Synthesis of Functional Photopolymerized Macroporous PolyHIPEs by Atom Transfer Radical Polymerization Surface Grafting

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A versatile platform to obtain highly functional macroporous materials was developed. A polymerizable initiator for atom transfer radical polymerization (ATRP) has been incorporated into a high internal phase emulsion (HIPE) without compromising the emulsion stability. Photopolymerization of this formulation led to polyHIPE with ATRP initiator groups on the surface available for polymer grafting reactions. The latter was first demonstrated by grafting of methylmethacrylate (MMA). Analysis by IR confirms the presence of PMMA in the polyHIPE. Moreover, scanning electron microscopy images show changes in the surface morphology of the polyHIPE after the grafting reaction. In accordance with the controlled character of ATRP, reinitiation from the PMMA-grafted polyHIPE with HEMA to afford block copolymers was possible. Moreover, functionalized polyHIPE was obtained by the grafting of glycidyl methacrylate. IR and SEM analysis confirm that this resulted in a smooth and homogeneous coverage of the polyHIPE surface with a high density of reactive epoxy groups. In a subsequent reaction these materials were rendered hydrophilic by ring opening of the epoxy rings and hydrophobic by subsequent reaction with pentafluorobenzoylchloride.

Introduction

Macroporous polymers are useful materials in a variety of applications. Examples include biomedical applications such as tissue engineering,[1] monoliths for separations in analytical chemistry, and supports for solid-state chemistry.[2] For these applications, the macroporous polymers should ideally be easy to prepare with controllable pore morphology and surface functionality. A class of macroporous materials which has drawn significant attention in that respect is polymers obtained from high internal phase emulsions (HIPEs). HIPEs are defined by an internal or droplet phase volume ratio of 0.74 or higher (i.e., the minimum volume of the emulsion comprised of droplets is 74%). This value represented by ϕ is the maximum ratio for packing, in the most efficient manner, of non-deformable spheres.[3] HIPE formation is related to the surfactant used which must be soluble only in the continuous phase in order to prevent emulsion inversion.[2] HIPEs have been used for many years in a vast number of industries including fuels, cosmetics, and food preparation.[3] Polymerization of a monomeric continuous phase of a HIPE leads to a highly porous cross-linked polymer material allowing foams with a well-structured morphology, void size, and interconnecting window size to be obtained. Generally, the system is composed of an organic (continuous) phase containing the monomer such as styrene, a cross-linker, e.g., divinyl benzene, a suitable emulsifier, and the aqueous (dispersed) phase containing the radical initiator. The addition of droplets of the aqueous phase into the organic phase with constant stirring results in a dilute reverse emulsion. If the amount of water in the organic phase is increased, a concentrated emulsion can be obtained with thin monomer films surrounding the water droplets. Polymerization of these thin films and the subsequent removal of the water produces a porous interconnected network. Initially, polymerization of HIPE was reported by Bartl and von Bonin[4,5] but the generic term PolyHIPE (pHIPE) was coined by Unilever, which over the past few decades carried out extensive research on these materials.[6] Considerable advances in this technology were made during this period and later by Hainey et al.[7] and Cameron and Sherrington.[8] A number of articles have discussed the variation of structural features as a function of the synthetic conditions.[2,9−13] The predominant work carried out in the synthesis of pHIPE involves thermal curing

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[†] Technische Universiteit Eindhoven.

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(1) Busby, W.; Cameron, N. R.; Jahoda, C. A. B. *Polym. Int.* **2002**, *51*, 871.
(2) Cameron, N. R.; Barbetta, A. *J. Mater. Chem.* **2000**, *10*, 2466.
(3) Cameron, N. R. *Polymer* **2005**, *46*, 1439.
(4) Bartl, H.; von Bonin, W. *Makromol. Chem.* **1962**, *57*, 74.
(5) Bartl, H.; von Bonin, W. *Makromol. Chem.* **1963**, *66*, 151.
(6) Deleuze, H.; Maillard, B.; Mondain-Monval, O. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1877.
(7) Hainey, P.; Huxham, I. M.; Rowatt, B.; Sherrington, D. C. *Macromolecules* **1991**, *24*, 117.
(8) Cameron, N. R.; Sherrington, D. C. *Adv. Polym. Sci.* **1996**, *126*, 163.
(9) Willilams, J. M. *Langmuir* **1988**, *4*, 44.
(10) Willilams, J. M.; Wrobleski, D. A. *Langmuir* **1988**, *4*, 656.
(11) Kranjc, P.; Leber, N.; Brown, J. F.; Cameron, N. R. *React. Funct. Polym.* **2006**, *66*, 81.
(12) Barbetta, A.; Cameron, N. R. *Macromolecules* **2004**, *37*, 3188.
(13) Barbetta, A.; Cameron, N. R. *Macromolecules* **2004**, *37*, 3202.

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of styrenic systems.[2,14] However, recent work by Pierre et al. described, for the first time, photopolymerization as a beneficial method for a faster and more benign polymerization.[15] In this fast curing system, acrylate-based monomers were used in the continuous phase. For example, ethylhexyl acrylate (EHA) and isobornyl acrylate (IBOA) were used in a balanced ratio to aid elasticity of the material.

Another direction of pHIPE research is the development of applications. Some of the primary applications to date worthy of mention are solid-phase peptide supports,[16] ion-exchange resins,[17] supports for cells and enzymes,[18,19] membrane filters for the removal of particulates from aerosol,[20] and materials for the removal of heavy metals.[21,22] A common denominator of all these applications is that they make use of two beneficial characteristics of pHIPE: (1) the fully interconnected network within the matrix of the pHIPE, induced by the physical properties of the emulsion, which allows for the easy flow of fluids through the monolith,[23,24] and,(2) the high surface area and the ability to introduce functional surface groups. Usually, the latter can be achieved by addition of a functional monomer to a formulation. However, this approach has its limitations since the stability of the HIPE is a delicate hydrophobic/hydrophilic balance; i.e., for every change of monomer composition the process conditions have to be optimized. Moreover, water-soluble polar monomers are fully excluded from this approach since they destabilize the emulsion. Alternatively, the pHIPE can be functionalized after cross-linking. Mondain-Monval and co-workers have shown that the polymers prepared from commercially available divinylbenzene consist of a highly cross-linked polystyrene matrix that still contains some unreacted pendant vinyl groups that can be functionalized postpolymerization, by reaction with a suitable reagent.[6,24] However, the density of functional groups is limited by the density of reactive groups on the pHIPE surface.

The ability to conveniently modify pHIPE surfaces with a high density of functional groups is crucial to opening new application areas. Surface grafting of polymer chains is an effective and versatile approach to afford this. Stable polymer brushes covalently attached to a surface possess excellent mechanical and chemical robustness and offer the flexibility to introduce a large variety of functional monomers. One of the most versatile methods for polymer grafting from solid supports is atom transfer radical polymerization (ATRP)[25−32] since it is tolerant toward many reaction conditions and allows a large array of monomer to be used.[33−35]

The aim of our research is to obtain highly functional, mechanically robust macroporous pHIPE for advanced applications. Inspired by the work of Moine et al. who reported initial work on ATRP from thermally cured styrene-based pHIPE[23,36] and by Huck et al. who have studied aqueous ATRP for the growth of polymer brushes from planar surfaces,[37,38] we investigated whether the advantages of fast acrylate UV curing for pHIPE formation could be combined with ATRP surface grafting. The advantage of this approach is that a standard monomer formulation can be optimized for best results in the pHIPE synthesis. Functionalization is accomplished in a secondary step by polymerization of functional vinyl monomers from the ATRP initiator functionalized pHIPE through surface grafting. This allows a high synthetic flexibility to be achieved since the surface can be decorated without compromising the pHIPE morphology.

In this paper we show that UV-curable pHIPEs can be obtained containing ATRP initiator groups. (For simplicity, further reference to these ATRP initiator containing pHIPEs will be denoted as I-pHIPE.) These initiator groups are available for the grafting reaction of methyl methacrylate (MMA). The retained activity of the ATRP end groups is demonstrated by polymerization of hydroxyethyl methacrylate (HEMA) from the reinitiation of pMMA-grafted pHIPE. Moreover, we show that highly functional pHIPE can be obtained by grafting of glycidyl methacrylate (GMA), which can be used as a reactive platform to obtain hydrophilic or hydrophobic surfaces. See Figure 1.

Experimental Section

Materials. Cu(I)Cl, Cu(I)Br, 2,2′-bipyridine (bpy), glycidyl methacrylate (GMA), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), 2-ethylhexyl acrylate (EHA), isobornyl acrylate (IBOA), trimethyloylpropanetriacrylate (TMPTA), 2,3,4,5,6-pentafluorobenzoyl chloride (PFBC), 4-dimethylaminopyridine (DMAP), 2-bromoisobutyryl bromide, and triethylamine were all used as received without further purification. Daracour 4265 (photoinitiator) was received from CIBA and Hypermer B246

(14) Moine, L.; Deleuze, H.; Maillard, B. *Tetrahedron Lett.* **2003**, *44*, 7813.
(15) Pierre, S. J.; Thies, J. C.; Dureault, A.; Cameron, N. R.; Hest, J. C. M. v.; Carette, N.; Michon, T.; Weberskirch, R. *Adv. Mater.* **2006**, *18*, 1822.
(16) Small, P. W.; Sherrington, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, 1589.
(17) Wakeman, R. J.; Bhumgara, Z. G.; Akay, G. *Chem. Eng. J.* **1998**, *70*, 133.
(18) Ruckenstein, E.; Wang, X.-B. *Biotechnol. Bioeng.* **1994**, *44*, 79.
(19) Ruckenstein, E.; Wang, X. *Biotechnol. Bioeng.* **1993**, *42*, 821.
(20) Akay, G.; Bhumgara, Z. G.; Wakeman, R. J. *Chem. Eng. Res. Des.* **1995**, *73*, 782.
(21) Benicewicz, B. C.; Jarvinen, G. D.; Kathios, D. J.; Jorgensen, B. S. *J. Radioanal. Nucl. Chem.* **1998**, *235*, 31.
(22) Alexandratos, S. D.; Beauvais, R.; Duke, J. R.; Jorgensen, B. S. *J. Appl. Polym. Sci.* **1998**, *68*, 1911.
(23) Moine, L.; Deleuze, H.; Degueil, M.; Maillard, B. *J. Polym. Sci. A: Polym. Chem.* **2004**, *42*, 1216.
(24) Mercier, A.; Deleuze, H.; Mondain-Monval, O. *React. Funct. Polym.* **2000**, *46*, 67.
(25) Jones, D. M.; Huck, W. T. S. *Adv. Mater.* **2001**, *13* (16), 1256.
(26) Matyjaszewski, K.; Dong, H.; Jakubowski, W.; Pietrasik, J.; Kusumo, A. *Langmuir* **2007**, *23*, 4528.
(27) Huang, X.; Wirth, M. J. *Macromolecules* **1999**, *32*, 1694.
(28) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. *Macromolecules* **1999**, *32*, 8716.
(29) Shah, R. R.; Mecerreyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33*, 597.
(30) Kim, J. B.; Bruening, M. L.; Baker, G. L. *J. Am. Chem. Soc.* **2000**, *122*, 7616.
(31) Zhoa, B.; Brittain, W. J. *Macromolecules* **2000**, *33*, 8813.
(32) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14.
(33) Nicolas, J.; Mantovani, G.; Haddleton, D. M. *Macromol. Rapid Commun.* **2007**, *28*, 1083−1111.
(34) Limer, A.; Haddleton, D. M. *Macromolecules* **2006**, *39*, 1353.
(35) Boyes, S. G.; Brittain, W. J.; Weng, X.; Cheng, S. Z. D. *Macromolecules* **2002**, *35*, 4960.
(36) Moine, L.; Deleuze, H.; Maillard, B. *Tetrahedron Lett.* **2003**, *44*, 7813.
(37) Edmondson, S.; Huck, W. T. S. *J. Mater. Chem.* **2004**, *14*, 730.
(38) Osborne, V. L.; Jones, D. M.; Huck, W. T. S. *Chem. Commun.* **2002**, 1838.

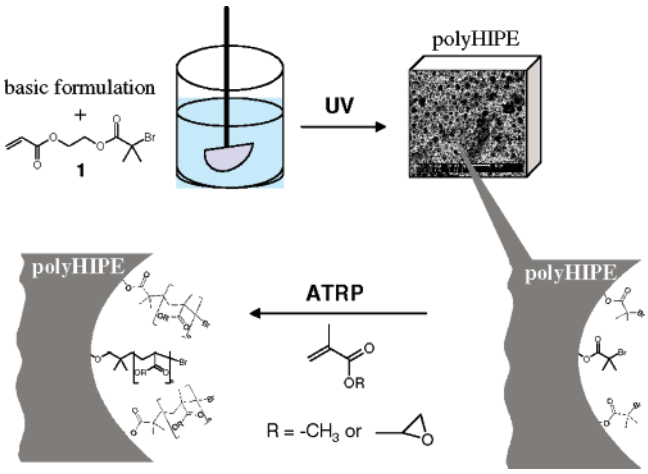

Figure 1. Synthesis of functional pHIPE in two steps: (1) Formation of stable high internal phase emulsion (HIPE) in the presence of **1** and UV curing to obtain pHIPE with ATRP initiator groups (I-pHIPE). (2) Grafting of MMA and GMA by ATRP from I-pHIPE surface.

(surfactant) from Uniqema. All deionized water used in reactions was obtained from a Millipore Milli-Q dispenser with a resistance of 18.2 MΩ·cm. All solvents were used as received. 2-Acryloxyethyl-2′-bromoisobutyrate, **1**, was synthesized according to a modified literature procedure.[39]

Characterization. Initiator characterization using nuclear magnetic resonance (^{1}H NMR) spectroscopy was carried out on a Bruker Avance Ultrashield 300 MHz FT-NMR spectrometer with solvent peak as reference. IR spectra were recorded using a PerkinElmer Spectrum One spectrometer fitted with the PerkinElmer Golden Gate diamond ATR accessory. Analysis of spectra was performed using BioMad KnowItAll software. Scanning electron microscopy (SEM) was performed using a Philips/FEI XL30 environmental SEM with samples previously coated with gold using vapor deposition.

Synthesis of the ATRP Initiator 2-Acryloxyethyl-2′-bromoisobutyrate, 1. 2-Hydroxyethyl acrylate (3.78 g, 32.6 mmol) and triethyl amine (3.30 g, 32.6 mmol) were added to a three-necked flask containing 200 mL of dry THF, stirred, and cooled to 0 °C. With use of an addition funnel, 2-bromoisobutyrl bromide (8.74 g, 38.0 mmol) was added dropwise. Upon completion of the addition, the reaction mixture was brought to room temperature and allowed to stand for 18 h. The product was extracted into ethyl acetate, dried over anhydrous $MgSO_4$, filtered and reduced in vacuo to yield a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.40 (CH_2═CH−, 1H, dd), 6.09 (CH_2═C*H*−, 1H, dd), 5.85 (CH_2═CH−, 1H, dd), 4.40 (O−CH_2−CH_2−O−, 4H, s), 1.95 (−C−CH_3−, 6H, s).

Synthesis of Control pHIPE without ATRP Initiator. The monomers 2-ethylhexyl acrylate (3.1 g, 16.82 mmol, 61.7 wt %), isobornyl acrylate (0.50 g, 2.40 mmol, 10.3 wt %), and trimethylolpropane triacrylate (0.90 g, 3.04 mmol, 18.2 wt %) were mixed together with the surfactant (Hypermer B246 (0.13 g, 2.6 wt %)) and the photoinitiator (Darocur 4265 (0.36 g, 7.2 wt %)) in a 50 mL wide-necked polyethylene bottle and were stirred with a steel stirring rod fitted with a D-shaped PTFE paddle, connected to an overhead stirrer motor, at 300 rpm. A nitrogen flux was maintained over the bottle. Deionized and degassed water (45 mL) was added dropwise, with constant stirring at room temperature, to form the HIPE. As the aqueous phase was added, the bottle was lowered to maintain stirring just below the surface of the developing HIPE, ensuring that no water pockets formed. Once all the aqueous phase had been added, stirring was continued for a further 5 min, to ensure homogeneity. A square-shaped PTFE frame was used to create a mold (5 cm side, 5 mm thickness) on a glass plate. The HIPE was poured inside and a second glass plate was used to close the mold. The mold was passed alternatively on each side three times (total UV dose: 6.0 J/cm^2) under a Fusion UV irradiator under N_2. The resulting polyHIPEs were then washed in acetone (4 × 500 mL) with a minimum of one overnight soak before being dried in vacuo at 50 °C overnight.

Synthesis of ATRP Initiator Functionalized PolyHIPE (I-pHIPE). 2-Ethylhexyl acrylate (2.6 g, 14.11 mmol, 51.4 wt %), isobornyl acrylate (0.50 g, 2.40 mmol, 10.3 wt %), and trimethylolpropane triacrylate (0.90 g, 3.04 mmol, 18.2 wt %) were mixed together with the ATRP initiator 2-acryloxyethyl-2′-bromoisobutyrate (0.5 g, 1.87 mmol, 10.3 wt %), surfactant (Hypermer B246 (0.13 g, 2.6 wt %)), and photoinitiator (Darocur 4265 (0.36 g, 7.2 wt %)) in a 50 mL wide-necked polyethylene bottle and were stirred with a steel stirring rod fitted with a D-shaped PTFE paddle, connected to an overhead stirrer motor, at 300 rpm. A nitrogen flux was maintained over the bottle. Deionized and degassed water (45 mL) was added dropwise, with constant stirring at room temperature, to form the HIPE. As the aqueous phase was added, the bottle was lowered to maintain stirring just below the surface of the developing HIPE, ensuring that no water pockets formed. Once all the aqueous phase had been added, stirring was continued for a further 5 min, to ensure homogeneity. The HIPE formulation was polymerized as outlined above.

Grafting of Methyl Methacrylate (MMA) from Nonfunctionalized and ATRP Functionalized polyHIPE. Grafting of MMA was performed based on a method described by Huck and co-workers.[25,40] MMA (10 g, 100 mmol), CuCl catalyst (174 mg, 1.8 mmol), and 2,2′-bipyridine (310 mg, 2.0 mmol) as ligand were added to a reaction vessel containing a previously degassed (15 min with N_2) mixture of methanol and deionized water (8:2) (10 mL). After some initial stirring using a mini magnetic stirring bar, the pHIPE samples (0.5 cm^3) were added to the reaction mixture and gently stirred at room temperature for 16 h. After this time the samples were removed from the reaction vessel and placed on filter paper in a small Buchner funnel over suction. The samples were thoroughly washed with MeOH, THF, and again with MeOH before being washed in a 0.1 M EDTA solution to remove any remaining catalyst[41] that had been absorbed into the pHIPE matrix. The EDTA solution was refreshed twice over an 18 h period. Finally, the samples were again washed with H_2O and MeOH before being dried in vacuo.

Grafting of 2-Hydroxyethyl Methacrylate (HEMA) Block from p(HIPE-*g*-MMA). CuBr catalyst (110 mg, 0.8 mmol), 2,2′-bypyridine (360 mg, 2.3 mmol) as ligand, HEMA (13.0 g, 100 mmol), and deionized water (10 mL) were placed in a two-necked round-bottom flask and degassed under a N_2 flow for 30 min. The mixture was extracted and added to a second, previously evacuated two-necked round-bottom flask, containing the p(HIPE-g-MMA) under a N_2 flow. The reaction was allowed to proceed for 18 h at room temperature. After this time, the modified samples were washed with MeOH, THF, and again with MeOH followed by 0.1 M EDTA overnight to remove any remaining catalyst that had been absorbed into the pHIPE matrix.[41] Upon removal, they were again rinsed with acetone, H_2O, and MeOH before being dried at 60 °C in vacuo for 48 h.

Grafting of Glycidyl Methacrylate (GMA) from Nonfunctionalized and ATRP Functionalized polyHIPE. Grafting of GMA was performed based on a method described by Huck and

(39) von Werne, T. A.; Germack, D. S.; Hagberg, E. C.; Sheares, V. V.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2003**, *125*, 3831.
(40) Jones, D. M.; Brown, A. A.; Huck, W. T. S. *Langmuir* **2002**, *18*, 1265.
(41) Shen, Y.; Tang, H.; Ding, S. *Prog. Polym. Sci.* **2004**, *29*, 1053.

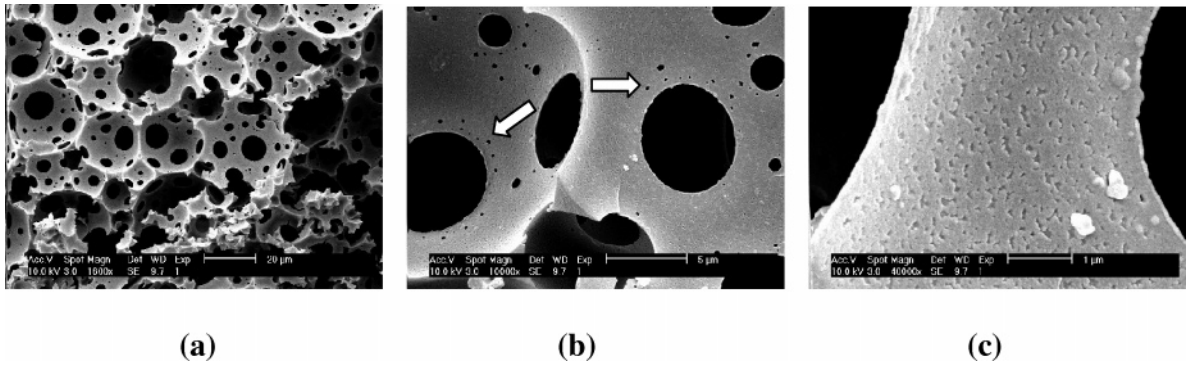

Figure 2. Scanning electron microscopy (SEM) images of I-pHIPE. Scale bar (a) = 20 μm, (b) = 5 μm, and (c) =1 μm.

co-workers.[25,40] GMA (14.2 g, 100 mmol), CuCl catalyst (174 mg, 1.8 mmol), and 2,2′-bipyridine (310 mg, 2.0 mmol) as ligand were added to a reaction vessel containing a previously degassed (15 min with N_2) mixture of methanol and deionized water (8:2) (10 mL). After some initial stirring using a mini magnetic stirring bar, the polyHIPE samples (0.5 cm^3) were added to the reaction mixture and gently stirred at room temperature for 16 h. After this time the samples were removed from the reaction vessel and placed on filter paper in a small Buchner funnel over suction. The samples were thoroughly washed with MeOH, THF, and again with MeOH before being washed in a 0.1 M EDTA solution to remove any remaining catalysts that had been absorbed into the polyHIPE matrix.[41] The EDTA solution was refreshed twice over an 18 h period. Finally, the samples were washed with H_2O and MeOH before being dried at 60 °C in vacuo for 48 h.

Epoxide Ring Opening of GMA-Modified PolyHIPE (p(HIPE-*g*-GMA)). Four samples of p(HIPE-*g*-GMA) were added to a beaker containing THF (10 mL). Twelve drops of concentrated HCl was added and the complete mixture was stirred at room temperature for 45 min. After this time the samples were thoroughly washed with THF, MeOH, and EtOH before being dried in vacuo at 37 °C to yield p(HIPE-*g*-GMA(*hyd*)).

Functionalization of p(HIPE-*g*-GMA(*hyd*)) with 2,3,4,5,6-Pentafluorobenzoyl Chloride (PFBC). CH_2Cl_2 (20 mL), triethylamine (148 mg, 0.15 mmol), and a catalytic amount of DMAP were added to a large sample vial and the mixture was split into two parts **a** and **b**. Into **a** was placed a sample of p(HIPE-*g*-GMA) and into **b** was placed a sample of p(HIPE-*g*-GMA(*hyd*)). PFBC (260 mg, 1.1 mmol) was added to both vials and the system was allowed to stand for 1 h, after which the samples were individually washed over suction with CH_2Cl_2, THF, acetone, and EtOH. The samples were then dried in vacuo at 37 °C.

Results

Preparation of I-pHIPEs. Our strategy involves the UV curing of an acrylate-based HIPE in the presence of **1**, i.e., a compound that contains a polymerizable monomer group for the incorporation into the pHIPE and an ATRP initiator group. UV curing of acrylates in the presence of ATRP initiators similar to **1** has been reported by Carter and co-workers for the modification of lithographically obtained microstructures.[39] ATRP after UV curing was successful and proves the general feasibility of the approach. For the incorporation of **1** into a stable concentrated HIPE, a number of parameters require attention, including the nature and concentration of the surfactant and continuous phase. This balance can easily be disrupted by the introduction of an additive to the system, leading to an unstable emulsion. Therefore, the selection of a monomer that must be soluble in the continuous phase as well as sufficiently hydrophobic to allow successful HIPE formation requires great care. The HIPE synthesis used here is a variation of a previously reported preparation.[15] A small ratio of monomer **1** (9.05 mol % with respect to total acrylates) was added to the emulsion which was then photopolymerized. No problems were encountered in the HIPE emulsion formation, which was stable up to the point of gelation. Therefore, any observed changes in structure, discussed in the coming section, are not due to emulsion breakdown but to chemical alteration after the functionalization steps. The obtained polymer materials were soft and rubbery.

All monoliths were subject to ATR-FTIR and SEM analysis. As the morphology of the materials is complex, the terminology to be used will be briefly defined based on the definitions laid down by Cameron and Barbetta.[2] The large spherical voids (on the order of micrometers) are termed voids. The interconnects between adjacent voids are referred to as windows (see Figure 2).

In the SEM images, we observed a highly porous material (approximately 90% porosity based on the formulation) and use of these images allowed us to visually estimate the average diameter of the voids as approximately 25 μm. The material also contained a large number of windows, which we visually estimated to have an average diameter of 8 μm, between adjacent voids (Figure 2a). What is also apparent here is the presence of extremely small pores in an almost uniform pattern around the larger windows (white arrows Figure 2b). The reason for the formation of these pores is unknown yet but they are important for three reasons. First, they give an indication as to the thinness of the wall; second, they give an indication as to the strength of the wall as they are not consumed by the larger windows; and third, due to the almost perfect alignment around the windows, they are most likely due to the polymerization effect. Figure 2c shows a divot effect in the morphology of the foam surface. This is a consistent character of the pHIPE samples prepared and will be a more important factor as we describe their functionalization.

Grafting of the MMA Monomer from the Surface of the pHIPE. A number of research groups have reported surface modification by ATRP. Despite the controlled growth of polymer, the technique usually requires insertion of the substrate into a solution of the monomer and the ATRP catalyst system, followed by thermal activation at high

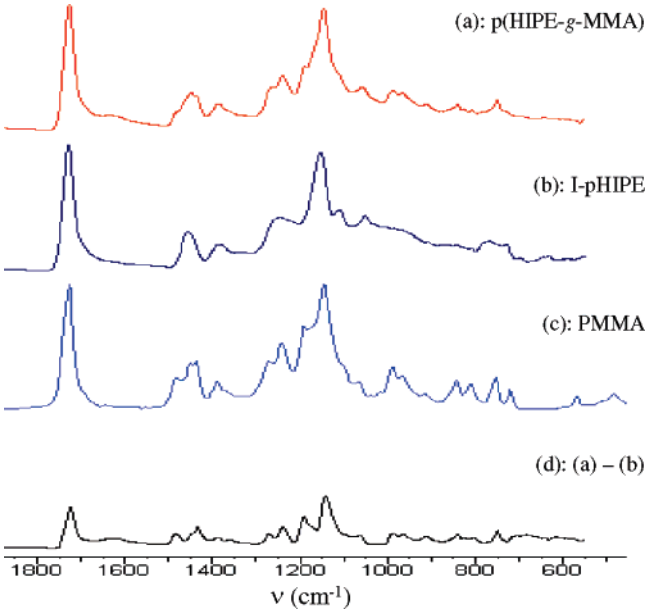

Figure 3. Infrared spectra showing in descending order: (a) spectrum of pHIPE after MMA grafting; (b) I-pHIPE; (c) PMMA (from unbiased data base); and (d) spectrum resulting from the subtraction of (b) from (a).

temperatures over long periods of time. In some cases the addition of a "sacrificial initiator" to the solution is required to control the polymerization, resulting in the formation of polymer in solution.[27−31] Recently, Huck and co-worker reported the very efficient surface ATRP in polar solvents like methanol and water from silicon waters. It is believed that the high dielectric constant of these solvents increases the activity of the catalyst. The polymerizations under these conditions are very fast and lead to high layer thicknesses without the addition of sacrificial initiator.[25] We therefore adopted this method for our attempts of ATRP from I-pHIPE surfaces. This allowed us to rapidly graft water-insoluble polymers from the pHIPE while maintaining reaction control and allowing us the possibility to grow block copolymers.

To exhibit the availability of the ATRP groups for grafting, we first used MMA as the monomer. Typically, a piece of I-pHIPE (0.5−1.0 cm^3) was added to the dark-colored polymerization mixture containing the MMA, catalyst (CuCl), and the ligand (bpy) in methanol/water. Initially, the pHIPE floated but eventually became immersed due to absorption of the reaction mixture. Following ATRP, the recovered pHIPE was brown in color due to the absorption of the copper catalyst. After intensive washing with suitable solvents to remove ungrafted polymer and EDTA to remove all catalyst, the polymer functionalized pHIPE returned to the original white color. At this point the material had become more brittle, which is a first indication of a successful modification. The obtained p(HIPE-*g*-MMA) was characterized by ATR-IR. Since the I-pHIPE and grafted pHIPEs are both produced using (meth)acrylates, distinguishing between the matrix and the grafted material is difficult using IR. For example, the strongly characteristic carbonyl band at around 1720 cm^{-1} could not be used to prove successful grafting, and so more attention was paid to the changes in the fingerprint region of the spectrum. Figure 3 shows the region of the recorded spectra between 1800 and 600 cm^{-1} of the pHIPE before and after grafting with MMA. A comparison of the spectra (a and b) shows only small changes in this area relating to the presence of pMMA. To make the differences between the spectra more evident, they were subtracted from each other and the resulting spectrum was confirmed by an unbiased electronic comparison with an IR database to be that of pMMA (Figures 3c and 3d).

Stronger evidence for the success of the grafting reaction was provided by SEM analysis. The images obtained from these samples (Figure 4) exhibit a change in surface morphology due to the presence of polymer on the surface. A clear change in surface roughness is observed when compared with the corresponding image in Figure 2. Here we can see that the divots present in the blank sample (Figure 2c) are now surrounded by smaller mounds. It should also be noted here that the small pores circling the windows are still visible.

Overall, the porosity of the monolith has been preserved with little change between these samples and the precursors. This is important as it shows that the pHIPE can be thoroughly washed out after grafting and that the porosity of the monolith remains intact. However, it is not possible from these images to determine the homogeneity and thickness of the grafted polymer layer.

Several control experiments were carried out to provide evidence that the detected pMMA was indeed grafted: (i) polymerization of MMA was not observed when the same reaction was carried out using pHIPE without ATRP initiator, (ii) polymerization of MMA was not observed when I-pHIPE was used in the absence of ATRP catalysts; and (iii) when an ATRP reaction was conducted with free ATRP initiator in solution in the presence of a pHIPE, polymerization occurred in solution but not in the pHIPE. After polymerization of the MMA, the monolith went through the same washing procedure, and although the reaction clearly produced pMMA, no corresponding signal was detected by IR for the pHIPE. This confirms the efficiency of the washing process and supports the conclusion that the pMMA is grafted from the pHIPE surface.

Having successfully polymerized MMA from the pHIPE surface, the next step was to further modify the grafted polymers. Since ATRP is a controlled living polymerization, the initiator remains attached to the end of the polymer as it grows, making it available for reinitiation. With use of the p(HIPE-*g*-MMA) matrix prepared above, we successfully carried out a second ATRP from the surface using HEMA to grow p(HIPE-*g*-(PMMA-*b*-PHEMA)). The IR spectra in Figure 5 show the presence of an O−H vibrational stretch at 3400 cm^{-1} corresponding to the hydroxy group of the HEMA and confirming the presence of p(HEMA) on the surface. Moreover, changes in the fingerprint region of this sample, when compared to the precursor, provide further evidence for the grafting of the HEMA and compare well with results reported by Brantley and Jennings.[42] These changes also provide evidence for the availability of the ATRP end groups of the pMMA grafts for reinitiation. Again, these samples were thoroughly washed and dried in vacuo prior to analysis.

(42) Brantley, E. L.; Jennings, G. K. *Macromolecules* **2004**, *37*, 1476.

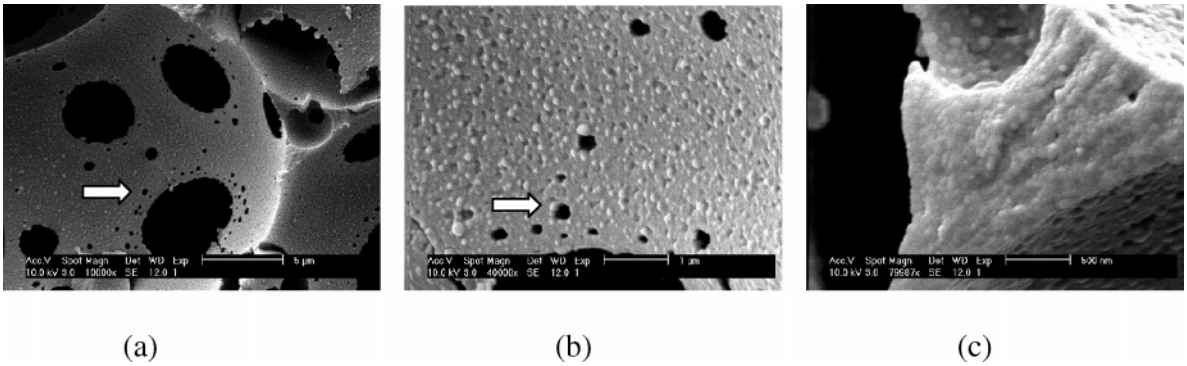

Figure 4. SEM images of p(HIPE-*g*-MMA), showing a distinct difference in the surface morphology of the matrix (compared with Figure 2). Scale bar (a) = 5 μm, (b) = 1 μm, and (c) = 500 nm.

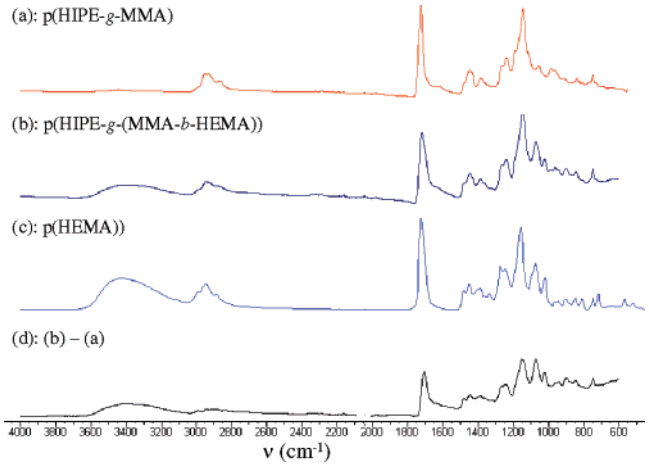

Figure 5. Infrared spectra showing in descending order: (a) spectrum of p(HIPE-*g*-MMA); (b) spectrum of p(HIPE-*g*-MMA) after ATRP of HEMA (block copolymerization); (c) p(HEMA); and (d) spectrum resulting from the subtraction of (a) from (b).

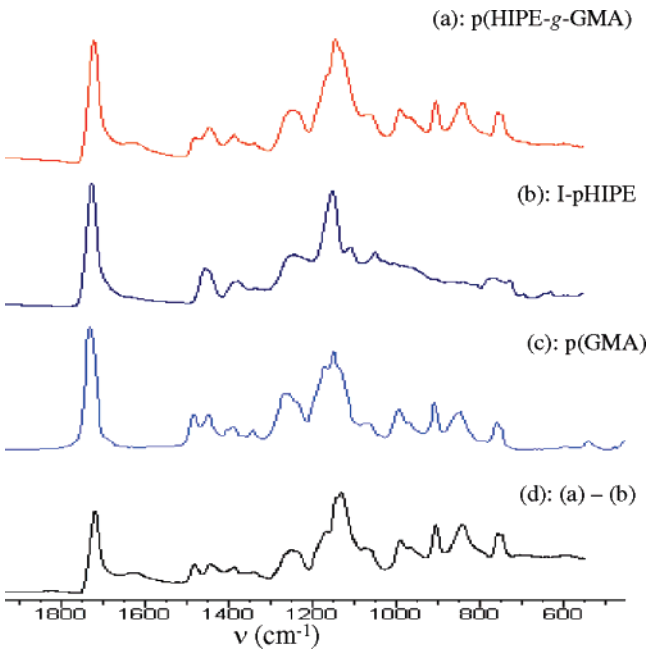

Figure 6. Infrared spectra showing in descending order: (a) spectrum of pHIPE after GMA grafting; (b) I-pHIPE; (c) p(GMA) (from unbiased data base); and (d) spectrum resulting from the subtraction of (b) from (a).

Grafting of the GMA Monomer from the Surface of the pHIPE. To obtain pHIPE with a high density of reactive surface functionalities, we attempted the grafting of glycidyl methacrylate (GMA). The epoxide group of GMA can further be modified by nucleophilic ring opening, e.g., by water, alcohols, amines, or carboxylic acids. pHIPE containing a successful surface coverage of pGMA would thus be a very versatile platform for the attachment of functional materials. The grafting reaction was carried out similarly to the MMA grafting. One significant observation of this grafting experiment was that the product material had become even more brittle than PMMA-modified pHIPE.

The fingerprint region of the IR spectra of the resulting p(HIPE-*g*-GMA) is consistent with that of pGMA. Furthermore, it revealed the presence of the epoxide groups (present between 900 and 800 cm^{-1}), showing that they are not opened under the reaction conditions used (Figure 6). Because the modified monoliths were thoroughly washed, no free monomer or polymer existed in the network and this change in the IR spectrum must exclusively be due to the grafted polymer.

Further analysis, using SEM, provided additional visual evidence for the extent of polymerization within the pHIPE matrix. Figure 7 clearly shows the presence of polymer on the surface. A clear change in surface morphology is observed when compared with the corresponding images in Figure 2. Here we can see that the divots that were present in the blank sample (Figure 2c) have completely disappeared and the surface has become extremely smooth. While the larger voids and windows remain and thus the porosity of the matrix is preserved, the pores around the windows have been filled in due to the thick coating that is blanketing the interior of the pHIPE (Figures 7a and 7b). Figure 7d shows an edge where the rough underlying structure is clearly coated in a blanket of approximately 40−50 nm depth.

From these results it can be concluded that the polymerization of GMA resulted in the very rapid growth of thick polymer layers within the matrix of the pHIPE. The rapid growth of the pGMA compared with that of the pMMA is in agreement with reports from Huck and co-worker, who attributed this effect to the coordination of the copper catalyst with the epoxide group of the GMA, resulting in the displacement of the ligand and increase in the activity of the catalyst.[25]

One concern that arose was whether the pGMA had grown by ATRP from the surface or whether it was deposited due to epoxide-induced cross-linking inside the matrix. To experimentally confirm that the polymerization had occurred due to the presence of the ATRP initiator in the bulk matrix,

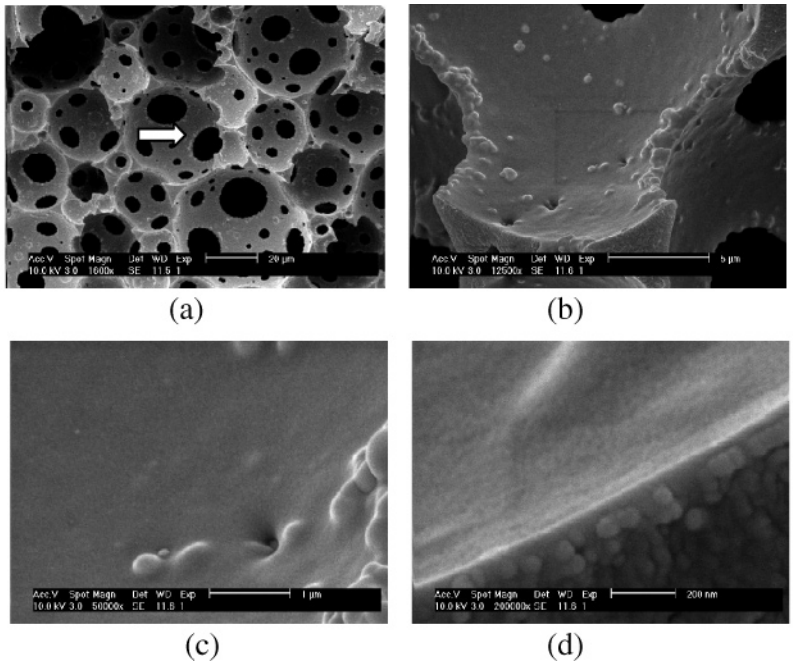

Figure 7. SEM images of p(HIPE-*g*-GMA) showing a distinctive coating on the surface. Scale bar (a) = 20 μm, (b) = 5 μm, (c) = 1 μm, and (d) = 200 nm.

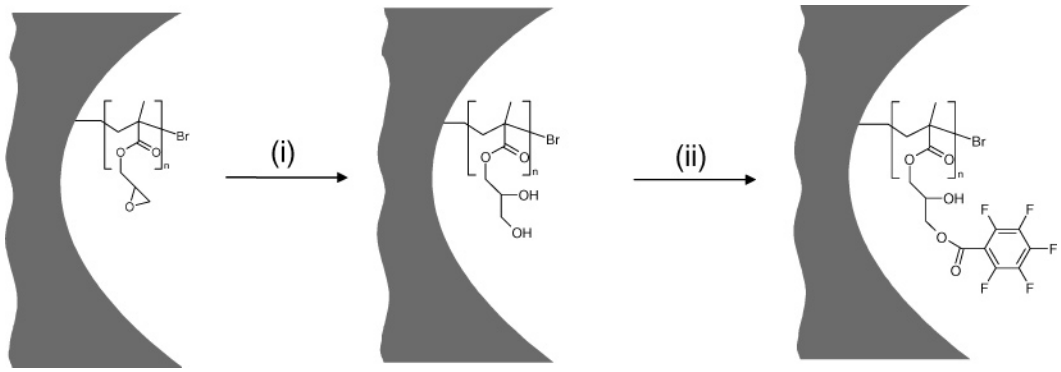

Figure 8. Synthetic approach for modification of p(HIPE-*g*-GMA). Conditions: (i) p(HIPE-*g*-GMA) (0.5 cm^3), 10 mL of THF, 12 drops of concentrated HCl, stirring r.t. for 45 min, washed with THF, MeOH, and EtOH, and dried in vacuo for 16 h at 37 °C; (ii) 20 mL of CH_2Cl_2, 148 mg of Et_3N, DMAP cat., 260 mg of PFBC, washed with CH_2Cl_2, THF, acetone, and EtOH, and dried in vacuo for 16 h at 37 °C.

a control experiment was performed. When a pHIPE without ATRP initiator was added to a solution-based ATRP reaction of GMA, the control pHIPE remained unmodified and the pGMA formed only in the solution and not in the matrix. Due to the porous nature of the pHIPEs, we expected that there could be absorption of the pGMA into the pHIPE. This did occur, but the polymer could be removed by thorough washing in a suitable solvent. Based on these results we conclude that the pGMA layer observed in Figures 7a−7d is chemisorbed to the surface by ATRP and not physisborbed by cross-linking. However, it cannot be excluded that partial cross-linking takes place in the coating.

Further Modification of p(HIPE-*g*-GMA). We further investigated the availability to promote modification of the p(HIPE-*g*-GMA). As previously mentioned, the epoxide groups of the pGMA are highly reactive. Hydrolysis of the ring in the presence of an acid generates a glycol which renders the pHIPE hydrophilic.[43] It also enables further functionalization of the grafted pGMA from the newly exposed hydroxyl groups. Using the acid chloride 2,3,4,5,6-pentafluorobenzoyl chloride (PFBC), we were able to modify the p(HIPE-*g*-GMA) with a fluorinated aromatic group, as shown in Figure 8.

Both reactions were monitored by ATR-IR spectroscopy and water contact angle measurements. Figure 9 shows a stacked IR plot of the product obtained after the reaction sequence. Inspection of the figure confirms the success of the hydrolysis reaction by the appearance of a broad O−H vibration around 3500 cm^{-1}. After reaction with PFBC, the spectrum changes with the presence of a residual O−H vibration band after PFBC modification, suggesting that the reaction was not quantitative. This might be due to sterical hindrance or differences in the reactivity between the primary and the secondary hydroxy group of the glycol unit. Other apparent features of the addition of the PFBC are the peak at 1000 cm^{-1}, which is characteristic of the −C−O−C− vibration of an ester and the presence of peaks at 1650, 1540, and 1500 cm^{-1}, which are in accordance with the presence of an aromatic ring. A definitive assignment cannot be made

(43) Nystrom, D.; Lindqvist, J.; Ostmark, E.; Hult, A.; Malmstrom, E. *Chem. Commun.* **2006**, *34*, 3594.

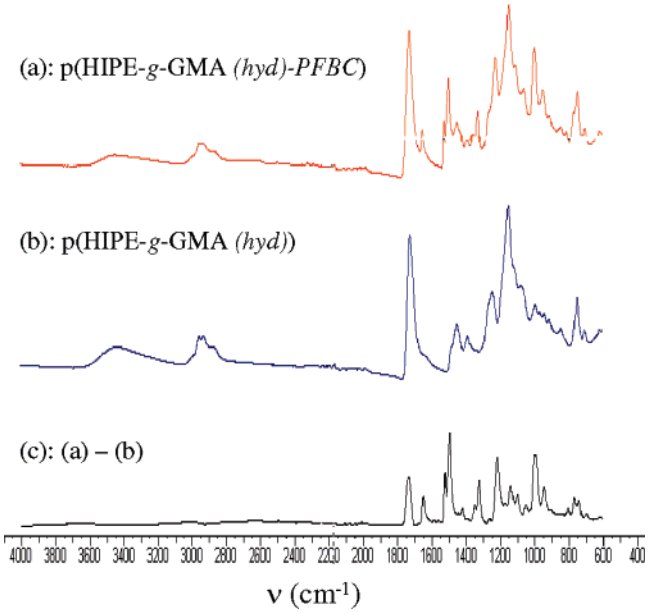

Figure 9. Infrared spectra showing in descending order: (a) spectrum of p(HIPE-*g*-GMA(*hyd*)-PFBC); (b) spectrum of p(HIPE-*g*-GMA) after acid hydrolysis; (c) spectrum resulting from the subtraction of (b) from (a).

as the bands are present in the fingerprint region and in many cases these peaks are caused by combined vibrations. However, the spectra in Figure 9 clearly show the additional bands appear after the modification with PFBC (Figure 9c).

That these modifications have an impact on the macroscopic properties, i.e., hydrophilicity, was shown by water contact angle measurements (Figure 10). Although it is not possible to accurately measure the contact angle due to the non-planar surface, the changes in hydrophobicity owing to hydrolysis of the epoxide ring of the GMA and the subsequent fluorination are evident.

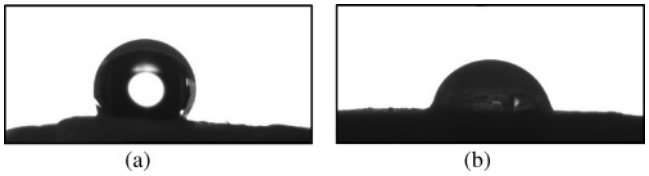

Figure 10. Water droplets on the surface of the modified pHIPES showing the increased hydrophobicity of (a) p(HIPE-*g*-GMA(*hyd*))-PFBC vs (b) p(HIPE-*g*-GMA).

Conclusions

In conclusion, we have shown that an ATRP initiator group can be chemically incorporated into an acrylate-based pHIPE formulation without compromising the emulsion stability. UV curing of this formulation led to pHIPE with ATRP initiator groups on the surface available for polymer grafting reactions. The latter was demonstrated by first grafting of pMMA and reinitiation of HEMA in a block copolymerization approach. Moreover, functionalized pHIPE was obtained by the grafting of GMA. This resulted in a smooth and presumably homogeneous surface coverage of the pHIPE surface with a high density of reactive epoxy groups. These materials can be used as a platform for further functionalization as has been demonstrated by the hydrolytic ring opening of the epoxy rings and subsequent reaction with PFBC to yield a hydrophobic fluorinated pHIPE.

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