

**Supplementary Information**  
**for**  
**Acid and base catalysed reactions in one pot with site-isolated polyHIPE**  
**catalysts**

Erdem Yavuz,<sup>a,b</sup> Nikolay Cherkasov<sup>a</sup> and Volkan Degirmenci<sup>\*a</sup>

<sup>a</sup>School of Engineering, University of Warwick, Coventry, CV4 7AL, United Kingdom.

<sup>b</sup>Istanbul Technical University, Department of Chemistry, Faculty of Science, 34469 Maslak, Istanbul, Turkey.

\*Corresponding author. E-mail address: v.degirmenci@warwick.ac.uk

## S1. Experimental details

### Materials

The following materials were used as purchased: 4-vinyl benzylchloride (90 %, Sigma-Aldrich) and styrene (99%, Sigma-Aldrich), divinylbenzene (80%, Sigma-Aldrich), CuBr (99%, Sigma-Aldrich), CaCl<sub>2</sub> hydrate (97%, Sigma-Aldrich), 2,2'-Bipyridyl (99%, Sigma-Aldrich), tert-butyl acrylate (98%, Sigma-Aldrich), toluene anhydrous (99%, Sigma-Aldrich), ethylenediaminetetraacetic acid (99%, Sigma-Aldrich), benzaldehyde dimethyl acetal (99%, Sigma-Aldrich), ethyl cyanoacetate (98%, Sigma-Aldrich), deionised water, tetradecane (98%, Sigma-Aldrich), ethanol (99%, Sigma-Aldrich).

Spectrum 100 instrument.

### Synthesis of polyHIPE: VBC-Styrene-DVB (80% pore volume)

VBC (5.41g, 33.42 mmol), Styrene (3.64 g, 34.83 mmol), DVB (1,21 g, 7.1 mmol) and surfactant Span 80 (2.05 g, 4.7 mmol) were mixed in a round-bottomed flask with an overhead stirrer fitted with a PTFE paddle. The mixture was purged with nitrogen gas for 15 min. The aqueous phase was prepared separately by dissolving potassium persulfate (0.2 g, 0.74 mmol) and calcium chloride dihydrate (1.0 g, 6.80 mmol) in de-ionised water (40 mL) and the resulting solution was purged with nitrogen for 15 min. The organic solution was stirred under nitrogen at 300 rpm and the aqueous phase was added dropwise over 30 min under constant mechanical stirring. After complete addition of the aqueous phase, stirring was continued for 1 h at 300 to produce a homogeneous emulsion and at 50 rpm to remove any entrapped air bubbles. The emulsion was transferred to the mold (PET container) and cured at 60 °C for 48 h. The resulting polyHIPE was purified by Soxhlet extraction (distilled water and IPA, both for 24 h) then dried in vacuo for 24 h.

### Poly(tert-Butyl acrylate) grafting onto polyHIPEs (PolyHIPE-g-PtBA)

Graft polymerization of tBA monomer was achieved through chlorine initiation sites on the polyHIPE. A typical procedure was as follows: CuBr, (0.288 g, 2.00 mmol), bipyridine (0.624 g 4.00 mmol) and tBA (12 mL, 84.0 mmol) were transferred in a 3 necked flask under a nitrogen atmosphere. The mixture was degassed under a stream of nitrogen for 15 minutes and then toluene (12 mL) was added rapidly via a syringe. The powdered polyHIPE foam (1.0 g) was

added quickly through the neck of the flask. The flask was then degassed again for a period of 15 min. The grafting reaction carried out at 80 °C for 20 h. At the end of the reaction, the content was poured into toluene (50 mL) to remove polymerization impurities then filtered under gravity. The material was then washed with ethanol (50 mL), distilled water (50 mL) and ethanol (50 mL). The grafted polyHIPE was transferred to EDTA solution (2.5 wt%) for 24 h to remove the remaining copper salt. The grafted powdered polyHIPE were filtered and washed with excess water and alcohol (30 mL). The resulting polymer was dried under vacuum at 40 °C for 24 h.

#### **Hydrolysis of polyHIPE-g-PtBA with Hydrochloric acid**

The polyHIPE-g-PtBA (Poly(tert-Butyl acrylate) grafted polyHIPE) (1.00 g) was transferred into a round bottom flask containing dioxane (10 mL) and HCl (5 mL) at room temperature. The mixture was left at reflux temperature for 6 h and then cooled down to temperature. The resulted polymer was transferred into dioxane (20 mL) and washed sequentially with ethanol (20 mL), deionized water (50 mL), and ethanol (20 mL). The hydrolysed polyHIPE was dried under vacuum at 40 °C for 24 h.

#### **Poly (GMA) grafting onto polyHIPEs (PolyHIPE-g-PGMA)**

Graft polymerization of glycidyl methacrylate (GMA) monomer was achieved through chlorine initiation sites on the polyHIPE. A typical procedure was as follows: CuBr, (0.288 g, 2.00 mmol), bipyridine (0.624 g 4.00 mmol) and GMA (11.1 mL, 83.6 mmol) were transferred in a 3 necked flask under a nitrogen atmosphere. The mixture was degassed under a stream of nitrogen for 15 minutes and then dioxane (10 mL) was added rapidly via a syringe. The powdered polyHIPE foam (1.0 g) was added quickly through the neck of the flask. The flask was then degassed again for a period of 15 min. The grafting reaction carried out at 65 °C for 20 h. At the end of the reaction, the content was poured into dioxane (50 mL) to remove polymerization impurities then filtered under gravity. It was then washed with ethanol (50 mL), distilled water (50 mL) and ethanol (50 mL), respectively. The poly(GMA) grafted polyHIPE (PolyHIPE-g-PGMA) was transferred to EDTA solution (2.5 wt%) for 24 h to remove the remaining copper salt. The grafted powdered polyHIPE were filtered and washed with excess water and ethanol (30 mL). The resulting polymer was dried under vacuum at 40 °C for 24 h.

#### **Modification of PolyHIPE-g-PGMA with Diethylamine (DEA)**

The polyHIPE-g-PGMA (1.00 g) was transferred into a round bottom flask containing DEA (10 mL) and ethanol (10 mL) at 0 °C and the mixture was stirred at room temperature for 24 h and then at 50 °C for 24 h. The resulted polymer was transferred into deionized water (50 mL) and washed with sequentially deionized water (50 mL) and ethanol (50 mL). The modified polyHIPE was dried under vacuum at 40 °C for 24 h.

#### **Determination of Amine content of Diethylamine(DEA) functional polyHIPE-g-PGMA**

To determine the amine content, 25 mg of the polymer sample was left in contact with 0.1 M of HCl for 24 h at room temperature. After filtration, 1 mL of the filtrate was transferred into 10 mL flask and the amine content of the solution was determined by titration with a 0.01 M NaOH solution in the presence of phenolphthalein indicator.

## **S2. Chemisorption of ammonia and propionic acid**

The polymer sample analysed was placed into a glass tube between 2 plugs of quartz wool, dried in an N<sub>2</sub> flow of 20 mL min<sup>-1</sup> (STP) at 130 °C for 5 h. The temperature was decreased to 100 °C to minimise possible ammonia physisorption. All the stainless steel piping was kept 110 °C to decrease ammonia adsorption. In a parallel line, a flow of 20 mL min<sup>-1</sup> (STP) 1 vol. % NH<sub>3</sub>, 1 vol. %Ar in N<sub>2</sub> was passed into a quadrupole mass spectrometer until getting stable readings. Afterwards, the gases were switched over with a 6-way valve and the flow of ammonia was introduced into the sample measuring the outlet gas concentrations. The concentration of Ar and NH<sub>3</sub> instantaneously decreased, Ar increased to the baseline over a few seconds corresponding to the dead volume of the reactor, while NH<sub>3</sub> concentration stayed low for the next about 30 min. The total area under the adsorption plot minus the dead volume was used for total ammonia capacity calculation.

Propionic acid chemisorption was performed similar to the ammonia chemisorption procedure, but instead of ammonia, vapours of propionic acid were introduced evaporated from liquid (99.8 wt. %) at 18 °C via the N<sub>2</sub> flow of 10 mL min<sup>-1</sup>.