



# Supercritical CO<sub>2</sub> mediated functionalization of highly porous emulsion-derived foams: ScCO<sub>2</sub> absorption and epoxidation



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## ABSTRACT

Highly macroporous polymers based on dicyclopentadiene (DCPD) have been successfully functionalized via a supercritical CO<sub>2</sub> method aimed at minimizing the usage of organic solvents typically necessary for functionalization of polymers. The macroporous morphology of DCPD-based polyHIPEs resists the high pressures and the material exhibits an unusually high uptake of scCO<sub>2</sub> at zero swelling. The scCO<sub>2</sub> treatment creates additional mesoporosity, facilitating for the functionalisation within the void walls. The use of scCO<sub>2</sub> as a solvent in the Prileschajew epoxidation and consecutive epoxide aminolysis of such epoxidized polydicyclopentadiene (pDCPD) monoliths is described. The procedure yields a high degree of functionalization with up to 6 mmol of  $\beta$ -amino alcohol derivatives per g of polymer.

## 1. Introduction

Heterogeneous-phase organic synthesis can combine the benefits of solid-phase chemistry with the advantages of solution-phase synthesis [1]. The essential advantage of heterogeneous-phase synthesis is that in just few reaction steps, libraries of molecularly diverse resins can be functionalized (synthesized), wherein excess reagents can be easily removed by extraction and filtration, and purification achieved, by washing [2]. Since heterogeneous-phase synthesis occurs at the interface boundary between the polymeric support and the liquid-phase, it requires longer reaction times to achieve comparable yields as classical solution phase synthesis [3]. Over the last two decades, polymeric supports for heterogeneous-phase synthesis evolved tremendously as morphology dictates the reaction kinetics due to the mass-transfer and diffusion limitations [4,5]. With increasing morphological complexity and decreasing feature sizes of porous morphologies down to the nanoscale, heterogeneous-phase synthesis was found destructive to the polymeric supports, as organic solvents damage the functional surfaces upon cycling due to the liquid's viscosity and surface tension.

Among the morphologies that have been used in heterogeneous-phase synthesis, a 3D-interconnected porous morphology of polyHIPE-based resins derived from high internal phase emulsions (HIPEs), makes this polymeric supports highly usable since it provides unobstructed diffusivity for reagents to access resin's reactive sites (functional

groups) [6]. Major advantage of polyHIPEs (polymerized high internal phase emulsions) [7] is their high porosity (between 74–95 vol.%) and a unique void and window structure that makes them further usable in low-pressure, continuous flow set-ups [8]. Gas-like diffusivity and liquid-like density of scCO<sub>2</sub> on the other hand, makes it an excellent choice as reaction medium. High diffusivity enhances mass transfer and reaction kinetics while low viscosity and surface tension of scCO<sub>2</sub> allow complete wetting of the polymeric supports without any damage of the surfaces [9]. The use of scCO<sub>2</sub> as the solvent in organic and polymer chemistry has been comprehensively explored during the last 30 years, since it can dissolve many organic compounds and sustain inherent environmental, health, and safety (EHS) [10] advantages due to its environmental benignness. Low viscosity of supercritical fluids (0.01–0.003 mPa s) as opposed to liquids (0.2–0.3 mPa s), make them as an attractive solvents for chemical synthesis [11]. ScCO<sub>2</sub> has been studied as an alternative solvent in polymer synthesis, [12,13] porous polymeric materials production, [14] polymer and bio-polymer processing [15,16], polymer particle synthesis [17], impregnation and dyeing of polymeric materials [18], polymer extraction and purification [19], and heterogeneous chemical modification of polymers [20]. However, the number of examples where scCO<sub>2</sub> is used as a solvent in the heterogeneous-phase organic synthesis is as yet fairly small.

Combination of polyHIPE-based resins and compressed (supercritical) CO<sub>2</sub> (scCO<sub>2</sub>) as it will be disclosed herein, is a promising

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solution to avoid aggressive and hazardous organic solvents in the heterogeneous-phase organic synthesis and to improve the sustainability of the process. In this article we describe a straightforward, environmentally friendly supercritical CO<sub>2</sub> technology for the post-functionalisation of polymeric foams through the Prileschajew epoxidation of pDCPD followed by the aminolysis towards  $\beta$ -amino alcohol derivatives. pDCPD is known as an industrially important cross-linked polymer with high E-modulus, impact strength, high ductility, chemical resistance and high operating temperature. DCPD-based polyHIPEs exhibit very favourable mechanical properties such as high modulus of 330 MPa and sample could tolerate a stress of 12 MPa before breaking [21]. After being oxidized, E-modulus of DCPD-based polyHIPEs significantly increased to extraordinarily high 770 MPa. As a consequence of the metathesis polymerisation, DCPD-based polyHIPEs bears a high degree of unsaturation offering ways for further functionalisation [22]. Accordingly, pDCPD foams ideally fulfil the prerequisites for the preparation of highly functionalised porous materials.

## 2. Experimental

### 2.1. Materials

The monomer was dicyclopentadiene (DCPD, Aldrich). The surfactant was a commercial triblock copolymer (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol), Pluronic L-121 with a molecular weight of 4400 g/mol, Sigma-Aldrich). The initiator was (H<sub>2</sub>IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru(3-phenyl-indenylid-1-ene) (M2, Umicore's 2nd generation initiator). The internal phase was deionized water (Milli-Q ultra-pure water). The solvents used included toluene (p.a. Aldrich) and acetone (Sigma-Aldrich) and CO<sub>2</sub> (Messer; purity 99.5%). The functionalization of pDCPD was done using 3-chloroperbenzoic acid (mCPBA, Sigma-Aldrich) and ethylenediamine (Sigma-Aldrich). All the materials were used as received.

### 2.2. Synthesis of DCPD based polymers

#### 2.2.1. DCPD-based polyHIPEs

Dicyclopentadien (8 g) and surfactants (Pluronic<sup>®</sup>L-121; 0.62 g) were placed in a three necked 250 mL flask and the mixture was stirred with an overhead stirrer at 400 rpm. The corresponding amount of deionized water (65 mL) was added drop wise under constant stirring. After addition of water, the water-in-oil high internal phase emulsion was further stirred for 1 h until a uniform emulsion was produced. The initiator M2 (8.13 mg) dissolved in toluene (0.6 mL), was added to the emulsion and the mixture was stirred for further 1 min. Subsequently, the emulsion was transferred into the mold (polystyrene container) and was cured at 80 °C for 4 h. Resulting polymers were purified via Soxhlet extraction with acetone and dried under vacuum until constant weight was obtained. The polyHIPE organogel composition was described using the sample name pDCPD\_90, where 90 reflect the HIPE internal phase content (the polyHIPE porosity).

#### 2.2.2. DCPD-based bulk organogels

The referenced bulk organogels were polymerized using the same amounts as described above for polyHIPEs, but without the Pluronic<sup>®</sup>L-121 and without the water. The reference bulk organogels are described using the sample name pDCPD\_0.

### 2.3. Supercritical CO<sub>2</sub> uptake

CO<sub>2</sub> uptake in the polymer was determined gravimetrically with a magnetic suspension balance with accuracy of 20  $\mu$ g in high-pressure cell (NWA GmbH, Lorrach, Germany). A detailed description can be found in the literature [23]. Briefly, the cell is made of stainless steel (AISI 316). The apparatus can be used at pressures up to 300 MPa and temperature of 250 °C and has a volume of 60 cm<sup>3</sup>. The inlet nozzle

provided the inlet of CO<sub>2</sub> into the autoclave into the middle of the autoclave, so the inlet was as close as possible to the polymer. The outlet nozzles are the macrometric and micrometric nozzles before the capturing flask. The cell is provided with two sapphire windows for visual observation of the interior. The polymer was cut in a shape of a cube with side length of 0.5 cm and put in a sample container and placed in the high pressure measuring cell. The system was heated to the temperature of 40 °C. Firstly, the mass of the polymer in vacuum was measured until equilibrium was reached. This represents the mass of the polymer without absorbed gas ( $m_0$ ). Then the pressure was increased (either to 100 or 200 bar) and the measurements were continued at these conditions till equilibrium was established, which represents the mass of the polymer with absorbed gas ( $m_1$ ). The mass ( $\Delta m$ ) difference is the amount of gas that was absorbed in the polymer under pressure and temperature. The measurements were corrected due to the buoyancy effect.

### 2.4. Prilezhaev epoxidation and aminolysis

After the polymer was synthesized it was kept in acetone at a temperature below 0 °C. Before the polymer was used for functionalization a surface layer of 2 mm was removed from the polymer (this layer might have already oxidized). Then the polymer was dried at ambient temperature with an evaporator under pressure of 250 mbar for 24 h. Afterwards, 1 g of pDCPD (15.13 mmol of double bonds) was suspended in scCO<sub>2</sub> at 40 °C and 100 bar for 24 h in the autoclave of the experimental setup shown in Fig. 1. The mCPBA was dissolved in DCM (concentration of 2 g/mL). The syringe hand pump with capacity of 12 mL was filled with the mCPBA solution and 12 mL or 24 mL of the solution was slowly injected into the autoclave. The solution was injected under pressure (the syringe pump was connected to the autoclave) and the pressure increased from 100 to 120 bar after 24 mL was injected. After 24 h, the autoclave was set at 100 bar and the polymer was cleaned with constant flow of carbon dioxide at 40 °C. Approximately 0.7 kg of CO<sub>2</sub> (at flow rate 1 dm<sup>3</sup>/min) were used for

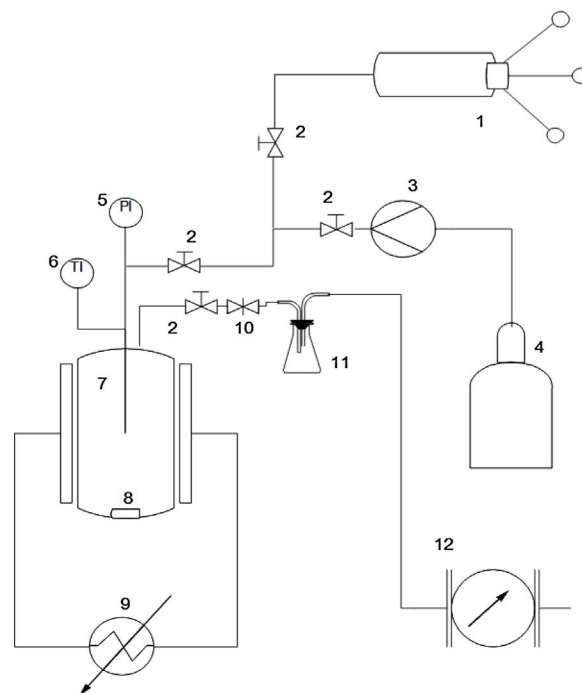


Fig. 1. Schematic representation of the equipment used for the functionalization under supercritical conditions. The set-up consist of syringe hand pump (1), valve (2), high pressure pump (3), CO<sub>2</sub> supply (4), pressure (5) and temperature indicator (6), autoclave (7), magnetic stirrer (8), heating system (9), micrometric valve (10), capturing flask (11), gas flow meter (12).

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