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Chemical Functionalization of Emulsion-templated Porous Polymers by Thiol-Ene "Click" Chemistry

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Highly porous polymers (polyHIPEs) have been prepared by the photopolymerization of high internal phase emulsions (HIPEs) with varying ratios of thiol and acrylate monomers. The resulting polymers have a nominal porosity of 80%, and are seen to have a well-defined, interconnected pore morphology, with average pore diameters ranging from 30 to 60 μm. The polyHIPE polymers have been shown using a colourimetric (Ellman's) assay to contain residual thiols which are reactive towards a range of (meth)acrylates (hexfluoroisopropyl acrylate, fluorescein *O*-acrylate and poly(ethylene glycol) methyl ether methacrylate). Functionalization was explored using thermally- and UV-initiated radical-mediated "click" reactions and an amine-catalysed Michael addition reaction. The extent of functionalization was investigated qualitatively and quantitatively using a range of techniques (solid state NMR spectroscopy; FTIR spectroscopy; X-ray photoelectron spectroscopy (XPS); observation of fluorescence); high levels of conversion (up to 90-95%) were observed for the thermally-initiated radical reaction and the Michael reaction.

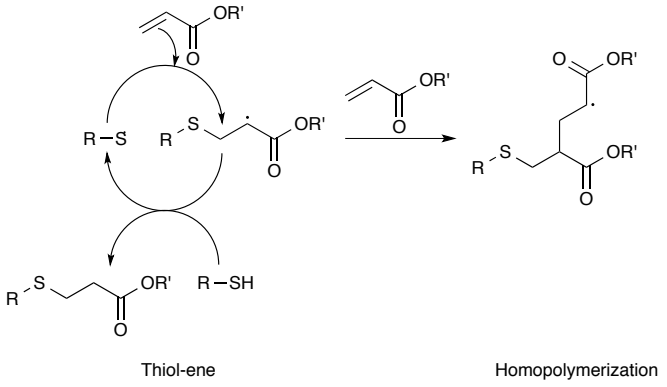
Introduction

Macroporous polymers have found a wide range of applications including as media for hydrogen storage[1], supports for catalysts[2] and for reagents used in synthesis[3], and in biotechnology[4]. Emulsion templating is an attractive method for producing macroporous polymers, as it allows a high level of control over the porosity and pore diameter in the final material[5-8]. The emulsion templating method involves the production of a high internal phase emulsion (HIPE) and the subsequent polymerisation of its continuous phase to give a porous material known as a polyHIPE [9]. Most polyHIPEs have been prepared by radical polymerisation, initiated either thermally or photochemically, however there are some notable examples that have been prepared by other methods[10, 11]. In recent years, polyHIPE materials have been prepared by radically initiated network formation between combinations of thiols and acrylates or alkynes[4, 6, 12], where the combined functionality of the monomers is at least 5. The resulting materials are being explored as scaffolds for tissue engineering[4].

Chemical functionalization is an attractive method to extend the functionality of these polyHIPE materials. Functionalization of polyHIPEs can occur either through the incorporation of a comonomer with the desired functionality into the HIPE system or via a post-polymerisation functionalization approach. Recent work explored the incorporation of the comonomer pentafluorophenyl acrylate (PFPA) into a thiol-acrylate polyHIPE as a route to introducing functionality[13]. After curing, functional amine-bearing molecules could be added to the polyHIPE by amidation of the reactive pentafluorophenyl ester. While this method proved effective, PFPA caused destabilization of the HIPEs and polyHIPE materials with high levels (15 wt. %) of PFPA had large pore diameters.

Post-polymerization functionalization allows for greater control over the morphology and pore diameter of the polyHIPE. Using this method a HIPE with the desired droplet diameter can be prepared and cured to 'lock in' the required pore diameter. After this, chemical functionality can be added. Several routes to the post-polymerization functionalization of polyHIPEs have been described. Poly(styrene/divinylbenzene) materials were functionalized by sulfonation, bromination and nitration [14]. PolyHIPEs produced from 4-vinylbenzyl chloride (VBC) have also been functionalized post-polymerization with a wide range of nucleophiles, including the amines tris(2-aminoethyl)amine and hexamethylenetetramine[15]. Reactive methacrylates, such as glycidyl methacrylate (GMA)[16], and acrylate esters, such as *N*-acryloxysuccinimide (NASI)[17], have also been used in polyHIPE production in order to form polymer networks with reactive handles that can be functionalized post-polymerization. Both the GMA epoxy groups and the *N*-succinimide ester moiety in the NASI monomer are susceptible to nucleophilic attack. As a result of the ease with which each can be functionalized post-polymerization, GMA and NASI polyHIPEs have been explored as supports for biocatalysts[18].

Two competing reactions occur during the formation of thiol-acrylate polymer networks; that between thiols and C=C bonds (enes); and acrylate-acrylate homopolymerization[19, 20] (Scheme 1). The latter leads to the presence of unreacted thiols in the polyHIPE. It has already been shown that residual vinyl groups in the polymer network of a vinyl(polystyrene) polyHIPE can be functionalization with thiol-bearing molecules[21]. Similarly, it is believed that unreacted thiol groups in a thiol-acrylate polyHIPE will open up these polyHIPEs to a wide variety of functionalization chemistries including thiol-ene "click" reactions, Michael additions and disulphide bond formation. The facile reaction conditions of thiol-ene "click" chemistry in particular make it an attractive route to the functionalization of thiol-acrylate polyHIPEs. In recent years, "click" chemistry has been the focus of much interest, with copper catalysed azide-alkyne cycloadditions (CuAAC) receiving much of the attention[22]. However, the need for biocompatible materials that avoid the use of copper has led to increasing emphasis on reactions between thiols and carbon-carbon double or triple bonds. Reactions between thiols and olefins that proceed via a thiyl radical are often referred to as thiol-ene reactions[23]. Their main advantage over CuAAC is that they do not require heavy metal catalysts. They also proceed via a highly selective reaction to yield a single, regioselective product[24]. Michael additions are also an attractive route for the addition of thiols to electron deficient enes[25], such as those found in acrylates. The wide range of commercially available thiols and C=C bond containing molecules is another attractive feature of thiol-ene "click" and thiol-Michael chemistry.



Scheme 1. Competing reactions occurring during network formation between thiols and acrylates: thiol-ene reaction (left cycle); and acrylate homopolymerization (right)

In this paper, we describe post-polymerization functionalization of thiol-acrylate polyHIPE materials using a method that relies on the presence of unreacted thiols[6]. Functionalization has been carried out by i) radical-mediated "click" reaction that can be initiated either thermally or by UV irradiation; and ii) base-catalysed Michael addition.

Experimental Section

Materials

All chemicals were purchased from Sigma Aldrich with the exception of the surfactant Hypermer B246 (a block copolymer of polyhydroxystearic acid and polyethylene glycol), which was obtained from Croda. All were used without further purification. The molecular weight of the poly(ethylene glycol) methyl ether methacrylate (PEGMA) monomer was 300 Da.

UV Curing

All UV curing was carried out using a Fusion UV Systems, Inc. Light Hammer 6 variable power UV curing system with LCE-6 bench-top conveyer. The operating wavelength of the hydrogen bulb is 200-450 nm and the maximum intensity is 200 $W.cm^{-2}$.

Characterization

Scanning Electron Microscopy

PolyHIPE morphology was investigated using a Philips/FEI XL30 ESEM operating at 20 kV. Fractured polyHIPE pieces were sputter-coated with gold and mounted on carbon fibre pads adhered to aluminium stubs. Average void sizes were then calculated using Image J Version 1.44p and applying a statistical correction factor[8].

NMR Spectroscopy

Solid-state ^{19}F NMR spectra were obtained using a Varian VNMRS 400 spectrometer using a direct polarisation experiment at a frequency of 282.087 MHz. Solid-state ^{13}C NMR spectra were obtained using a Varian VNMRS 400 spectrometer using a direct polarisation experiment at a frequency of 100.56 MHz.

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectra were obtained at the National EPSRC User's Service (NEXUS) at Newcastle University, an EPSRC Mid-Range Facility. XPS analysis was performed using a K-Alpha instrument equipped with monochromated Al Ka source (Thermo Scientific) in NEXUS. A pass energy of 200 eV and a step size of 1.0 eV was employed for all survey spectra while a pass energy of 40 eV and a step size of 0.1 eV was used for high resolution spectra.

PolyHIPE Preparation

PolyHIPEs of 80% nominal porosity and with three different thiol:acrylate molar ratios were prepared: 60% thiol, 40% acrylate; 50% thiol, 50% acrylate; and 40% thiol, and 60% acrylate. Since the polymer network formation relies on a 1:1 reaction between thiols and alkenes, the monomer mixture cannot be too rich in either thiol or acrylate. The quantities of monomer used are shown in Table 1. The HIPE oil phase, consisting of trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), trimethylolpropane triacrylate (TMPTA), 1,2-dichloroethane (7ml), surfactant Hypermer B246 (3 wt% of organic phase) and photoinitiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide/2-hydroxy-2-methyl-propiophenone blend (7 wt% of monomer content) was added to a 250 ml two-necked round bottom flask with continuous stirring at 350 rpm from an overhead stirrer fitted with a D

shaped PTFE paddle. Water (56 ml) was added dropwise to form the HIPE, which had an 80% internal phase volume fraction. This was then stirred for a further minute in order to ensure that the emulsion was homogeneous. The emulsion was then poured into a mould consisting of two glass slides and a 5 cm by 5 cm PTFE square. Once in the mould the HIPE was then cured by passing under the UV lamp six times (three times on each side of the mould) at a speed of approximately 3.5 m min^{-1}. Once cured the polyHIPE was then washed by immersion in acetone. The solid polyHIPE was then washed further by soxhlet extraction with dichloromethane overnight. The polyHIPE was then dried under reduced pressure for several hours.

Table 1. Components used to prepare thiol-acrylate polyHIPEs and their residual thiol content

PolyHIPE	Thiol[a] (mmol)	Acrylate[a] (mmol)	Residual thiol conc. ($mmolg^{-1}$)[b]	Theoretical residual thiol conc. ($mmolg^{-1}$)[c]
60% Thiol	12.1	8.07	0.35 ± 0.07	1.67
50% Thiol	10.0	10.0	0.25 ± 0.08	0.00
40% Thiol	8.07	12.1	0.09 ± 0.12	0.00

[a] thiol = trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), acrylate = trimethylolpropane triacrylate (TMPTA); [b] obtained by colorimetric assay using Ellman's reagent, values quoted are averages (n=3) and errors are the standard deviation; [c] calculated according to eq. 1.

Calculation of Unreacted Thiol Loading in PolyHIPE Materials

A theoretical concentration of unreacted thiol was calculated for the 60% thiol polyHIPE using Equation 1[26].

$$ThiolLoading = \frac{(n_{initial\ thiol\ groups} - n_{initial\ \pi\ bonds})}{Total\ mass\ of\ reagents} \quad (1)$$

where n = number of moles.

Determination of Thiol Loading using Ellman's Reagent

The determination of the thiol loading of thiol-acrylate polyHIPEs was performed via a colorimetric assay using a previously described method[27]. Briefly: 5-10 mg polyHIPE was frozen in liquid nitrogen and then ground to a powder with a mortar and pestle. This powder was then transferred to a 5 ml volumetric flask and 1 ml THF was added. The polyHIPE was left to swell for 10 minutes. During this time a 1 ml solution of Ellman's reagent (5 µmol) in ethanol was prepared. This solution was then added to the polyHIPE along with 5 µl diisopropylethylamine. The flask was then shaken for 30 minutes and then diluted to 5 ml with ethanol. This solution was then filtered and diluted to a concentration between 5 µmol and 5mmol in a 96 well plate and the absorbance measured at 412 nm.

Thermally Initiated Functionalization

100 mg polyHIPE was frozen in liquid nitrogen and then ground to a powder with a mortar and pestle. This powder was then transferred to a glass vial and 10 ml toluene added. The polyHIPE was left to swell in the toluene for 10 minutes. Two molar equivalents of the desired acrylate and 0.5 equivalents AIBN, relative to the calculated thiol loading (eq 1), were added to the polyHIPE and the resulting solution was left in an oven at 60 ^{o}C overnight. The polyHIPE was then washed by immersion in toluene (the reaction solvent) and dried under reduced pressure. The quantities of acrylates used are shown in Table 2.

UV Initiated Functionalization

100 mg polyHIPE was frozen in liquid nitrogen and then ground to a powder with a mortar and pestle. This powder was then transferred to a glass vial and 10 ml chloroform added. The polyHIPE was left to swell in the chloroform for 10 minutes. Two molar equivalents of the desired acrylate and 0.5 equivalents AIBN, relative to the calculated thiol loading (eq 1), were added to the polyHIPE and the resulting solution was exposed to UV radiation under the same conditions as those described previously. The polyHIPE was then washed with chloroform (the reaction solvent) and dried under reduced pressure. The quantities of acrylates used are shown in Table 2.

Michael Addition

100 mg polyHIPE was added to a glass vial and 10 ml ethanol added. The polyHIPE was left to swell in the ethanol for 10 minutes. Two molar equivalents of the desired acrylate and 2.5 mol % triethylamine, relative to the calculated thiol loading (eq 1), were added. The resulting solution was left to react at room temperature for 48 hours without stirring. The polyHIPE was then washed in ethanol (the reaction solvent) and dried under reduced pressure. The quantities of acrylates used are shown in Table 2.

Table 2. Quantities of acrylates used to functionalize thiol-acrylate polyHIPEs

Acrylate	Mass (g)
Hexafluoroisopropyl Acrylate	0.070
Fluorescein *O*-Acrylate	0.120
Poly(ethylene glycol) Methyl Ether Methacrylate	0.154

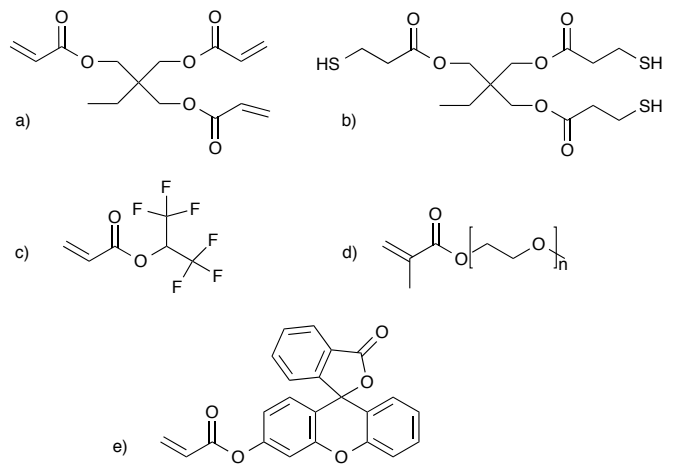
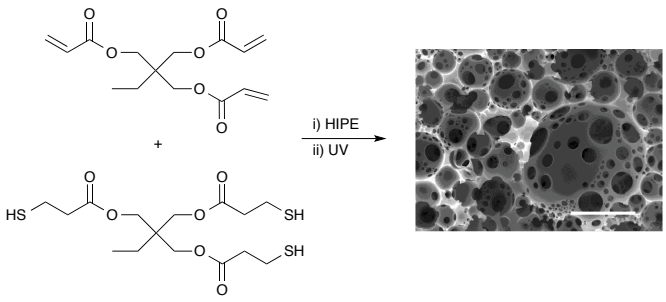


Figure 1. Chemical structure of the monomers used to prepare and functionalize thiol-acrylate polyHIPEs. **a)** trimethylolpropane triacrylate (TMPTA), **b)** trimethylolpropane tris(3-mercaptopropionate) (TMPTMP), **c)** hexafluoroisopropyl acrylate (HFIPA), **d)** poly(ethylene glycol) methyl ether methacrylate (PEGMA), **e)** fluorescein *O*-acrylate (FA).

Results and Discussion

Preparation of Thiol-Acrylate PolyHIPEs

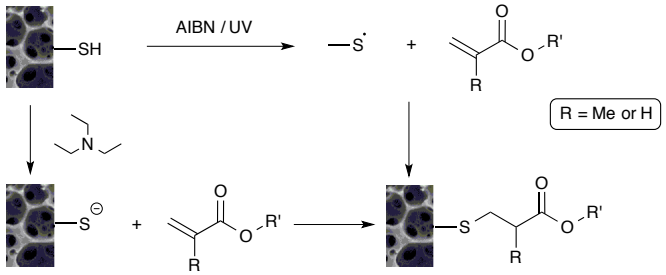
The monomers used in the preparation of the HIPE, namely trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) and trimethylolpropane triacrylate (TMPTA) (Figure 1), are sufficiently hydrophobic to produce an emulsion that has enough kinetic stability for the photopolymerization reaction to occur without significant emulsion collapse[6] (Scheme 2). This produced polyHIPE materials with a well-defined and interconnected porosity. The average pore diameter was found to be between 30 and 40 μm and the nominal porosity defined by the HIPE aqueous phase content is 80%. There are two competing reactions during the formation of the polyHIPE, as shown in Scheme 1. The first reaction is the thiol-ene "click" reaction between the two comonomers; the second is the homopolymerisation of the acrylate monomer. The occurrence of the second reaction leads to unreacted residual thiols in the polyHIPE, the presence of which can be quantified by a colourimetric assay using Ellman's reagent[27] (Table 1). As would be expected, polyHIPEs with a higher percentage of the thiol monomer TMPTMP are found to have a higher concentration of thiol groups at the polymer surface. A TMPTMP level of 40 mol% is sub-stoichiometric, while 50% represents an exact balance with the number of moles of acrylate groups. Consequently, if the acrylates were consumed solely by reaction with thiols, no residual thiol groups should be present in the cured materials. Since the 40 and 50% samples show significant levels of residual thiol (Table 1) we can conclude that another reaction that consumes acrylates is occuring, most probably acrylate homopolymerisation[19, 20]. The stiffness of the samples was observed (by tactile inspection) to increase as the ratio of acrylate : thiol increased.



Scheme 2. Synthesis of thiol-acrylate polyHIPEs from TMPTMP and TMPTA. Scale bar = 50 μm.

Post-polymerisation Functionalization of Residual Thiols

The residual thiols were then used as reactive 'handles' with which to functionalize the polyHIPEs using various (meth)acrylates. The same thiol-ene "click" reaction that was used to form the polyHIPE can also be used to react the thiols and the mechanism by which the reaction occurs is shown in Scheme 3. Another reaction that commonly occurs between thiols and electron defficient alkenes is the amine-catalysed Michael addition, also shown in Scheme 3. This reaction was also investigated as a route to the chemical functionalization of thiol-acrylate polyHIPEs. We chose three representative acrylates: hexafluoroisopropyl (HFIPA) acrylate, fluorescein *O*-acrylate (FA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA) (structures shown in Figure 1). The quantity of acrylate used was calculated as 2 equivalents relative to the highest residual thiol content determined (Table 1). The functionalized samples were analysed by ^{19}F NMR spectroscopy, ^{13}C NMR spectroscopy and XPS.



Scheme 3. Functionalization of residual thiols by radical-mediated "click" and Michael addition reactions.

HFIPA was chosen due to its high fluorine content, which can be detected by ^{19}F NMR spectroscopy and by XPS. In Figure 2, a strong fluorine resonance by solid state ^{19}F NMR spectroscopy is shown for the 50% TMPTMP material functionalised by the UV method. The intensity of the peak does not diminish following extensive washing in THF, indicating that the fluorinated acrylate is bound chemically to the surface of the material[28].

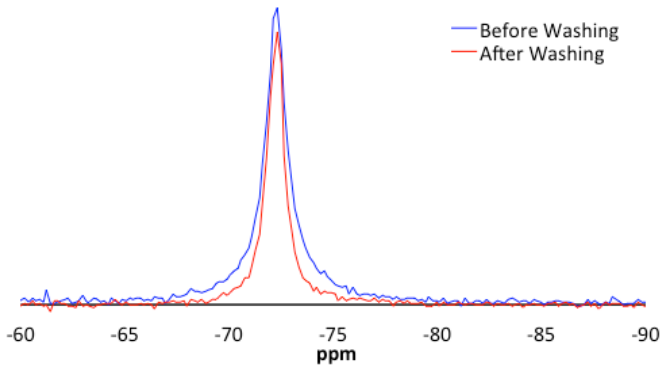


Figure 2. ^{19}F NMR spectra of thiol-acrylate polyHIPE containing 50% TMPTMP functionalized with HFIPA by a UV initiated reaction, before (dark trace) and after washing with THF.

XPS was also used to show the presence of fluorine on the surface of the polyHIPE samples. The high-resolution F(1s) spectrum (Figure 3) suggests that the thermally initiated "click" and Michael addition reactions give a higher level of functionalization than the UV initiated "click" reaction. The low conversions observed for UV initiated "click" reactions are suspected to be due either to the shorter reaction times associated with this method or the opacity of the polyHIPE materials, preventing sufficient penetration of UV light.

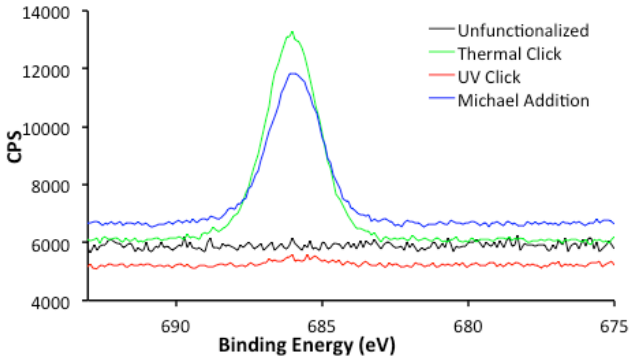


Figure 3. High resolution F(1s)[29] XPS spectra of HFIPA-functionalized thiol-acrylate polyHIPEs containing 50% TMPTMP. From top to bottom: thermal click reaction; Michael addition reaction; unfunctionalized sample; UV click reaction.

The concentration of free thiol in the polyHIPE materials were quantified using Ellman's reagent; results are shown in Table 3. In agreement with the XPS data, the thermally initiated "click" reaction gives a significantly higher level of functionalization; almost 90%, while the UV reaction gives around 55% conversion. The highest levels of functionalization achieved were obtained via the Michael addition, with conversions of over 90% being observed.

Table 3. Functionalization of polyHIPEs with HFIPA determined by colourimetric assay using Ellman's reagent.

Sample	Functionalization (%)
Thermally Functionalized, 60% TMPTMP	89
Thermally Functionalized, 50% TMPTMP	87
Thermally Functionalized, 40% TMPTMP	88
UV Functionalized, 60% TMPTMP	59
UV Functionalized, 50% TMPTMP	55
UV Functionalized, 40% TMPTMP	29
Michael Addition, 60% TMPTMP	94
Michael Addition, 50% TMPTMP	93
Michael Addition, 40% TMPTMP	82

The morphology of polyHIPEs is of crucial importance for any intended application. Changes in morphology during functionalization may lead to polyHIPEs that are not fit for their desired purpose. SEM was used to investigate the polyHIPE morphology both before and after functionalization and the average void diameters were calculated. The polyHIPEs have an open cell morphology with an interconnected network of pores (Figure 4), making them potentially suitable for applications such as tissue engineering[4]. The SEM images indicate that post-polymerization functionalization either via a "click" or Michael addition reaction has no major influence on the morphology of the polyHIPE. After functionalization the polyHIPEs retain their open cell structure and the average void size remains between 30-40 μm.

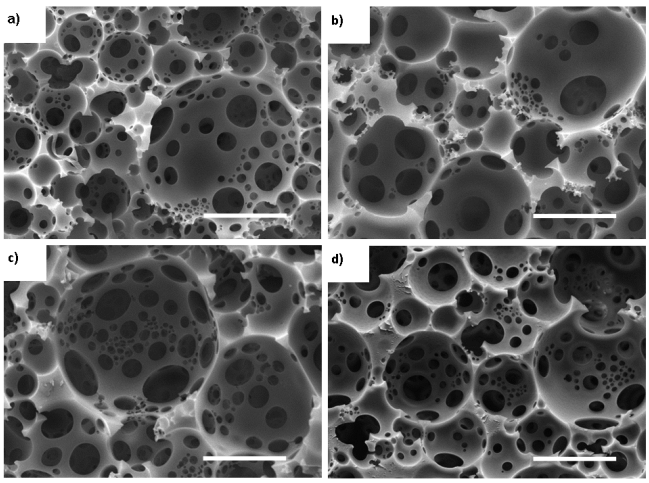


Figure 4. Morphology of 60% TMPTMP polyHIPEs functionalized with HFIPA post-polymerization as obtained by SEM. **a)** before functionalization, **b)** after functionalization by a thermally-initiated "click" reaction. **c)** after functionalization by a UV-initiated "click" reaction. **d)** after functionalization by a Michael addition. Scale bar = 50 µm.

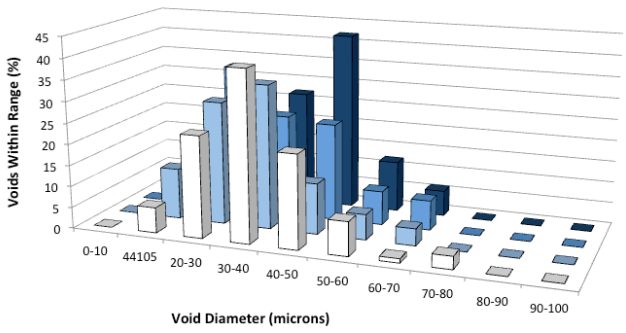


Figure 5. Void diameters of 40% TMPTMP polyHIPEs obtained by image analysis of SEMs. Front to back: unfunctionalized polyHIPE; after functionalization by thermally-initiated "click" reaction; after functionalization by UV-initiated "click" reaction; after functionalization by Michael addition reaction.

In order to give a visual confirmation of the functionalization of thiol-acrylate polyHIPEs containing residual thiols, the Michael reaction was carried out with fluorescein *O*-acrylate. After reaction, samples were washed thoroughly with ethanol in order to remove any unbound dye from the polyHIPE. After drying the material was examined under UV light. Strong green fluorescence was observed for the modified sample (Figure 6), indicating the dye was successfully bonded to the polyHIPE surface.

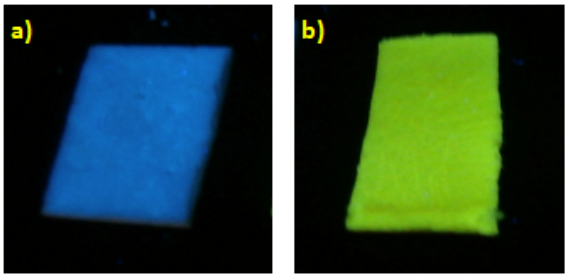


Figure 6. 40% TMPTMP polyHIPEs functionalized with fluorescein O-acrylate via a Michael addition reaction, observed under illumination by UV light (λ = 254 nm, TLC lamp). **a)** Unfunctionalized polyHIPE. **b)** Functionalized with fluorescein *O*-acrylate.

Thiol-acrylate polyHIPEs are hydrophobic; however, there is interest in making hydrophilic polyHIPEs for applications in biotechnology. The availability of methacrylate terminated poly(ethylene glycol) (PEG) chains provides a route to hydrophilic thiol-acrylate polyHIPEs via post-polymerization functionalization. A short chain PEG methacrylate (M_n = 300 Da) was chosen as PEG has been shown to prevent non-specific protein adsorption onto polymer surfaces[30]. The presence of peaks corresponding to PEG C-O-C ester bonds (around 71 ppm) in the solid-state ^{13}C NMR spectrum (Figure 7) indicates that the PEGMA is bonded chemically to the polyHIPE.

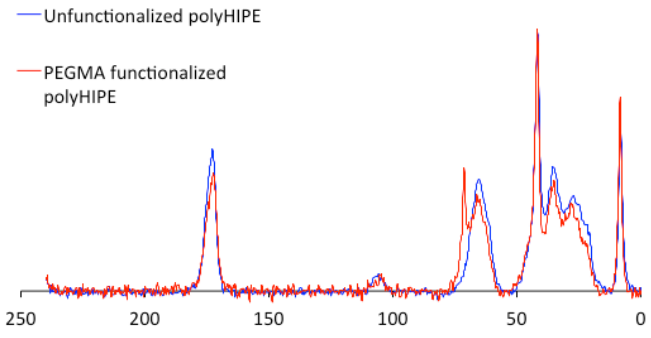


Figure 7. Solid state ^{13}C NMR spectrum of 40% TMPTMP polyHIPE functionalized with PEGMA.

The hydrophilicity of the PEG functionalized polyHIPE was tested by dropping deionized water containing a blue food dye onto a dry piece of the functionalized polyHIPE, as shown in Figure 8. PolyHIPEs functionalized with PEGMA using thermally-initiated "click" and Michael addition reactions were found to be sufficiently hydrophilic to allow absorption of the water droplet within a few minutes of application to the polyHIPE surface. In contrast, the water droplet remained on the surface of the unfunctionalized material and of that modified by the UV-initiated click reaction. These results agree with the findings of the HFIPA modification reactions whereby the thermally-initiated click and the Michael addition reactions give the greatest extent of functionalization.

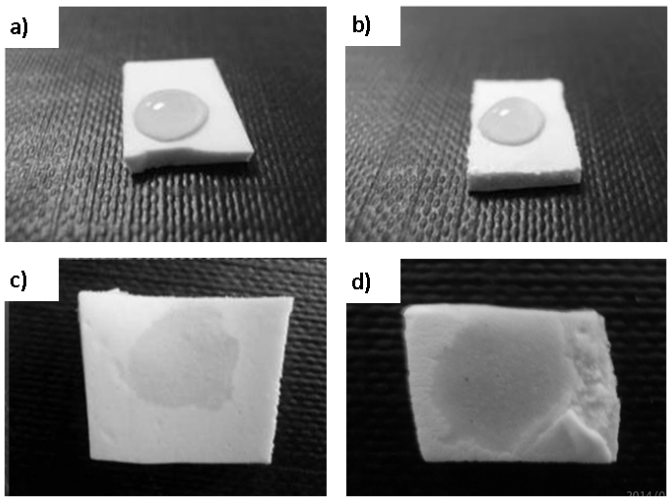


Figure 8. Wetting of 60% TMPTMP polyHIPEs. **a)** before attachment of PEGMA to the surface, **b)** after attachment of PEGMA by a UV-initiated "click" reaction, **c)**

after the attachment of PEGMA by a thermally-initiated "click" reaction, **d)** after the attachment of PEGMA by a Michael addition reaction.

Conclusions

Three thiol-ene reactions (UV- and thermally-initiated radical thiol-ene "click" reaction and base catalysed Michael addition) were utilized in order to functionalize thiol-acrylate polyHIPE post-polymerization. Thermally initiated "click" functionalizations were shown to proceed with high levels of conversion, as were the Michael additions. The conversions observed for UV initiated "click" functionalization were lower than expected, due either to the shorter reaction times associated with this method or the opacity of the materials. Both thermally-initiated thiol-ene "click" and Michael addition chemistries offer an attractive route to the functionalization of thiol-acrylate polyHIPEs. We have shown that the functionalization reactions can occur with a range of readily available (meth)acrylates and do not have a negative impact on the morphology of the polyHIPEs. The reactions are quick and can be carried out under mild conditions, which potentially would allow the attachment of sensitive molecules. These functionalization methods could be used to attach a wide range of molecules, including biologically relevant molecules such as proteins, or enzymes and catalysts, to the surface of thiol-acrylate polyHIPEs.

Acknowledgements

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Notes and references

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