

Ultra-High Surface Area Functional Porous Polymers by Emulsion Templating and Hypercrosslinking: Efficient Nucleophilic Catalyst Supports

Irena Pulko,^[b, c] Jennifer Wall,^[a] Peter Krajnc,^{*,[b]} and Neil R. Cameron^{*,[a]}

4-Dimethylaminopyridine (DMAP) is a highly efficient and important organocatalyst used for a variety of organic reactions,^[1] including the acylation^[2] and silylation^[3] of hindered alcohols, the Baylis–Hillman reaction^[4] and the ring-opening polymerisation of lactide and other lactones.^[5] Heterogeneous versions^[6] supported on soluble^[7] and cross-linked polymers^[8] as well as inorganic nanoparticles^[9] have been described. Soluble catalysts and nanoparticles can show high activities but require extra isolation steps for catalyst recycling. On the other hand, catalysts supported on insoluble polymer beads, whilst being simple to recycle, tend to suffer from a drop in activity compared to the homogeneous catalyst. Furthermore, the performance of catalysts supported on gel-type polymer beads is limited by solvent-dependent access to the reactive sites inside the beads.^[10] The use of permanently porous (often referred to as ‘macroporous’) polymer beads overcomes these solvent limitations,^[11] however reactions with these supports can be slow as mass transfer to the active sites on the internal surface of the porous bead occurs by diffusion only.

The mass transport limitations of permanently porous beads can be overcome by using emulsion-templated porous polymers (polyHIPEs), which possess very large pores (1–

100 µm) permitting mass transfer by convection rather than diffusion.^[12] PolyHIPE materials are produced from high internal phase emulsions (HIPEs), where the dispersed phase occupies >74 % of the emulsion volume. PolyHIPEs have been prepared from either oil-in-water (o/w) or water-in-oil (w/o) emulsions and have been used in a flow through manner as scavengers,^[13] reagents,^[14] solid-phase synthesis supports^[15] and chromatography media.^[16]

For polyHIPEs to function as a heterogeneous catalyst support, a high surface area is required. PolyHIPE materials with surface areas up to 690 m² g^{−1} can be prepared by the addition of an organic porogen to the monomer phase together with careful choice of HIPE stabilising surfactant.^[17] However the resulting materials are rather weak mechanically. An alternative approach to introducing high surface areas is the hypercrosslinking method.^[18] Hypercrosslinked polymers contain a very high density of crosslinks together with molecular-sized pores (micropores), and exhibit important properties such as an ultra-high surface area (up to 2000 m² g^{−1}) and the ability to sorb large amounts of both thermodynamically good and poor solvents, due to high matrix rigidity and a much reduced degree of chain entanglement. Hypercrosslinked polystyrene, in the form of beads, can be prepared by Lewis acid catalysed post polymerisation crosslinking of poly(4-vinylbenzyl chloride) (pVBC) (Scheme 1).^[19] High surface area polyHIPE materials for gas storage have recently been prepared by this method.^[20]

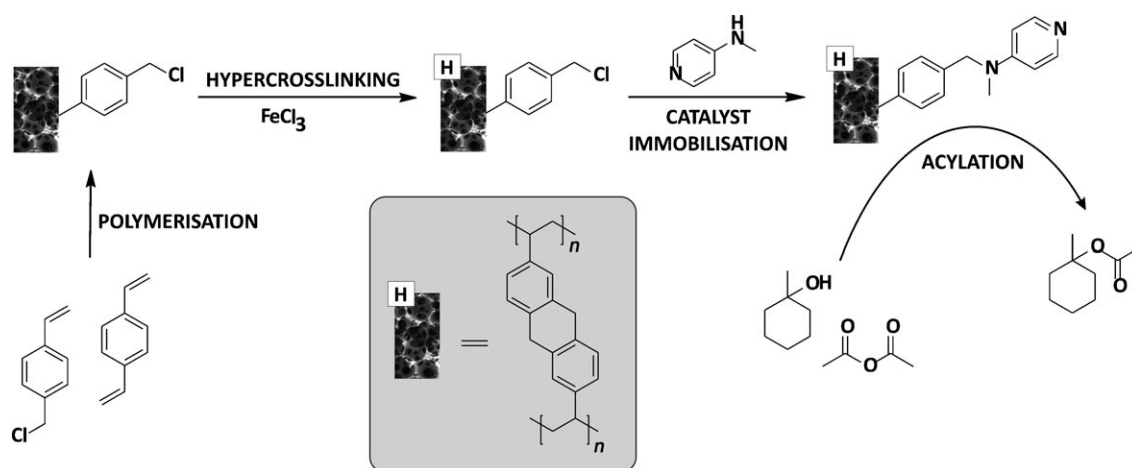
Hypercrosslinked polyHIPE is a potentially attractive catalyst support material due to the combination in one material of an interconnected network of macropores, facilitating access of reagents to the surface, with an ultra-high surface area produced by the hypercrosslinking induced microporosity. Furthermore, hypercrosslinking VBC polyHIPEs to less than full conversion would leave residual chloromethyl functionality for the attachment of catalysts. In this work, we demonstrate proof of this concept; the hypercrosslinking of VBC polyHIPEs is controlled to leave unreacted benzyl chloride moieties with which to anchor DMAP, leading to a highly efficient, recyclable nucleophilic catalyst (Scheme 1).

[a] J. Wall, Prof. N. R. Cameron
Department of Chemistry and Biophysical Sciences Institute
Durham University
South Road, Durham, DH1 3LE (UK)
Fax: (+44) 191-3844737
E-mail: n.r.cameron@durham.ac.uk

[b] Dr. I. Pulko, Prof. P. Krajnc
Faculty of Chemistry and Chemical Engineering
University of Maribor
Smetanova 17, 2000 Maribor (Slovenia)
Fax: (+386)2-2527-774
E-mail: peter.krajnc@uni-mb.si

[c] Dr. I. Pulko
Polymer Technology College
Pod gradom 4, 2380 Slovenj Gradec (Slovenia)

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.200903043>.



Scheme 1. Formation of hypercrosslinked, PolyHIPE-based DMAP supports and use as acylation catalysts.

VBC polyHIPEs were prepared by an established procedure of polymerising the continuous phase of a w/o HIPE with 4-VBC and 2% (w/w) of DVB in the oil phase, and a volume ratio of aqueous to oil phase of 9 to 1.^[21] Production of such a polyHIPE generally leads to a material with a relatively low surface area. In this case, the BET surface area of the VBC polyHIPE (PHP) was $5.7 \text{ m}^2 \text{ g}^{-1}$, as measured by nitrogen adsorption (Table 1). A typical polyHIPE architec-

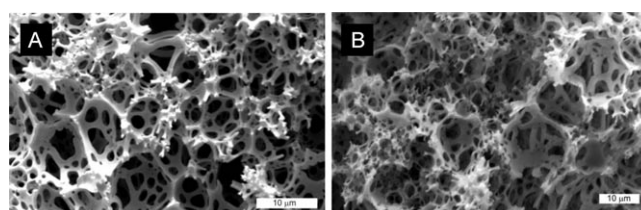


Figure 1. SEM of VBC polyHIPE before (A) and after (B) hypercrosslinking reaction. Scale bars = 10 μm .

Table 1. Hypercrosslinking and functionalisation of polyHIPEs and polymer beads.

Polymer ^[a]	% Cl ^[b]	% N ^[b]	Loading [mmol g ⁻¹] ^[c]	Surface area [m ² g ⁻¹]
PHP	13.02	0	3.67	5.7
HXL-PHP	8.07	0	2.27	990
PHP-MAP	1.32	7.86	2.81	6.4
HXL-PHP-MAP	2.41	3.33	1.19	715
B	17.65	0	4.97	^[d]
HXL-B	8.04	0	2.26	1100
B-MAP	5.52	4.79	2.26	^[d]
HXL-B-MAP	3.23	2.18	0.78	935

[a] PHP = polyHIPE, B = beads, HXL = hypercrosslinked, MAP = 4-(N-methylamino)pyridine. [b] Determined by elemental analysis. [c] For samples reacted with MAP: MAP loading, from % N value; otherwise, Cl loading from % Cl. [d] Samples have no dry state porosity so have no significant sorption of N₂.

ture, with large voids created by droplets of the internal phase of the precursor emulsion together with an extensive network of interconnecting pores, is produced (Figure 1). For the hypercrosslinking procedure, powdered polyHIPE was allowed to react with FeCl₃ in dichloroethane for 15 min at 80 °C. An enormous enhancement of the BET surface area to $990 \text{ m}^2 \text{ g}^{-1}$ was found (Table 1; HXL-PHP). It was established previously that FeCl₃ is the most suitable Lewis acid for the hypercrosslinking reaction^[19a] and that a short reaction time is sufficient.^[18d]

Since post polymerisation crosslinking involves reactions between pre-formed polymer chains, the supramolecular structure is affected and this could lead to a change in the

morphological features of the material. The sample HXL-PHP (polyHIPE after hypercrosslinking) was therefore investigated by SEM and no significant change in morphological features was observed compared to the unreacted material (Figure 1). Unlike the use of porogenic solvents to enhance surface area,^[17] the HXL process does not affect negatively the mechanical properties of the material.

The chloromethyl groups in VBC polymers allow post-polymerisation functionalisation. The same groups are consumed during the hypercrosslinking reaction, and if the reaction is allowed to proceed to near-completion, the resulting hypercrosslinked matrix will be difficult to functionalise. Therefore, controlling the degree of hypercrosslinking to leave a certain amount of unreacted chloromethyl groups, is required to produce ultra-high surface area, functional polymers. The results of chlorine analysis versus duration of hypercrosslinking reaction (Figure 2) indicate the possibility to control the degree of reaction of the chloromethyl groups. From an initial loading of chloromethyl groups of 3.6 mmol g^{-1} , after one hour of crosslinking reaction the loading was reduced to 2.1 mmol g^{-1} , and the BET surface area increased from 10 to $990 \text{ m}^2 \text{ g}^{-1}$. Continuing the reaction further decreased the loading to 1.3 mmol g^{-1} and increased the BET surface area to $1085 \text{ m}^2 \text{ g}^{-1}$.

As a comparison, hypercrosslinking reactions were similarly performed on gel-type polymer beads prepared by the suspension polymerisation method. Polymer beads (B) with a 2% degree of crosslinking by divinylbenzene and a chloro-

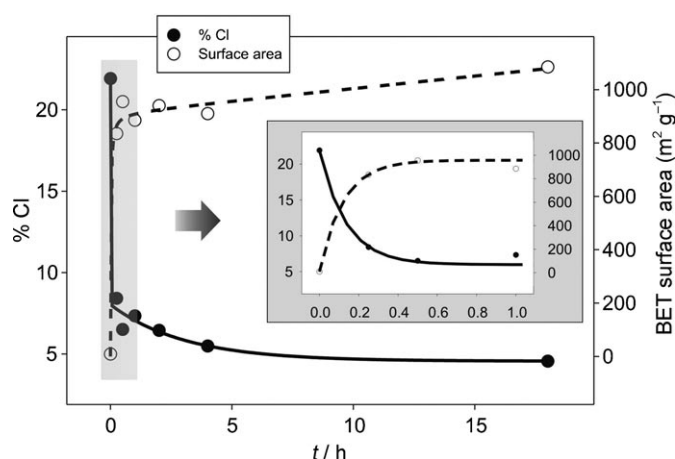


Figure 2. Increase in surface area (open circles) and decrease in chlorine loading (closed circles) with progress of hypercrosslinking reaction. Inset shows period up to 1 h (axes labels the same as the main figure).

methyl group loading of 5 mmol g⁻¹ were subjected to the same hypercrosslinking treatment with FeCl₃. After 15 min of reaction, beads (HXL-B) were obtained with a reduced loading of chloromethyl groups (2.3 mmol g⁻¹) and an increased BET surface area of 1100 m² g⁻¹ (the beads exhibited no nitrogen-accessible porosity prior to hypercrosslinking).

To demonstrate the applicability of the hypercrosslinked polyHIPE materials, their use as a support material for the nucleophilic catalyst DMAP was investigated. HXL-PHP was suspended in THF with NaH while 4-(N-methylamino)-pyridine (MAP) was added in excess. Characterisation by FTIR (see Figure S3 in the Supporting Information) and elemental analysis (Table 1) confirmed the presence of the immobilised MAP moiety (see also Scheme 1). In a similar manner, three control polymer supported DMAP samples were prepared: non-hypercrosslinked polyHIPE (PHP), to probe the effect of surface area; hypercrosslinked beads (HXL-B), to study the influence of reactive site accessibility; and non-hypercrosslinked beads (B), which have been used previously to support DMAP.^[8a] These polymers (see Table 1 for loadings) were used as catalysts for the acylation of methylcyclohexanol with acetic anhydride (Scheme 1).^[8a] The amount of catalyst used was 1 mol% relative to the starting material (methylcyclohexanol). To test the solvent compatibility influence on catalyst reactivity, two solvents were chosen for the reaction: diethyl ether and toluene, which are non-swelling and swelling solvents, respectively, for crosslinked polystyrene. The results are presented in Figure 3.

It is evident that hypercrosslinking produces polyHIPE materials that give more efficient supported DMAP catalysts (Figure 3A). Conversion reaches 100% after 3 h for HXL-PHP-MAP in diethyl ether, while the un-hypercrosslinked polyHIPE support (PHP-MAP) reaches only 65% conversion after the same time period. A similar difference is evident when toluene, a swelling solvent for PHP, is used. Figure 3A also reveals solvent-induced differences in perfor-

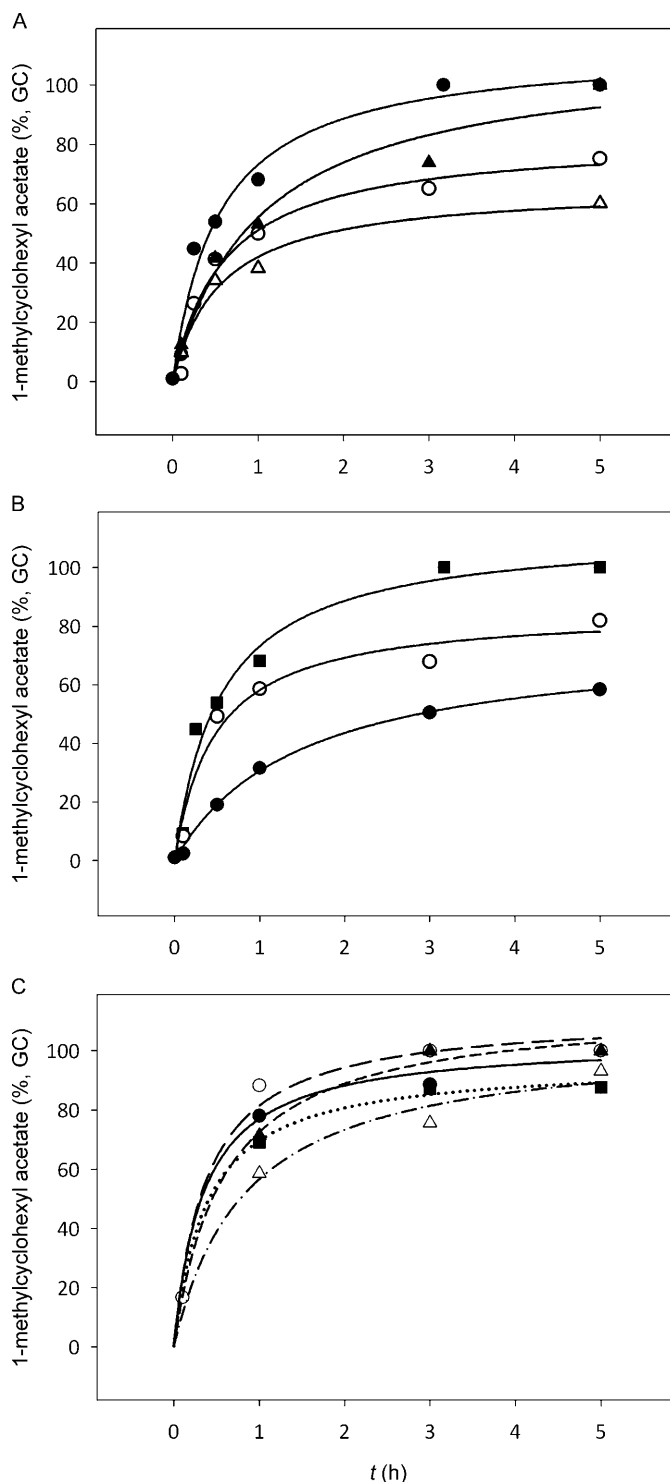


Figure 3. Conversion of methylcyclohexanol with supported DMAP (1 mol% catalyst relative to methylcyclohexanol). A) comparison of hypercrosslinked and un-hypercrosslinked polyHIPEs in diethyl ether and toluene (open triangles: PHP-MAP in toluene; open circles: PHP-MAP in diethyl ether; closed circles: HXL-PHP-MAP in diethyl ether; closed triangles: HXL-PHP-MAP in toluene); B) comparison of polyHIPE and beads in diethyl ether (squares: HXL-PHP-MAP; open circles: HXL-B-MAP; closed circles: B-MAP); C) recycling of HXL-PHP-MAP (five runs; closed circles: run 1; open circles: run 2; closed triangles: run 3; open triangles: run 4; closed squares: run 5). See Table 1 footnote for definition of PHP, HXL and B.

mance: the most efficient catalytic performance is obtained with HXL-PHP-MAP in diethyl ether, possibly due to the higher polarity of this solvent and, therefore, its better suitability for nucleophilic reactions. HXL-PHP-MAP outperforms HXL-B-MAP, as is shown in Figure 3B. After three hours, conversion of methylcyclohexanol is only 68%, compared to 100% with HXL-PHP-MAP. This indicates the more rapid mass transfer to the surface enabled by the much more open pore morphology of polyHIPE, which permits convective flow within this material. Un-hypercrosslinked beads (B-MAP) similarly are outperformed by HXL-B-MAP due to low swellability of the former in diethyl ether. The performance of these beads in toluene is similar to that reported previously for the same polymer supported catalyst and catalytic reaction (data not shown), although the catalyst loadings are different.^[8a] The ability of these beads to give any conversion of methylcyclohexanol in diethyl ether is presumably due to the presence of significant quantities of MAP on the surface of the beads (the overall loading is quite high, see Table 1). To investigate catalyst recyclability, a sample of HXL-PHP-MAP was used five times without significant loss of activity (Figure 3C). This confirms the covalent attachment and minimal leakage of the catalyst, as well as the possibility of reusing the supported catalyst.

In conclusion, we have demonstrated the ability to control the extent of hypercrosslinking of pVBC polyHIPE materials to derivatise the surface with molecules of interest. This has been demonstrated by attaching 4-(N-methylamino)pyridine (MAP) to give a polyHIPE-supported version of the nucleophilic catalyst DMAP. The MAP immobilised on hypercrosslinked polyHIPE is shown to be highly efficient in the acylation of a tertiary alcohol and significantly outperforms both un-hypercrosslinked polyHIPE and hypercrosslinked beads. The materials in monolithic form could be installed in columns to conduct such catalytic transformations under flow.

Experimental Section

Preparation of 4-vinylbenzyl chloride/divinylbenzene polyHIPE material: 100 mL of an aqueous phase, consisting of $K_2S_2O_8$ (0.11 g, 0.41 mmol) in deionised water (100 mL), was added dropwise with continuous stirring at 300 rpm to an oil phase, consisting of 4-vinylbenzyl chloride (11.62 g, 76 mmol), divinylbenzene (0.25 g, 1.9 mmol), and the surfactant sorbitan monooleate (Span 80; 2.20 g). The emulsion was stirred for another 30 min after addition of the aqueous phase, then transferred to a mold for curing (24 h at 60°C). The resulting polyHIPE was purified by Soxhlet extraction (deionised water and acetone, both for 24 h) then dried in vacuo for 24 h.

Hypercrosslinking of polyHIPE: Powdered polyHIPE (1 g, 3.67 mmol chlorine per gram) was placed in a flask, 1,2-dichloroethane (80 mL) was added and the neck was fitted with a rubber septum. The mixture was degassed under a stream of nitrogen for 15 min with constant stirring, after which time the nitrogen supply was removed and the sealed flask left for a further 45 min (with stirring) to swell the polymer. The flask was then placed in an ice bath and $FeCl_3$ (1.09 g, 6.7 mmol) was added quickly through the neck of the flask. The flask was then resealed and degassed again for a period of 15 min. After removal of the nitrogen supply, the

flask was left stirring in the ice bath for a further 45 min to ensure uniform dispersion of $FeCl_3$. The sealed flask was then placed in an oil bath at 80°C and heated for a period of 18 h. The reaction was then quenched by the addition of methanol (40 mL) then filtered under gravity. It was then washed with methanol (3 × 20 mL) and 0.1 M HNO_3 (aq) (3 × 20 mL) then in soxhlet apparatus with acetone for 24 h. The product was then dried at 50°C in vacuo for 24 h. A similar procedure was used for polymer beads.

Functionalisation of HXL-PHP with 4-(methylamino)pyridine: A dry, 250 mL 3-necked flask equipped with a reflux condenser and magnetic stirrer bar was purged with nitrogen, then dry NaH (0.68 g, 28.5 mmol), and dry THF (10 mL) were added. 4-(Methylamino)pyridine (1.10 g, 10.2 mmol) dissolved in dry THF (20 mL) was injected into the flask and the resulting solution was heated to reflux in an oil bath for 1 h. After this time, HXL-PHP (0.55 g, 2.03 mmol of reactive groups) was added quickly through the central neck, maintaining a blanket of nitrogen. The flask was then heated to 50°C for a period of 30 min. The reaction was quenched and the product precipitated by pouring the reaction mixture into an excess of methanol. The polymer was filtered and washed with THF/ H_2O (3 × 20 mL), THF/0.1 M HNO_3 (aq) (3 × 20 mL), THF/ H_2O (3 × 20 mL) and methanol (3 × 20 mL). The washed product was then dried in vacuo for 24 h. A similar procedure was used for other polymers.

Catalytic testing: 1-Methylcyclohexanol (1.0 mL, 8.1 mmol), toluene (7 mL) or diethyl ether and the catalyst (1 mol%) were added to a flask and stirred under nitrogen for 15 min. After this time, acetic anhydride (1.5 mL, 15.8 mmol) was injected into the flask. The reaction mixture was allowed to react at room temperature for a given period of time, after which the polymer was filtered, washed with solvent (toluene or diethyl ether) and transferred to a sealed vial and submitted for analysis by gas chromatography.

Acknowledgements

This work was supported by an International Joint Project grant from the Royal Society [JP062046].

Keywords: acylation • microporous polymers • organocatalysts • porosity • supported catalysts

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Received: November 4, 2009
Published online: January 26, 2010