



# Preparation of high loading PolyHIPE monoliths as scavengers for organic chemistry<sup>☆</sup>

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**Abstract**—A novel microcellular polyHIPE monolith of high functional group capacity has been prepared by a two-step process including the synthesis of the scaffold by polymerization of a highly concentrated emulsion and then the in situ surface polymerization of methacrylate monomers. Application of the resulting functionalized monolith is demonstrated in a scavenging reaction of poly(glycidyl methacrylate)-grafted polyHIPE with 1-hexylamine. The open-cellular structure of the core combined with the good accessibility of the grafted functional polymer chains allows total scavenging of the amine in a relatively short period.

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Over the last few years, the use of immobilized scavengers in organic chemistry has gained in popularity as a result of their ability to facilitate the purification process.<sup>1</sup> The support interacts with the excess of reagents and then by an easy filtration step, the complex is removed from the reactive medium leaving the desired product in solution. For optimum efficiency, the chemical and structural design of the solid support has to satisfy several conditions. It must be chemically inert to all other reagents used during the synthesis, mechanically stable and have a shape allowing easy and rapid manipulation. Moreover, a high loading and a good accessibility of functional groups are essential for scavenging chemistry.

Surface grafting of polymer chains has been investigated as an effective and versatile method to afford high capacity supports.<sup>2</sup> Commonly, the grafting process is performed by an in situ surface initiated polymerization from immobilized initiators that allows monomers to diffuse easily. In the majority of cases, azo-based initiators are used to initiate radical polymerization<sup>3</sup> but this process leads to the formation of free polymer which is then difficult to remove from the reaction medium. One approach to overcome this is

to modify the support surface by atom transfer radical polymerization (ATRP). The mechanism of ATRP has been fully described elsewhere.<sup>4</sup> It is based on a reversible homolytic cleavage of a carbon–halogen bond by a redox reaction between an organic halide and a transition metal such as copper(I). Such polymerization is tolerant towards many functional groups and allows the use of a large panel of monomers. ATRP has previously been used for surface modification of gold,<sup>5</sup> silica<sup>6</sup> and various polymer materials.<sup>7</sup>

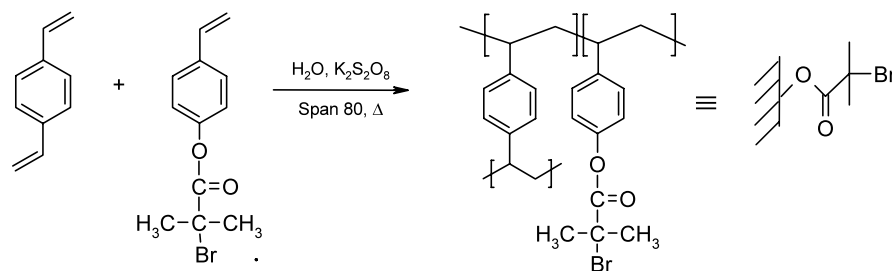
PolyHIPE is a microcellular polymer monolith prepared from a highly concentrated emulsion (HIPE) following the procedure initially developed by Unilever.<sup>8</sup> After polymerization of the emulsion, a permanent well-organized structure is formed which consists of large interconnected cells exhibiting excellent flow properties.<sup>9</sup> The choice of this material as matrix for our support was mainly driven by its characteristic of promoting good diffusion of fluids towards immobilized functional groups.<sup>10</sup> Moreover, and importantly for our requirements, the fully open structure combined with the monolithic format offers opportunities for flow-through applications such as rapid separation media.

To overcome the low capacity usually observed with these materials,<sup>11</sup> we report here the synthesis and the application of a novel high loading polyHIPE based on in situ surface polymerization using ATRP. Recently, Cameron et al.<sup>12</sup> have reported the preparation of

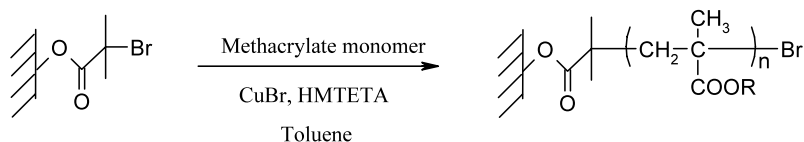
**Keywords:** PolyHIPE; microcellular; monolith; ATRP; scavenger.

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**Scheme 1.** Synthesis of bromoester functionalized polyHIPE.



**Scheme 2.** ATRP from the surface of functionalized polyHIPE.

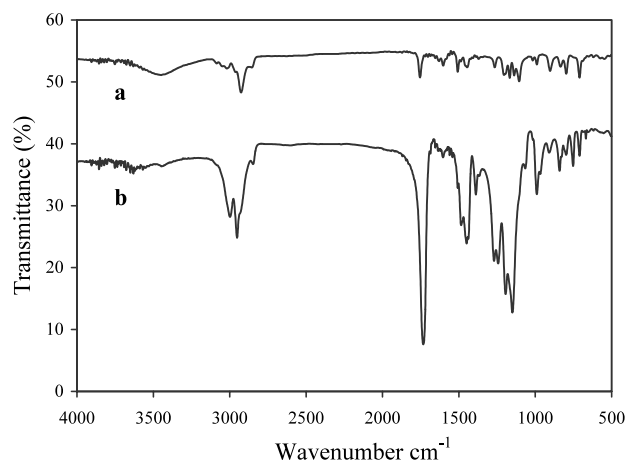
scavengers by amine functionalization of poly(4-vinylbenzyl chloride-co-divinylbenzene) polyHIPE. They have shown the effectiveness of this material when used for scavenging in a flow-through manner. This represents an alternative approach to our method for producing high-loading scavenger monoliths.

A polyHIPE bearing tertiary bromoester groups was first prepared by polymerization of a concentrated inverse emulsion. The dispersed phase containing water and 1 mol% of initiator ( $K_2S_2O_8$ ) was slowly added to the continuous phase composed of divinylbenzene (84 mol%), 4-vinylphenyl 2-bromo-2-methylpropanoate (16 mol%), and a suitable surfactant (Span 80) to allow the formation of the concentrated emulsion (Scheme 1). After heating for 6 h at 60°C, the polymerized material was thoroughly washed with tetrahydrofuran and dried under vacuum to remove all traces of surfactant and water. The final loading of bromoester on the support was calculated as ca. 0.8–0.9 mmol  $g^{-1}$  from elemental analysis.

The polymerization of methacrylate monomers [methyl methacrylate (MMA) or glycidyl methacrylate (GMA)] from these initiator sites was accomplished by dipping the polyHIPE in a solution containing the monomer, CuBr, hexamethyl triethylenetetramine (HMTETA) and toluene (Scheme 2).<sup>13</sup> Polymerizations were carried out at 80°C for 24 h.

After completion of the polymerization, the monoliths were subjected to intense washing by solvent reflux using  $CHCl_3$  and THF. A large increase in the relative absorbance of the carbonyl peak at 1730  $cm^{-1}$  in the FTIR spectrum (Fig. 1) confirmed the grafting of the poly(methacrylate). To verify that the polymer formed was not a result of thermal polymerization, a blank experiment was carried out (Table 1). A monolith without immobilized initiators on its surface was treated similarly. No polymer was produced on the monolith surface. The presence of tertiary bromoester groups is therefore essential to initiate the polymerization.

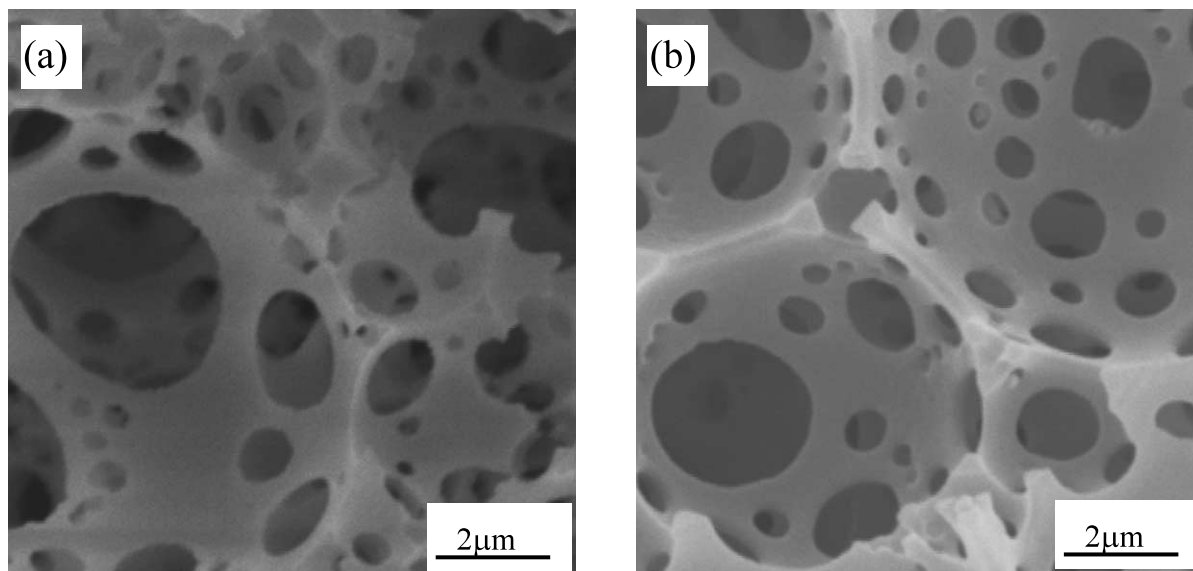
Table 1 summarizes the results of the surface polymerization. Quantitative evaluation of the grafting was carried out by elemental analysis based on oxygen and correlated with the weight increase determined gravimetrically, after drying under reduced pressure. For both monomers, the conditions led to high loading polyHIPEs with capacities of around 5 mmol  $g^{-1}$  either in the presence of MMA or GMA. In order to obtain a better knowledge of the characteristics of the ATRP surface initiated polymerization, it would be desirable to cleave off the grafted polyesters and analyze them separately. We expected that the phenolic ester function at their point of attachment should be sufficiently labile to be easily cleaved. Unfortunately, we were not able to detach the polymer chains from the surface. All attempts to achieve this by hydrolysis (KOH/ $CH_3OH$ ) were unsuccessful. This shows that the ester link between the monolith and the polyester chains is more robust than expected. Despite the fact that we could not analyze the detached polymer, this is a tremendous advantage for our supports since no chains would be lost to the medium during their use as scavenger.



**Figure 1.** FT-IR of (a) ungrafted and (b) PMMA grafted polyHIPE.

**Table 1.** Synthesis parameters and capacity data for the surface polymerization of functionalized polyHIPE by ATRP

Entry	Monomer	[MMA] <sub>0</sub> :[I] <sub>0</sub> [CuBr]:[HMTETA]	Capacity (mmol g <sup>-1</sup> )	
			Gravimetry	Elemental analysis
Blank <sup>a</sup>	MMA	100:0:1:1	0	0
1	MMA	100:1:1:1	4.9	5.1
2	GMA	100:1:1:1	4.5	4.2

<sup>a</sup> Polyhipe with no immobilized initiator.**Figure 2.** SEM images of (a) ungrafted and (b) PMMA grafted polyHIPE.

It is important to retain the overall morphology of the microcellular monolith during the polymerization step. Since the permeability of the support is directly connected to the size of the pores, the grafted polymer should not obstruct the flow through the network. The internal structure of the monolith before and after ATRP reactions was characterized by SEM (Fig. 2). The ungrafted polyHIPE has an open-cell structure fully interconnected which is typical of this material. Cell size is around 6–7  $\mu\text{m}$  in average with holes of ca. 1.2–1.4  $\mu\text{m}$ . After polymerization, the morphology of the polyHIPE is preserved and the cell and hole sizes are similar to those of the precursor. The presence of the grafted polymer does not affect the porous structure of the material. We could therefore legitimately assume that the flow characteristics of the monolith will be preserved.

To test the accessibility in solution of the grafted functions inside the monolith network, a model reaction was performed with the PGMA grafted polyHIPE in the presence of a primary amine. The monolith was immersed in a solution of dry THF containing 0.5 equiv. of 1-hexylamine based on polymer loading and heated at 80°C. The consumption of amine was followed by gas chromatography. After 18 h, all of the 1-hexylamine had reacted with the support. For comparison, the same reaction was performed with a com-

mercial resin<sup>14</sup> bearing 3 mmol g<sup>-1</sup> of glycidyl groups. After 18 h, only 50% of the amine had been consumed. This initial study reveals that the grafted glycidyl groups on the polyHIPE support have excellent site accessibility and demonstrates the effectiveness of this new system.

In summary, we have shown that it is possible to prepare microcellular monolith supports of high loading with the help of in situ surface polymerization using ATRP. The overall morphology of the precursor matrix is also preserved. These materials fulfill all the requirements for a good scavenger, i.e. high loading, good accessibility given by the mobility of the grafted chains and a structure which allows the rapid diffusion of fluids. Moreover, the monolith format permits easy and rapid manipulation. Further work is now in progress to evaluate the effectiveness of our supports for scavenging applications via a flow-through system.

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13. General grafting procedure: A Schlenk tube was charged with a given amount of polyHIPE monolith and CuBr (1 mol equiv. with respect to the bromoester group) under nitrogen. A solution of MMA, anhydrous toluene and HMTETA (1 mol equiv. with respect to the bromoester group) was prepared in a second Schlenk tube. Oxygen was removed by three freeze–pump–thaw cycles and then the solution was added to the first Schlenk tube by syringe. The mixture was placed in an oil bath at 80°C for 24 h. The resulting monolith was separated and washed with CHCl<sub>3</sub>. Traces of monomers, ligand and copper were extracted in a Soxhlet apparatus with THF for 48 h. The monolith was then dried under vacuum at 60°C for 24 h.
14. Glycidyl methyl ether, polymer-bound, 50–90 mesh, 1% crosslinked, loading 3 mmol g<sup>-1</sup> (Aldrich).