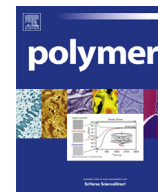




Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Emulsion-templated porous polymers prepared by thiol-ene and thiol-yne photopolymerisation using multifunctional acrylate and non-acrylate monomers

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ARTICLE INFO

Article history:

Received 9 January 2017

Received in revised form

4 April 2017

Accepted 6 April 2017

Available online xxx

Keywords:

Porous polymers

Photopolymerisation

Emulsions

ABSTRACT

The chemical and mechanical properties of macroporous polymer substrates play a crucial role in the determination of their end-application. The preparation of highly (macro)porous monolithic polymers (polyHIPEs) by emulsion templating and thiol-ene/yne photopolymerisation, using multifunctional acrylate, allyl ether and alkyne-based monomers with trimethylolpropane tris (3-mercaptopropionate) (TMPTMP), is described in this work. Issues associated with monomer solubility and/or stability of the produced high internal phase emulsions (HIPEs) are tackled. Scanning electron microscopy (SEM) is used to study the morphology and porosity (average void diameters) of the obtained materials. Due to the nature of the photoinitiated thiol-ene reactions, materials obtained from acrylate monomers display residual thiols that are quantified by a colourimetric (Ellman's) assay. Raman spectroscopy is also shown to be a complementary technique to evaluate the residual thiol content. The influence of the monomer functionality on the mechanical properties of the material is explored using compression tests. Significant differences in the surface functionality and mechanical behavior between materials prepared with comonomers able to homopolymerise (acrylates) and those unable to homopolymerise (allyl ethers; alkynes) are demonstrated.

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1. Introduction

Macroporous polymers [1] have a wide range of potential applications, including in (bio)catalysis [2], gas storage [3], separation science [4] and tissue engineering [5]. They can be prepared by either templating or non-templating methods [6]. In non-templating approaches, phase separation or solvent evaporation can create a porous material from a single-phase precursor. Commonly employed non-templating methods for preparing porous polymers include thermally-induced phase separation and gas foaming. Due to its high degree of control over porosity,

templating methods have gained much attention recently and have now become some of the most attractive methods of synthesising macroporous polymers [7]. Highly porous polymers can be prepared by the emulsion templating method, which involves the formation of a high internal phase emulsion (HIPE) followed by polymerisation of its continuous phase. Once polymerised, the continuous phase of the HIPE contracts allowing droplets to connect with nearby droplets, leading to a fully interconnected, low density polymer foam – known as a PolyHIPE [3,8–14]. The rapid curing time provided by photo-polymerisation allows the potential of synthesising polyHIPE materials from monomers which produce highly unstable emulsions [15–19].

Although thiol-ene (and thiol-yne) click chemistry has been employed extensively in recent years to prepare a wide range of novel materials [20–22], its application in the synthesis of macroporous materials has been reported only rarely. For example, thiol-ene and thiol-yne photopolymerisation were combined with microfluidics to prepare monodisperse macroporous polymer

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beads [23]. Thiol-ene photopolymerisation inside capillary columns was used to prepare monolithic stationary phases for capillary liquid chromatography [24,25]. Enzymatic microreactors were produced by conducting thiol-ene photopolymerisations of emulsions inside microfluidic devices [26]. In 2011, Cameron et al. first introduced the preparation of well-defined polyHIPE materials by combining emulsion templating with thiol-ene and thiol-yne photopolymerisation using a tri-acrylate and a bis-alkyne as comonomers [16]. Subsequent work explored the use of these materials as scaffolds for the *in vitro* culture of cells in 3D [27–30], and in the production of layered materials [31]. Acrylate-based monomers undergo homopolymerisation in addition to thiol-ene reaction, which results in residual thiols in the final material [32]. Residual thiols were found in thiol-acrylate polyHIPE materials prepared with different thiol:acrylate stoichiometries, even when the acrylate groups were in significant excess. For that reason, we sought to explore further the use of commercially available, non-acrylate comonomers with which to prepare polyHIPE materials by thiol-ene/yne photopolymerisation. Accordingly, we employed allyl ether-based comonomers (tetraallyl ether and diallyl ether) and an alkyne-based comonomer (1,7-octadiyne), in addition to a range of multifunctional acrylates, for polyHIPE preparation by photopolymerisation. We also undertook a thorough investigation of the morphology, surface functionality and compression behavior

of the resulting materials. Compression data for methacrylate [33] and carbon black-filled [34] polyHIPEs have been reported previously, however, as far as we can tell, data for acrylate-, allyl ether- or alkyne-based polyHIPEs have not yet been reported. We show that non-acrylate monomers tend to give rise to an elastomeric material, whereas an acrylate counterpart produces a more rigid foam. It is also shown that non-acrylate comonomers give rise to very low levels of residual thiol groups.

2. Experimental

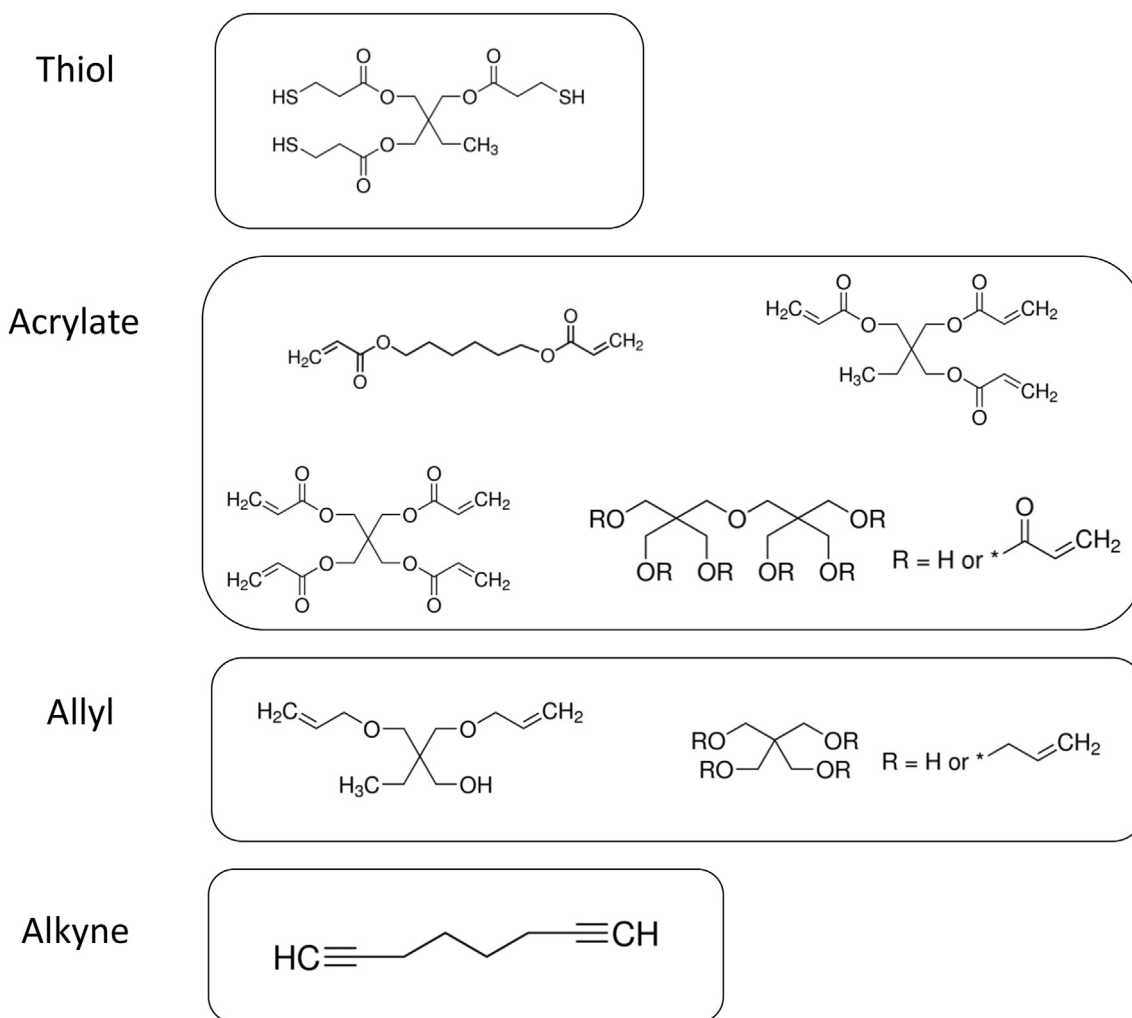
2.1. Materials

All chemicals were obtained from Sigma Aldrich apart from the surfactant Hypermer B246 (a block copolymer of polyhydroxystearic acid and polyethylene glycol), which was obtained from Croda International. All were used without further purification.

3. Methods

3.1. PolyHIPE preparation

In a 250 mL two-necked round-bottomed flask, an oil phase



Scheme 1. Monomers used in this study. Thiol: trimethylolpropane tris(3-mercaptopropionate) (TMPTMP); acrylates (clockwise from top left): 1,6-hexanediol diacrylate (HDDA), trimethylolpropane triacrylate (TMPTA), dipentaerythritol penta-/hexa-acrylate (DPEHA) and pentaerythritol tetraacrylate (PETA); allyl ethers (left to right): trimethylolpropane diallyl ether (TMPDAE) and pentaerythritol allyl ether (PEAE); alkyne: 1,7-octadiyne (ODY).

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