



# Preparation of porous polyurethanes by emulsion-templated step growth polymerization



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## ABSTRACT

A new class of emulsion-templated macroporous polymers (polyHIPEs) was prepared by step-growth polymerization involving a low molecular weight triol and a commercially available diisocyanate. Several water-in-oil High Internal Phase Emulsions (HIPEs) were formulated by varying the nature of the monomer and the volume fraction of the inner phase. The addition of particles in the continuous phase to obtain composites was studied. The preparation of Pickering emulsions and non-aqueous emulsions was also investigated. The addition of a catalyst to the HIPE and subsequent polymerization followed by solvent elimination led to the corresponding polyurethane polyHIPEs. These materials were characterized by Scanning Electron Microscopy (SEM), FT-IR,  $^{13}\text{C}$  solid NMR, mercury intrusion porosimetry, nitrogen adsorption and thermal analysis. The materials obtained shows porosities up to 80% and a thermal stability comparable to commercial polyurethane foams.

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## 1. Introduction

PolyHIPEs are cellular materials obtained through polymerization within High Internal Phase Emulsions (HIPEs) [1]. HIPEs are emulsions where the internal phase occupies at least 74% of the total emulsion volume [2]. Thus, PolyHIPEs have a low density and high interface area, which makes them useful for drug encapsulation [3], as catalyst supports [4], and as supports for the immobilization of bio-molecules [5]. PolyHIPEs are generally obtained through free-radical polymerization [6], restricting the potential monomers that can be used to styrene, (met)acrylates and their derivatives [7]. However, several other approaches have been reported, including interfacial polycondensation of cyanuric chloride with 2-nitroresorcinol [8], urea-formaldehyde and formol-formaldehyde resins [9], polysiloxane elastomer network [10], thiol-ene and thiol-yne chemistry [11], polycondensation [12], Ring Opening Metathesis Polymerisation [13,14].

Nowadays, polyurethane foams constitute one of the most important classes of polymeric materials [15]. Very few reports on the preparation of porous polyurethane (PU) polyHIPEs can be found in the open literature. Emulsion templated poly(styrene-co-divinylbenzene)/polyurethanes interpenetrated polymer networks

were synthesized by Lépine et al. whereby the poly(styrene-co-divinylbenzene) network was required to maintain the structural integrity of the polyurethane network [16]. Dganit et al., produced PU polyHIPEs by reacting poly( $\epsilon$ -caprolactone) macromonomers with diisocyanate [12]. More recently, Qixiang et al. used polyurethane diacrylate as crosslinker for styrene-based polyHIPEs [17].

Polyurethane polymers are usually prepared by polycondensation of a diol and a diisocyanate using dibutyl tin dilaurate (DBTDL) as catalyst [18]. In our case, in order to obtain a 3D polymeric network, we decided to employ an  $A_2+B_3$  strategy, meaning the reaction of difunctional with trifunctional monomers [19]. However, by using this configuration, the usual structure obtained is soluble hyperbranched polymers, as predicted by Flory [20]. To obtain an insoluble PU network, the gel point of the system must be reached and exceeded. Predicting the formation of the gel point is, however, a difficult task as its formation depends on a large number of parameters (such as the dilution of the monomers and their molar ratio) and the PU case is particularly complex [21]. Strategies to obtain a gel in step-growth polymerizations include: long reaction times, polymerization in concentrated solutions, monomers with functional groups of similar reactivity and excess of one of the monomers [22].

Non-aqueous (oil-in-oil) HIPEs have been scarcely studied. In their seminal work, Cameron et al., [23] came to the conclusion that reasonably stable non-aqueous HIPEs ( $\Phi = 0.90$ ) could only be obtained by using a certain solvent couples: alkane (petroleum

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ether)-in-formamide being the best one, alkane-in-DMSO and alkane-in-DMAc being less stable. Following this work, poly(aryl ether sulfone) (PES) PolyHIPE were prepared from petroleum ether-in-DMF emulsions [24]. Similar results have been obtained by Imhof et al., [25] for non-aqueous MIPE ( $\Phi = 0.50$ ). In both cases commercially available PEO-PPO-POE triblock copolymers were used as surfactants. Non-aqueous Pickering HIPEs have also been reported [26]. More recently, formulation of ionic liquid-in-monomers HIPEs ( $\Phi = 0.80$ ) permitted the encapsulation of an ionic liquid in a polymeric matrix [27].

The aim of this work is the preparation of PU polyHIPEs using low molecular weight triols and diisocyanates as sole monomers. Parameters such as the nature of the solvent emulsion and the stabilizing agent were changed to study their effect on the morphology of these newly obtained PU polyHIPEs. Interestingly the technique used in this work allows, contrary to gas foaming, to encapsulate a phase change materials (PCM) as droplets into a solid matrix. These types of materials have many applications as smart insulation materials [28].

## 2. Experimental

### 2.1. Materials and methods

Aleuritic acid, myo-inositol (MOI), isopropanol, triethylamine (TEA), trimethylorthoalderate, p-toluenesulfonic acid monohydrate (PTSA), Dibutyl tin dilaurate (DBTDL), 4,4'-diphenylmethane diisocyanate (4,4'-DMI), were purchased from Sigma Aldrich. Anisole was purchased from Acros organics, Polyglycerol polyricinoleate (PGPR 4150) was kindly supplied by Palasgaard, Pluronic F-127 was purchased from BASF. Aluminium flakes (AF), were kindly supplied by Met flake under the commercial name Metabrite A9-15MO. Multiwalls Carbon nanotubes (CN), were kindly supplied by Arkema, modified Silica (HDK20) was kindly supplied by SPCI. PU foam was kindly supplied by GTT France.

#### 2.1.1. Monomers preparation

**2.1.1.1. Isopropyl aleuritate (IA).** Isopropyl aleuritate, was synthesized according to [29]. Aleuritic acid (5 g, 16.42 mmol) was dissolved in isopropanol (148 mL, 1.9 mol), the mixture was stirred and heated at 90 °C. After complete dissolution of aleuritic acid, concentrated H<sub>2</sub>SO<sub>4</sub> (0.5 mL) was added drop wise and the mixture refluxed for 12 h. After cooling to RT, the reaction mixture was neutralized by addition of K<sub>2</sub>CO<sub>3</sub> and all volatiles were evaporated under reduced pressure. Cold water was added to the yellow residue obtained while cooling in an ice bath. The solution containing a light yellow precipitate was stirred for 5 h while cooling. The precipitate was filtered over a Buchner funnel with a double paper filter and washed with cold water. The residue was dried in an oven under vacuum (48 h, 40 °C) followed by drying using a high vacuum line (RT, 8 h) to give a light yellow solid. Yield: 85%.

FTIR: ( $\nu_{\max}/\text{cm}^{-1}$ ): 3356 (OH), 1732 (C=O), 1244 (C-O-C). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 4.92 (1H, m), 4.16 (2H, m), 3.37 (2H, m), 3.19 (1H, s), 2.22 (2H, t), 1.24–1.52 (m, 22H), 1.18 (d, 6H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 172.86, 73.60, 67.25, 61.20, 34.29, 33.03, 32.71, 29.67, 29.57, 29.20, 28.88, 26.22, 26.05, 25.00, 22.08. + TOF MS: C<sub>19</sub>H<sub>38</sub>O<sub>5</sub>Na calcd. 369.2611; found: 369.2612.

**2.1.1.2. Myo-inositol orthoalderate (MIO).** The synthesis was adapted from [30]. To a suspension of myo-inositol (12.0 g, 66.7 mmol) in DMF (100 mL), trimethyl orthoacetate (12 mL, 94 mmol), and p-toluenesulfonic acid monohydrate (1.0 g, 5.8 mmol) were added. The resulting mixture was heated at 100 °C for 2 h until the mixture became homogeneous. After cooling, triethylamine (4 mL) was added to the solution. The solution was

concentrated under reduced pressure. The resulting residue was dissolved in a minimum amount of ethyl acetate and chromatographed on a short silica gel column (eluent: ethyl acetate). The resulting solution was concentrated under reduced pressure, and the resulting residual solid was crystallized from methanol. Yield: 60%.

FTIR: ( $\nu_{\max}/\text{cm}^{-1}$ ): 3332 (OH), 1717 (C=O). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 5.37 (2H, s), 5.17 (1H, d), 4.21 (2H, s), 3.99 (2H, m), 3.92 (2H, t), 1.26 (3H, s). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>,  $\delta$ ): 108.19, 74.76, 68.79, 66.02, 58.04, 24.26. HRMS [M+] C<sub>11</sub>H<sub>19</sub>O<sub>6</sub> calcd. 247.11816; found: 247.11900.

#### 2.1.2. PolyHIPE preparation

**2.1.2.1. Nomenclature of the samples synthesized.** In the following, HIPEs have been abbreviated PU $\Phi$ - $\Delta$ - $\theta$  where  $\Phi$  represents the volume ratio of inner phase,  $\Delta$  the modification of the standard W/O emulsion formulation (if applicable), and  $\theta$  the nature of the triol employed. For example, PU<sub>80</sub>-Pick-MIO refers to a Pickering emulsion with  $\Phi = 0.80$  using myo-inositol orthoalderate as triol. The final polyHIPEs bears the same name as their HIPEs precursors.

**2.1.2.2. Aqueous emulsions stabilized by a surfactant.** In a typical experiment, myo-inositol orthoalderate (656 mg, 2.7 mmol) and PGPR (730 mg, 20% according to the continuous phase) were first dissolved in anisole (1 mL) at 50 °C under stirring (500 rpm) during 30 min. The temperature was then decreased to 30 °C and a solution of 4,4'-diphenylmethane diisocyanate (1 g, 4 mmol) in anisole (1 mL) was then added, the mixture was stirred at 500 rpm during 30 min. When a homogenous liquid is obtained, the aqueous phase consisting of pure H<sub>2</sub>O was added dropwise at a rate of 1.0 mL min<sup>-1</sup> using a syringe pump under continuous stirring (300 rpm). After the total addition of the water the stirring was maintained for 5 more minutes. Emulsions presenting a final internal phase volume fractions of  $\Phi = 0.50, 0.80$  and 0.90 were thus prepared. The highly viscous HIPEs obtained were transferred into a beaker and the catalyst DBTDL (0.2 mmol, 5% according to the isocyanate) was added. The mixture was gently stirred with a spatula and quickly transferred in a PTFE mold. The mold was sealed and placed 72 h in an oven at 70 °C. The samples were further removed from the molds, washed at RT with stirred diethyl ether during 72 h, then dried at room temperature during one week.

Solid <sup>13</sup>C NMR (sample PU<sub>80</sub>-MOI, 400 MHz,  $\delta$ ): 182; 143; 135; 83. FT-IR: (sample PU<sub>80</sub>-MIO  $\nu_{\max}/\text{cm}^{-1}$ ): 2277 (NCO isocyanates); 1730 (C=O urethane); 1540 (CNH urethane).

**2.1.2.3. Emulsion stabilized by particle (Pickering emulsion).** In a typical experiment, myo-inositol orthoalderate (656 mg, 2.7 mmol) was first dissolved in anisole (1 mL), HDK20 silica (109 mg, 3% according to continuous phase) was added and dispersed using ultrasounds. The same procedure as for aqueous emulsions stabilized by surfactants was then followed.

**2.1.2.4. Non-aqueous emulsions.** In a typical experiment myo-inositol orthoalderate (656 mg, 2.7 mmol) and Pluronic F-127 (1 g, 30% according to the continuous phase) were first dissolved in DMF (1 mL) at 70 °C, the heating and the stirring (500 rpm) were maintained during 30 min. The temperature was then decreased to 30 °C and a solution of 4,4'-diphenylmethane diisocyanate (1 g, 4 mmol) in DMF (1 mL) was then added, the mixture was stirred at 500 rpm during 30 min. The dispersed phase consisting of hexadecane was added dropwise at a rate of 1.0 mL min<sup>-1</sup> using a syringe pump and the stirring was maintained at 300 rpm. The same procedure for aqueous emulsions stabilized by surfactants was then followed. The polymerization took place in an oven

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