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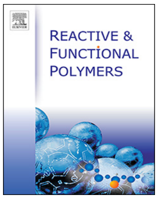

Novel hypercrosslinking approach toward high surface area functional 2-hydroxyethyl methacrylate-based polyHIPEs

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ABSTRACT

Highly porous poly(2-hydroxyethyl methacrylate-*co*-*N*,*N′*-methylenebisacrylamide) (poly(HEMA-*co*-MBAA)) frameworks were prepared from oil-in-water high internal phase emulsions (HIPEs). After subsequent functionalization through a two-step synthetic pathway involving i) activation of the hydroxyl functions exposed at the pore surface and ii) functionalization with allylamine or propargylamine, two different functionalized porous polymers were obtained and characterized in terms of porosity and chemical composition through mercury intrusion porosimetry, nitrogen adsorption-desorption porosimetry, and Raman spectroscopy, respectively. A final step relying on radical thiol-ene/yne "click" additions with di- or tetrathiols was further investigated so as to hypercrosslink the resulting porous materials and eventually decorate the pore surface with thiol functions. Very high specific surface area values as determined by nitrogen sorption porosimetry were found, namely up to 1500 $m^2.g^{-1}$ for HEMA-based material functionalized with allylamine after hypercrosslinking with pentaerythritol. *In-situ* generated gold nanoparticles were immobilized at the pore surface, and one such strategy allowed for the preparation of hybrid materials that were successfully applied for the supported heterogeneous catalytic reduction of a nitroaromatic compound, *i.e.p*-nitrophenol, and of a pollutant dye used in textile industry, *i.e.* Eosin Y.

1. Introduction

Porous materials have encountered a tremendous interest in the last decade in different research fields, including separation sciences, bioreactors, controlled drug delivery, gas transport or nanomaterials design, to cite but a few. [1] Porous polymer-based materials present some intrinsic properties that render them very appealing when compared to their inorganic counterparts. They notably possess tunable mechanical properties in a large range, and they can be easily functionalized in rather mild conditions. Additionally, they present a higher compatibility with (bio)organic (macro)molecules and can be chemically engineered with low-cost processes. [1,2] Different strategies have hitherto been developed to produce such organic (nano)porous frameworks, including molecular imprinting, [3] selective removal of a porogen homogeneously blended within a thermostable matrix, [4] selective removal of one partner from (semi-) Interpenetrating Polymer Networks (IPNs), [5,6] selective degradation of block copolymers (BCPs), [7] selective destruction of supramolecular assemblies, [8] leaching of macromolecular porogenic templates, [9,10] extraction of porogenic solvents [11,12] or polymerization of high internal phase emulsions (polyHIPEs). [13,14] Organic porous materials have notably been intensively developed within the last decade in the field of heterogeneous supported catalysis, following a preliminary step consisting in the immobilization of noble or transition metal nanoparticles. Despite rather good results obtained concerning the reduction of nitroaromatic compounds or dyes commonly used in textile industry, C—C homo- [15] or hetero- [16] cross-coupling reactions or even cascade reactions constituted of C—C homocoupling reaction followed by reduction of nitroaromatic moieties, [15] such porous polymer-based supports generally suffer from a major drawback closely related to their rather low specific surface area. A higher specific surface area could notably allow for higher nanometal content to be immobilized at the pore surface of the polymeric materials. One of the strategy commonly used to address this issue relies on the so-called hypercrosslinking procedure during which pendant chains exposed at the pore surface of the materials are linked together through a covalent bond with a homodifunctional chemical crosslinking agent. [17,18] The hypercrosslinking strategy has been applied to polyHIPE materials in order to

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obtain porous polymers with a distinct bimodal pore size distribution, thus creating materials constituted of large pores along with nanopores induced by the hypercrosslinking. Vinylbenzylchloride-based polyHIPEs were functionalized in this way to obtain materials with specific surface areas up to 990 $m^2.g^{-1}$, while retaining the polyHIPE macroporosity and the possibility of further chemical functionalization and catalyst immobilization. [19] Unreacted double bonds in divinylbenzene/styrene polyHIPEs were utilized for the same purpose yielding hypercrosslinked polyHIPEs with induced nanoporosity and specific surface areas up to 355 $m^2.g^{-1}$. [20] A similar strategy was used to obtain high surface area polyHIPEs with pyridyl groups to be used for catalysis. [21] Similarly to other functional monomers, 2-hydroxyethyl methacrylate (HEMA) is a very suitable monomer for the preparation of hydrophilic functionalizable polymers, and monolithic (bi)porous polymers have been prepared from HEMA using *e.g.* emulsion templating, [22–24] double porogen templating [25] or temperature-induced phase separation. [26]

Herein, we report on the preparation of monoliths *via* the polymerization of high internal phase emulsions consisting of 2-hydroxyethyl methacrylate as the functional monomer and *N,N′*-methylenebisacrylamide as the crosslinker. Investigations regarding hypercrosslinking of these poly(2-hydroxyethyl methacrylate) (PHEMA)-based monoliths were then engaged. Prior to the hypercrosslinking reaction, hydroxyl groups were first activated with 1,1′-carbonyldiimidazole (CDI), and the intermediate activated hydroxyl moieties were reacted with either allylamine or propargylamine. Hypercrosslinking of these porous polymeric frameworks was then achieved through radical-mediated thiol-ene/yne addition of a di- or tetrathiol on the alkene- or alkyne-functionalized monoliths. A dramatic increase of the specific surface area of such hypercrosslinked porous materials was immediately noticed by nitrogen sorption porosimetry and the presence of thiol functions at the pore surface was demonstrated by Raman spectroscopy, both allowing for the preparation of ideal supports for the immobilization of gold nanoparticles and subsequent catalyzed reduction of nitroaromatic and dye compounds.

2. Experimental

2.1. Materials

1,1′-Carbonyldiimidazole (CDI, 97%) and hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4$, 99.9%) were purchased from Alfa Aesar. Absolute ethanol (EtOH, 99%) was obtained from VWR chemicals. Acetone (99.8%), cyclohexane (99.5%) and isopropanol (99.7%) were supplied by Carlo Erba. Allylamine (98%), propargylamine (98%), pentaerythritol (3-mercaptopropionate) (**T4**, > 95%), 4-nitrophenol (*p*-nitrophenol, 99%), 2,2′-azobisisobutyronitrile (AIBN, 98%), sodium borohydride ($NaBH_4$, ≥99%), 1,4-dioxane (99.9%), 1,3-propanedithiol (**T2**, 99%), hydroxyethyl methacrylate (HEMA, 97%), Eosin Y (EY, ~99%), and poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic® F68) were purchased from Aldrich. *N,N′*-Methylene bisacrylamide (MBAA, ≥99%), ammonium peroxodisulfate (APS, ≥98%), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA, ≥99%), and aluminium oxide (Al_2O_3, purum p.a.) were obtained from Fluka. All reagents and solvents were used without any further purification, except AIBN that was recrystallized from methanol and stored at 4 °C prior to use. HEMA was flushed through an Al_2O_3 column before use to remove the radical inhibitors.

2.2. HEMA-based polyHIPE preparation

Deionized water (5.2 mL), monomer HEMA (2.322 g), crosslinker MBAA (0.334 g), initiator APS (0.073 g) and surfactant Pluronic® F68 (1.565 g) were placed in a two-necked round bottom flask. Cyclohexane (22 mL, 75 vol% of emulsion) was added dropwise to the monomer solution while stirring with an overhead stirrer at 180 rpm (D-shaped paddle stirrer). Once all cyclohexane has been added, stirring was continued for a further 180 min to form a milky white oil-in-water (o/w) emulsion. Stirring rate was then reduced to 20 rpm and the reducing agent TMEDA (60 μL) was added. Afterwards, the emulsion was transferred to the mould (polyethylene container) and cured at room temperature for 24 h. The monolithic product (**P1**) was purified *via* Soxhlet extraction with isopropanol for 24 h, and dried for 24 h in air.

2.3. HEMA-based polyHIPE functionalization and hypercrosslinking

2.3.1. Functionalization of polyHIPEs with CDI

2 equiv. of CDI (compared to hydroxyl groups in pristine polyHIPE **P1**, *i.e.* 1 g) were dissolved in 10 mL of acetone. The solution was then added to 500 mg of HEMA-based polyHIPEs (3.6 mmol of hydroxyl groups). The reaction medium was stirred on an orbital shaking plate during 24 h at room temperature. The CDI-activated material **P2** was then filtered, washed for three times with an abundant volume of acetone, and dried under vacuum.

2.3.2. Functionalization of CDI-activated polyHIPEs with propargylamine or allylamine

5 equiv. of propargylamine (800 mg, compared to hydroxyl groups in the precursor **P1**) were added to the freshly prepared CDI-activated polyHIPE material **P2** in the presence of 10 mL of acetone. The sample was shaken during 24 h at room temperature. The materials were dried under vacuum after being filtered and washed three times with an abundant volume of acetone. In parallel, 5 equiv. of allylamine (57 mg, compared to hydroxyl groups in the precursor **P1**) were added to the freshly prepared CDI-activated polyHIPE material **P2**. The same procedure as for the propargylamine functionalization was followed.

2.3.3. Hypercrosslinking of PHEMA@CDI@allylamine and PHEMA@CDI@ propargylamine polyHIPEs P3 and P4 with pentaerythritol

A solution of 5 mL of 1,4-dioxane and 263 μL of pentaerythritol (**T4**) in the presence of 1 wt% AIBN was prepared and added to PHEMA@CDI@allylamine and PHEMA@CDI@propargylamine polyHIPEs **P3** and **P4** (containing 1.38 mmol of alkene and alkyne functions). The vials were then immersed in an oil bath overnight at 70 °C. The samples were then filtered off, washed three times with an abundant volume of 1,4-dioxane and dried under vacuum.

2.3.4. Hypercrosslinking of PHEMA@CDI@propargylamine P3 and P4 with 1,3-propanedithiol

5 equiv. of 1,3-propanedithiol (**T2**, 373 mg, compared to alkyne functions in the precursor) were added to PHEMA@CDI@propargylamine **P4** material (6.9×10^{-1} mmol of alkyne functions) in the presence of 10 mL of acetone. The sample was stirred on an orbital shaking plate during 24 h at room temperature. The material was filtered off, washed three times with an abundant volume of acetone and dried under vacuum.

2.4. Immobilization of gold nanoparticles on PHEMA@CDI@ allylamine@T4 polyHIPEs

A 10 wt% $HAuCl_4$ aqueous solution was added to PHEMA@CDI@allylamine@tetrathiol polyHIPE **P5** and let to react overnight. The materials were then washed three times with an abundant volume of deionized water to insure that residual Au^{3+} ions non-specifically adsorbed on the pore surface were totally removed. Upon immersion in a $NaBH_4$ aqueous solution (7 mg of $NaBH_4$ in 2 mL water) for 2 h, the resulting materials were washed three times with 1 mL water. The sample was finally dried under vacuum overnight and was examined by SEM to observe the *in-situ* generated GNPs immobilized at the pore surface of **P5**.