be extremely stable with shelf life stabilities of months.[13]

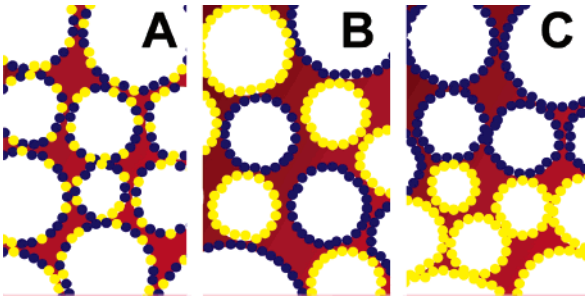

Figure 1. Three possible designs using two different particles as Pickering stabilizers of cellular polymer monoliths. Two-dimensional projections are from the side (*y*,*z* plane). In example A, the particles are randomly distributed over each water droplet, or cell; B shows a random blend of two Pickering emulsions with each droplet stabilized by only one type of particle; and in C, we pack one Pickering emulsion on top of the other creating distinct zones or layers, in the cellular monolith.

These characteristics can produce a number of benefits in poly(HIPE) manufacturing, not achievable when using conventional low-molecular-weight surfactants. The use of Pickering stabilized emulsion droplets as templates will functionalize the cell walls of the poly(HIPE)s with a layer of solid particles. These particles could for example contain functional groups for substrate, for example, protein, interaction. Moreover, the irreversible adhesion of the particles to the interface of the emulsion droplets will allow for the functionalization of individual cells with different types of particles, via one simple synthetic procedure. This creation of different micro-environments among the cells could be of great potential benefit in the design of porous monoliths for multistep reactions. We will demonstrate this principle by using a combination of fluorescently labeled and non-labeled cross-linked latex particles as stabilizers in three possible poly(HIPE) designs projected in Figure 1.

The synthesis strategy can be set out in three consecutive steps:

(i) Microgels of submicrometer dimensions synthesized via miniemulsion polymerization (See Supporting Information, S1, for details) were used as solid stabilizers to create Pickering water-in-oil emulsions.[14] The cross-linking of these latex particles was essential to prevent disintegration via swelling once assembled at the liquid−liquid interface, which ultimately results in loss of Pickering stabilization. For the poly(HIPE)s containing two different types of particle stabilizers we used both hostasol-labeled and non-labeled microgels. As tag we used 2-(6-methacryloyloxyhexyl)-

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(1) Gibson, L. J.; Ashby, M. F. *Cellular Solids: Structure and properties,* 2nd ed.; Cambridge University Press: New York, 1999.
(2) Zhang, H.; Cooper, A. I. *Soft Matter* **2005**, *1*, 107−113.
(3) Imhof, A.; Pine, D. J. *Chem. Eng. Technol.* **1998**, *21*, 682−685.
(4) Pickering, S. U. *J. Chem. Soc., Trans.* **1907**, *91*, 2001−2021.
(5) Binks, B. P. *Adv. Mater.* **2002**, *14*, 1824−1827.
(6) Bartl, H.; v. Bonin, W. *Makromol. Chem.* **1962**, *57*, 74−95.
(7) Bartl, H.; v. Bonin, W. *Makromol. Chem.* **1963**, *66*, 151−156.
(8) Lissant, K. J.; Mayhan. K. G. *J. Colloid Interface Sci.* **1973**, *42*, 201−208.
(9) Barby, D.; Haq, Z. EP0060138, 1982.
(10) Williams, J. M. *Langmuir* **1991**, *7*, 1370−1377.
(11) Barbetta, A.; Cameron, N. R. *Macromolecules* **2004**, *37*, 3202−3213.
(12) Pieranski, P. *Phys. Rev. Lett.* **1980**, *45*, 569−572.
(13) Binks, B. P. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21−41.
(14) (a) Fujii, S.; Read, E. S.; Binks, B. P.; Armes, S. P. *Adv. Mater.* **2005**, *17*, 1014−1018. (b) Ngai, T.; Behrens, S. H.; Auweter, H. *Chem. Commun.* **2005**, *3*, 331−333. (c) Bon, S. A. F.; Cauvin, S.; Colver, P. J. *Soft Matter* **2007**, *3*, 194−199.

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thioxantheno[2,1,9-dej]iso-quinoline-1,3-dione, a hostasol methacrylate derivative.[15] A variety of monomers were used to make up the oil phase, such as divinylbenzene, mixtures of styrene/divinylbenzene, and mixtures of *n*-butyl and *n*-lauryl methacrylate/ethylene glycol dimethacrylate. The oil phase also included approximately 1.0 wt % of a radical initiator, being di-*tert*-butylperoxyoxalate (CAUTION: see Supporting Information, S1)[16] or 2,2′-azobis(2,4-dimethyl valeronitrile) (V-65). The microgel stabilized water-in-oil emulsions were generated by either shaking (large droplets) or using an ultra-turrax (small droplets). Note that the microgels are dispersed in the aqueous phase prior to mixing.

(ii) The Pickering emulsions were allowed to settle via gravitation/buoyancy, typically for about 1 h for large droplets with occasional gentle shaking to increase the packing efficiency. According to Stokes's law (1851) this is the time needed for a "hard sphere" of water with a diameter of 10 μm to drop 4.42 cm in toluene, conditions which are easily met for our monolith designs. For the Pickering emulsions generated with the ultra-turrax (small droplets) we used centrifugation (1000*g*, 2 times for 5 min) and removed the excess organic phase prior to polymerization. Because the emulsion droplet size distributions were not monodisperse this generated high internal phase Pickering emulsion layers (volume fraction > 0.74). A pre-made mixture of hostasol-labeled (yellow) and non-labeled (white) microgels dispersed in the waterphase was used for system **A**. The random blend of emulsion droplets each stabilized with one type of particles, **B**, was generated by gentle mixing of two pre-made Pickering emulsions via tumbling by hand of the vials. For the layered systems, **C**, one high internal phase Pickering emulsion template was carefully placed on top of the other using a pipet.

(iii) The stacked high internal phase Pickering emulsions were susbequently polymerized via radical polymerization of the continuous monomer phase either at room temperature, using di-*tert*-butylperoxyoxalate[16] (CAUTION: See Supporting Information, S1), or at 51 °C using V-65 as initiator. Note that in some experiments the excess bulk phase of pure monomer was not removed. Typically the polymerization was allowed to proceed for a minimum of four initiator half-lives. The poly(HIPE) monoliths produced were obtained by removal of the cylindrical glass reaction vessel and were dried in air and subsequently under vacuum. In case of isolated cell structures the monoliths were crushed.

Figure 2 depicts three possible monolith scenarios using two different particle stabilizers, the continuous phase being poly (*n*-butyl methacrylate). From the two right-most images it is evident that schematic design **C** has been achieved with the hostasol-labeled microgels embedded at the bottom and the top of the cellular monolith, respectively. To distinguish between designs **A** and **B**, we performed confocal microscopy. The results are given in Figure 3 for scenario **B** (see also Supporting Information, S4, for a movie). From this image it can be clearly seen that only a fraction of the cells

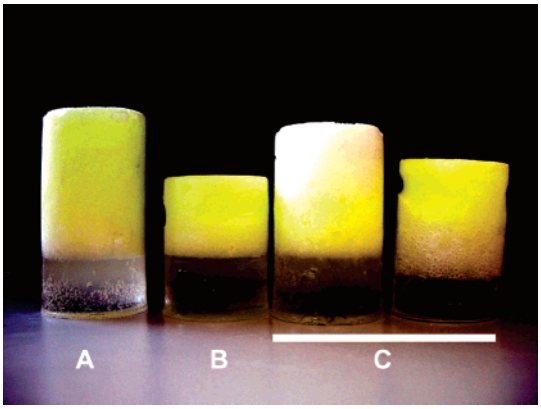

Figure 2. Collection of poly(*n*-butyl methacrylate) based cellular polymer monoliths produced via Pickering high internal phase emulsions after removal of the reaction vial. The monoliths are placed upside down. The clear bottom layer in the image is bulk polymerized *n*-butyl methacrylate. The yellow/white top layers are the polymerized w/o emulsion templates. Indexes A, B, and C correspond with the three possible poly(HIPE) designs as given in Figure 1. The difference in heights is caused by the use of different overall amounts of material in the different experiments.

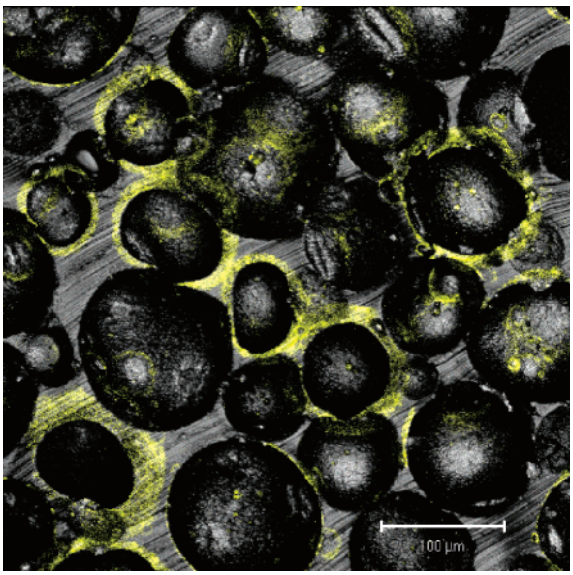

Figure 3. Cumulative projection of *z* slices obtained via dual channel confocal microscopy. The first channel (white) represents the reflected light signals of the Pickering poly(HIPE), whereas the second channel (yellow) exclusively shows the fluorescent emission and thus position of the hostasol labeled particle stabilizers. The presence of the yellow rings around some of the poly(HIPE) cells clearly matches design B from Figure 1. For a movie, see Supporting Information, S4.

are covered with fluorescent microgels, in the image colored yellow. The location of the yellow "rings" shows that the fluorescent particles are located mostly at the cell interfaces. Moreover, it proves that no interchange of particles between the Pickering stabilized emulsion droplets is observed, otherwise all cells would show some fluorescent emission. These findings are to be expected because the energy well at the liquid−liquid interface is too large for the particles to escape.[12]

The clear bulk polymer phase was removed from the monoliths after which their overall density was calculated via gravimetry assuming cylindrical cellular polymer monolith geometry and a known density of the scaffold polymer. All Pickering poly(HIPE) materials showed values for the volume fraction of air between 0.76 and 0.87.

(15) Tronc, F.; Li, M.; Lu, J.; Winnik, M. A.; Kaul, B. L.; Graciet, J.-C. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 766−778.
(16) Bartlett, P. D.; Benzing, E. P.; Pincock, R. E. *J. Am. Chem. Soc.* **1960**, *82*, 1762−1768.

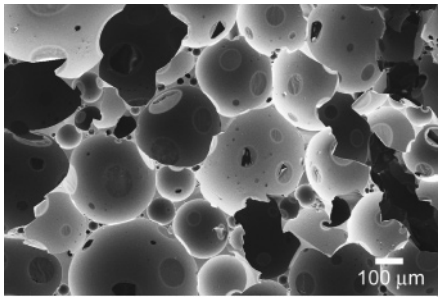

Figure 4. FE-SEM image of cellular monoliths scaffolded with poly(divinyl benzene).

Upon evaporation of the water under vacuum the monoliths made from poly(*n*-butyl methacrylate) buckled (for details see Supporting Information, S2). Clearly the pure poly(*n*-butyl methacrylate) scaffold is not robust enough to withstand pressure differences/capillary forces upon drying. Permanent shape deformation of the cellular monoliths was not observed when 10.1% divinylbenzene was used as a comonomer, in the cases of pure divinylbenzene or its mixtures with styrene or in the case of a mixture of *n*-lauryl methacrylate and ethylene glycol dimethacrylate (4.7 wt %). The latter cellular monolith was very flexible and showed spongy reversible behavior (for movies, see Supporting Information, S3). These types of elastomeric poly(HIPE) materials have been made before by Cameron and Sherrington using conventional surfactants.[17]

The size of the cells could be controlled by varying the amount of microgels used. As a crude indication for cell dimensions, that is, the diameter of the Pickering stabilized emulsion droplets, we can use the following equation:[14c]

$$D = \pi \mathrm{Cov}\left(\frac{1}{w_{\mathrm{part}}}\right)\left(\frac{\rho_{\mathrm{part}}}{\rho_{\mathrm{water}}}\right)d_{\mathrm{part}}$$

in which Cov represents the coverage expressed as the ratio of the effective area covered by the particle stabilizers and the total area of the water droplet, w_{part} is the weight fraction of particle stabilizers used with respect to the amount of water phase, ρ_{water} and ρ_{part} being the densities of the water phase and the microgel particles in g cm^{-3}, D and d_{part} being the diameters of the emulsion droplet and the particle stabilizers in μm. In the case of the preparation of a purely divinylbenzene scaffolded cellular monolith we used cross-linked microgels as stabilizers with an average diameter of 153 nm and a polydispersity of 0.1 as measured by dynamic light scattering. We used 8.43 g of water at pH 9, 10.03 g of divinylbenzene, 0.011 g of microgels, and shaking to generate the Pickering emulsion. When we assume full coverage, Cov = 1, this would produce a poly(HIPE) having cells with an average diameter of approximately 400 μm. From Figure 4 it can be observed that this approximate value is of the right order of magnitude. Note that the excess of divinylbenzene was removed prior to polymerization. The overall porosity of this poly(HIPE) was 82%.

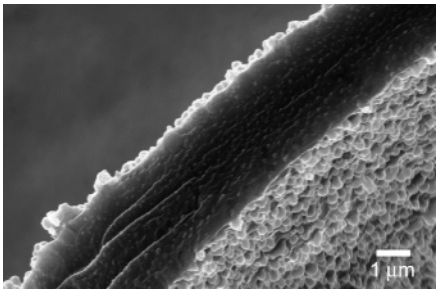

Figure 5. FE-SEM image of point of contact between two cells in Pickering poly(HIPE). It can be seen that particles are present on both sides of the thin interconnecting film.

The cellular structure in our Pickering poly(HIPE)s can be open and/or closed. In the case of the poly(divinyl benzene) monoliths we see from field-emission scanning electron microscopy (FE-SEM) analysis (Figure 4) that cells sometimes are interconnected but in most cases show the presence of a thin film at the points of contact of two cells. This thin film occasionaly is broken as can clearly be observed from the image. It seems logical that these films are present since Pickering emulsions are highly stable, even upon direct contact. We invisage that these films could be used as pressure release valves in two pack systems where each individual cell is filled with different reagents, provoking a desired chemical reaction upon rupture.

Figure 3 already indicated that the fluorescent particles are present at the interface of the cells. A question arising is whether we are having a film with particles on both sides or a monolayer of particles at the point of contact between two cells. The latter was recently observed by Horozov and Binks.[18] In all of our cases we have not been able to find bridging monolayers. As clearly can be seen from Figure 5 microgel building blocks are present at both sides of the interconnecting scaffolding polymer.

In summary we have demonstrated the production of poly(HIPE)s using Pickering stabilization. We have demonstrated that the individual cells of the poly(HIPE)s are covered with particles and that by using two types of particle stabilizers a variety of Pickering poly(HIPE)s can be designed.

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Supporting Information Available: Experimental procedures and images of buckled monoliths from poly(*n*-butyl methacrylate) (PDF), two movie clips of reversible deformation of cellular monoliths from cross-linked poly(*n*-lauryl methacrylate) (AVI), and a confocal microscopy movie to support Figure 3 (AVI). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Cameron, N. R.; Sherrington, D. C. *J. Mater. Chem.* **1997**, *7*, 2209−2212.

(18) Horozov, T. S.; Binks, B. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 773−776.