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Glycidyl methacrylate and ethylhexyl acrylate based polyHIPE monoliths: Morphological, mechanical and chromatographic properties

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ABSTRACT

Using water-in-oil emulsions with a high volume share of aqueous (droplet) phase as precursors (High Internal Phase Emulsions; HIPEs), highly porous polymers (polyHIPEs) were prepared from glycidyl methacrylate (GMA) and ethylhexyl acrylate (EHA), their morphology investigated and mechanical and chromatographic characteristics evaluated. All polyHIPE monoliths had open cellular porous morphology with primary pores (cavities) between 4.8 μm and 26.2 μm and secondary level of interconnecting pores. Introduction of EHA into the oil phase and consequently into the polymer matrix of polyHIPEs had a significant effect on the mechanical properties; both tensile strength and elasticity were increased. On the other hand, chromatographic properties, such as protein binding capacity and back pressure, did not dramatically change.

1. Introduction

Emulsions with a high volume fraction of internal phase are known as HIPEs (High Internal Phase Emulsions) where the droplet phase occupies typically more than 74 vol.% [1,2]. By polymerisation of a HIPE, with the continuous phase containing monomers, monoliths with a high level of porosity and open porous morphology are obtained (Scheme 1, Fig. 1). Such polymers, usually termed polyHIPEs, can be prepared from either oil in water emulsions containing oil soluble monomers or from water in oil emulsions where hydrophilic monomers are contained in the aqueous phase of the emulsion [3–5]. Among other applications of polyHIPEs, chromatography is a prospective field. Chromatographic monoliths are a particular group of chromatographic stationary phases that consist of a single piece of highly porous material with interconnected channels which enable the flow of the mobile phase. Due to this particular structure several properties, such as flow unaffected resolution and dynamic binding capacity, low pressure drop, and high dynamic binding capacity for very large molecules, are exhibited. Polymer based monoliths are widely used for separation [6] and purification of biologic macromolecules [7,8] due to their scalability [9,10] and chemical stability [11] required for sanitation. Despite polymeric chromatographic monoliths which were prepared to exhibit various microstructures [12] there are very few reports regarding polyHIPE materials applied for chromatography. Glycidyl methacrylate (GMA) is a reactive monomer, which is frequently used for the preparation of functional polymers. For the preparation of monolithic polymeric chromatographic columns, especially, GMA has been extensively used [13]. Majority of porous columns, prepared from GMA, make use of the phase separation process with included porogenic solvents to induce the porous morphology of polyGMA. On the other hand, preparation and applications of GMA based polyHIPEs have also been demonstrated [4,14–19]. The possibility of preparation of monoliths with a high level of porosity (up to 90%) and pore size tuning make GMA based polyHIPEs good candidates for chromatographic applications. The use of GMA polyHIPEs for protein separation has already been reported, both in the form of discs [17] and membranes [18]. Especially in the case of high levels of porosity, the brittleness of the material presents a drawback for chromatographic applications. We have therefore intended to influence the mechanical properties of GMA polyHIPEs by introduction of a co-monomer, namely

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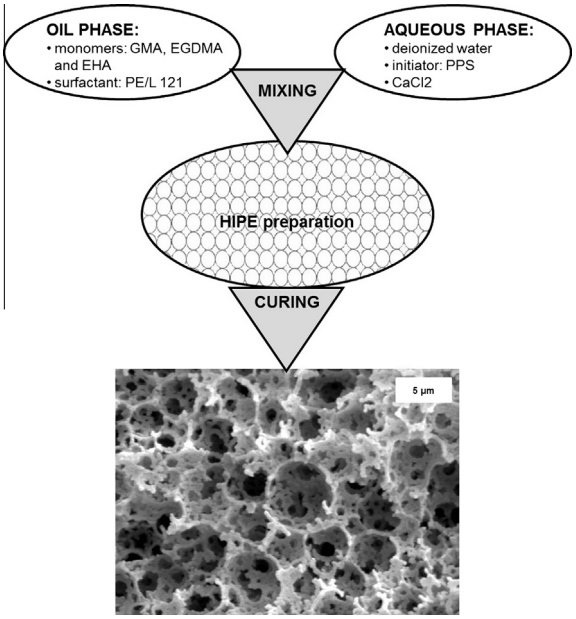

Scheme 1. polyHIPE preparation.

ethylhexyl acrylate which is known to influence the plastic behaviour of polymers. Herein we report on the morphological, mechanical and chromatographic properties of GMA based polyHIPE material, with included EHA.

2. Experimental section

2.1. Chemicals

Monomers glycidyl methacrylate (GMA, Sigma–Aldrich), ethylene glycol dimethacrylate (EGDMA, Sigma–Aldrich), 2-ethylhexyl acrylate (EHA, Sigma–Aldrich) were passed through a basic alumina column prior to use in order to remove the inhibitors. Potassium persulfate (PPS, Fluka), N,N,N′,N′-tetramethylethylene diamine (TEMED, Fluka), calcium chloride hexahydrate (Sigma–Aldrich), surfactant Synperonic PEL 121 (Sigma–Aldrich), toluene (Sigma–Aldrich) and diethyleneamine (DEA, Sigma–Aldrich) were used as received. Proteins myoglobin, conalbumin from chicken egg white and soybean trypsin inhibitor (STI) were obtained from Sigma–Aldrich.

2.2. Preparation and functionalization of polyHIPE monoliths

Organic and aqueous phase were prepared separately. Organic phase consisted of monomers EGDMA, GMA and EHA, surfactant PEL 121 and toluene. Aqueous phase contained water, $CaCl_2$ and potassium persulphate. Aqueous phase was added dropwise to the organic phase in a three necked flask within a half an hour period while stirred with an overhead stirrer at 250 rpm. After the addition of aqueous phase stirring was continued for one hour continued by the addition of N,N,N′,N′-tetramethylethylenediamine (TEMED). The emulsion was transferred to a polypropylene container and cured at 40 °C for 24 h. Monoliths were purified by extraction in Soxhlet apparatus with water and isopropanol for 48 h. The amounts of components are presented in Table 1. For chromatographic evaluation, polyHIPE monoliths were functionalised with diethyleneamine introducing weak anion exchange diethylaminoethyl groups (DEAE) as described previously [17].

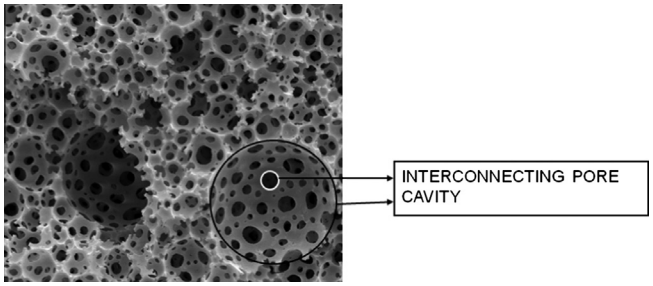

Fig. 1. SEM picture of polyHIPE material.

2.3. Structutral characterisation

SEM pictures were taken on a Quanta 200 3D (FEI Company; samples were gold sputtered (gold coating layer thickness under 40 nm) and an acceleration voltage of 20 kV was used). Cavity size distribution was determined by SEM image analysis; measuring the diameter of at least 100 cavities. Cavity sizes were adjusted for random sectioning using the correction factor $2/\sqrt{3}$. Nitrogen adsorption/desorption measurements were done on a Micromeritics TriStar II 3020 porosimeter using a BET model for surface area evaluation. All samples were degassed and measured three times.

2.4. Determination of mechanical properties

Mechanical properties of monoliths were measured at a constant room temperature using Instron 3345 device (Norwood, USA). Cylindrical shaped monoliths had a diameter of 12 mm and height of 12 mm for compression and approximately 100 mm for tensile experiments. To estimate monolith initial volume monolith dimensions were measured for compression test while for tensile test monolith diameter and distance between two grips within which monolith was fixed, were measured. Compression or pulling was performed at a constant velocity of 1.0 mm/min till material breakage for determination of strain and stress at break. From the linear part of stress–strain curve modulus was calculated.

2.5. Chromatographic experiments

Chromatographic experiments were performed on a gradient HPLC system consisting of two Pumps 64, an injection valve with 20 µl sample loop, a variable wavelength monitor with a 10-mm optical path set to 280 nm and HPLC hardware/software (data acquisition and control station), all from Knauer (Berlin, Germany).

For separation of standard protein mixture and determination of dynamic binding capacity loading buffer was 20 mM Tris–HCl, pH 7.4 and elution buffer 20 mM Tris–HCl + 1 M NaCl, pH 7.4. Flow rate was 4 ml/min.

Standard protein mixture consisted of myoglobin (c = 0.5 mg/ml), conalbumin (c = 1.5 mg/ml), soybean trypsin inhibitor (c = 2.5 mg/ml) dissolved in loading buffer. Linear gradient from 0% to 100% elution buffer in 30 s was applied and retention times of proteins were recorded. Dynamic binding capacity was measured with bovine serum albumin (c = 1.0 mg/ml) dissolved in loading buffer. Capacity was determined at 50% of break through curve. All proteins were from Sigma–Aldrich (USA)

3. Results and discussion

3.1. Preparation of GMA/EGDMA/EHA monoliths

Preparation of polyHIPE monoliths with GMA as a functional monomer and crosslinked with ethyleneglycol dimethacrylate