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Reactive & Functional Polymers 65 (2005) 37–45
REACTIVE & FUNCTIONAL POLYMERS
www.elsevier.com/locate/react

4-Vinylbenzyl chloride based porous spherical polymer supports derived from water-in-oil-in-water emulsions

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Received 6 September 2004; received in revised form 28 December 2004; accepted 3 January 2005
Available online 18 July 2005

Abstract

4-Vinylbenzyl chloride (VBC) based water-in-oil-in-water emulsions with 85% pore volume and 70% VBC in organic phase were prepared and polymerised by free radical polymerisation. Porous spherical particles of diameters between 50 and 150 μm were obtained and their morphological structure and reactivity studied by FTIR spectroscopy, elemental analysis, optical microscopy, scanning electron microscopy and mercury intrusion porosimetry. Strong influence of the suspension stabiliser, namely poly(*N*-vinylpyrrolidone) (PVP), on the particle form was found. Diameters of spherical polymers particles depend on the PVP concentration, being larger with the lower concentration of PVP. Reactivity of novel supports was demonstrated by the reactions with piperidine, piperazine, tris(hydroxymethyl)methylamine and tris(2-aminoethyl)amine, all yielding corresponding amine derivatives.

Keywords: Multiple emulsions; Polymer supports; 4-Vinylbenzyl chloride; Solid phase synthesis; High internal phase emulsions

1. Introduction

Research in the field of reactive polymer supports has been in a constant growth since Merrifield's breakthrough tetrapeptide synthesis in 1963 [1]. The advents of combinatorial chemistry and polymer assisted solution phase chemistry have contributed to the recent intense research in the field [2]. Polymer supports similar to the ones Merrifield used for peptide synthesis, are still commonly used today. Such beads, of chloromethylated polystyrene chemistry and typically cross-linked with ≈2% of divinylbenzene (DVB), are commercially available. Some of further functionalised resins can also be found on the market. Gel type beads posses no permanent pores and must therefore swell in the reaction medium in order for a transformation to be successful. This limits the range of solvents in which supports can be used. This problem can partly be overcome by

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doi:10.1016/j.reactfunctpolym.2005.01.007

using higher levels of crosslinker and porogens during the suspension polymerisation. Polymer beads prepared with a higher lever of crosslinker and porogen, usually termed macroporous beads have permanent pores, however, are usually mechanically quite fragile. An alternative approach for preparing porous polymer supports is the polymerisation of the continuous phase of a high internal phase emulsion (HIPE; volume fraction of internal phase exceeds 75% which represents maximum occupiable volume by spheres) [3]. The internal phase of an emulsion is used as a template for porosity and porous polymers with pore volume as high as 90% that are still mechanically stable can be prepared [4].

While the polymerisation of a HIPE leads to monolithic polymers, particles of PolyHIPE can be obtained by crushing and powdering of the monoliths. However, the irregular shape of powdered particles can be problematic for applications where bead shape particles are preferred.

In 1996 Li and Benson of Biopore Corporation have patented a method for the preparation of PolyHIPE styrene-DVB polymer particles in the shape of beads [5]. They prepared a water-in-oil high internal phase emulsion of which droplets were dispersed in a suspension medium and polymerised. Resulting polymer particles were beads with open cellular structure very similar to that known from monolithic PolyHIPE preparation. In order to introduce functional groups to PolyHIPE beads, Deleuze et al. [6] have added 4-vinylbenzyl chloride (VBC) to the continuous phase of HIPE, replacing as much as 45% of styrene, while Do Suh et al. [7] have used similar approach, namely water-in-oil-in-water (W/O/W) emulsion preparation (with lower level of aqueous phase in emulsion than normally used in a HIPE) introducing methyl methacrylate and ethylene glycol dimethacrylate as a crosslinker to produce polymers they called multihollow microcapsules. To the best of our knowledge, the report by the French group is the only one so far introducing VBC into PolyHIPE beads.

In order to enhance the loading of reactive chloromethyl groups, we were interested in the possibility of preparing stable W/O/W emulsions with high levels of 4-vinylbenzyl chloride using a procedure as simple as possible. Such polymer supports in monolithic form have already been prepared and their functionalisations and applications described [8,9]. In this paper, we present the preparation of beads of PolyHIPE with the level of 4-vinylbenzyl chloride as high as 70% and the nominal porosity as high as 85%. Functionalisations of these polymers with piperidine, piperazine, tris(2-aminoethyl)amine and tris(hydroxymethyl)methylamine and the influence of suspension stabilisation media on the structure is also described.

2. Experimental

2.1. Materials and analyses

4-Vinylbenzyl chloride (VBC, Aldrich) and divinylbenzene (DVB, Aldrich, 80%, tech., the rest ethylstyrene) were washed with 5% NaOHaq to remove the inhibitors. Azo-bis-isobutyronitrile (AIBN), potassium persulphate, sorbitan monooleate, tris(hydroxymethyl)methylamine tris(2-aminoethyl)amine and piperazine, were all purchased from Aldrich and used as received. Poly(*N*-vinylpyrrolidone) (PVP, Fluka, $M_w = 4.0 \times 10^4$ g mol^{-1}), pyridine (Kemika Zagreb), piperidine (Kemika Zagreb), nitric acid (Fluka, 65% aqueous solution), calcium chloride hexahydrate (Merck), methanol (MeOH, Merck), *N*,*N*-dimethylformamide (DMF, Carlo Erba Reagenti), dichloromethane (DCM, Fluka) and tetrahydrofurane (THF, Fluka) were also used as received. FTIR spectra were recorded on a Perkin–Elmer FTIR 1650 spectrometer (KBr pellets), SEM pictures were taken on a Jeol JSM-840A and CHN elemental analyses were done on a Perkin–Elmer CHN 2400 analyzer. Mercury intrusion porosimetry was performed on a Micromeritics – AutoPore III 9420 Mercury Porosimeter.

2.2. Preparation of VBC/DVB beads (1a, 1b, 1c, 1d)

2.20 g (14.43 mmol) of vinylbenzyl chloride, 0.81 g (6.18 mmol) of divinylbenzene, 0.85 g of sorbitan monooleate and 0.04 g of azo-bis-isobutyronitrile were placed in a reactor and the mixture