



## Hyperbranched polyglycerols containing amine groups — Synthesis, characterization and carbon dioxide capture

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### ABSTRACT

In this article we report an easy synthetic way towards hyperbranched polyglycerols containing primary amine groups (A-HBPGs). A-HBPGs were synthesized in a two-step procedure including an anionic ring opening copolymerization of the phthalimide-epoxy monomer with glycidol followed by hydrazinolysis of phthalimide groups. Polymeric products of both synthetic steps were characterized using NMR, MALDI-TOF, FTIR, viscosimetry and elemental analysis techniques. The maximum amount of the amine containing units in the products was estimated to be 31 mol%. Introduction of higher amounts of these units was limited by the reactivity (sterical) and viscosity reasons. A-HBPGs showed to be effective in CO<sub>2</sub> capture from the ambient air. Adsorbents consisting of A-HBPGs and fumed silica in the 1 to 1 wt ratio were capable of adsorbing up to 85.6 mg of CO<sub>2</sub>, representing 0.82 mmol CO<sub>2</sub> per gram or 36.3 mg CO<sub>2</sub> per gram of adsorbent. The measurements confirmed that the amount of adsorbed carbon dioxide was proportional to the number of amine sites in a polymer. The obtained CO<sub>2</sub> adsorbents could be regenerated upon by heating. Desorption took place above 80 °C, but the optimum temperature seemed to be at least 100 °C. The effect of easier CO<sub>2</sub> desorption in presence of HBPG structures reported in the literature in case of our materials has not been confirmed.

### 1. Introduction

Hyperbranched polyglycerols (HBPGs) are structurally defined, biocompatible macromolecular scaffolds, that have an aliphatic polyether backbone, and possess multiple hydroxyl terminal groups. The hydroxyl groups in polyglycerol not only increase the hydrophilicity of this polymer but also allow for its modification, leading to polymers with carboxyl, amine, and vinyl groups, as well as to polymers with bonded aliphatic and perfluorated chains, sugar moieties, and covalently immobilized bioactive compounds, in particular proteins [1]. HBPGs are easily synthesized by ring opening polymerization of glycidol [2] or glycerol carbonate [3].

Functional HBPGs have recently gained considerable interest due to their potential in biomedical applications [4–7]. Particularly interesting are branched polymers containing amine groups. A comprehensive review of amine containing hyperbranched polyglycerols and branched polyamines in general as gene carriers was given by Fischer et al. [8]. The most popular pathway leading to amine containing hyperbranched polyglycerol (A-HBPG) involves the use of azide intermediates [9]. Haag et al. reported polyglycerol [10,11] and polyglycerol based

nanogels [12] with different numbers of amine sites (different charge densities) that can function as cellular delivery systems. Polyglycerols were synthesized by ring opening polymerization of glycidol [2], while the nanogels by acid-catalyzed epoxide-opening polymerization based on an A<sub>3</sub>+B<sub>3</sub> system (glycerol and glycerol-tris(glycidylether)) using a mini-emulsion approach. For the surface modification of both types of polymers with amine groups, a three-step protocol was applied involving: mesylation of hydroxyl groups, a nucleophilic substitution with sodium azide and the final reaction with triphenylphosphine [9]. A-HBPGs obtained in the same way were also used as coatings for polypropylene surfaces [13]. The same research group developed also interesting polyglycerol-amine based nanocarriers for gene delivery containing a pH-cleavable benzacetal structures. Due to the acid lability of the acetal moiety, the cleavable A-HBPGs were found to be less toxic in vitro [14].

A simple route of formation of structures consisting of a HBPG core and a polyamine shell was reported by Oupicky et al. [15]. First, the hydroxyl groups of HBPG were activated with phenyl chloroformate, then a large excess of norspermine or N,N-bisethyl-norspermine was added resulting in the final polymers, which were used as gene delivery

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vectors with reduced toxicity. Another way to attach amine-functional molecules to the HBPG's outer sphere involved the use of sodium periodate as an activation agent [16]. Sodium periodate was used to transform the hydroxyl groups into aldehyde ones capable of reacting with amines. A core-shell polymers of reversed structure were also synthesized. Macromolecules containing a PEI core and HBPG shell were reported by Chen et al. [17].

While most of synthetic procedures of preparation of A-HBPGs includes the modification of existing HBPG macromolecules, the examples of preparation of these structures via copolymerization are particularly rare. A nice example of such an approach using a novel amino glycidyl ether monomer was presented by Kim et al. [4]. A Boc-protected butanolamine glycidyl ether monomer was copolymerized with glycidol through anionic ring-opening multibranching polymerization. The copolymerization and subsequent deprotection chemistry allowed the incorporation of an adjustable fraction of primary amine moieties (typically, 5 – 20% monomer ratio) within the HBPG backbones, thus providing potentials for varying charge densities and functionality in HBPGs.

Another method of obtaining HBPGs containing amine functionalities which has just emerged in the literature is the use of the Garbiel synthesis. Phthalimide monofunctional HBPGs were synthesized by applying a (phthalimide)/(potassium phthalimide) initiating system for the anionic ring-opening multibranching polymerization of glycidol [18]. The phthalimide group was then quantitatively cleaved by hydrazinolysis to form a monoamine functional HBPG. The amine functionality at the initiating site was then transformed into carboxylic, maleimide, and chloroacetamide groups. Dendritic polyglycerol sulphates containing multiple phthalimide functionalities were also obtained by a ring opening copolymerization of glycidol and N-(2,3-epoxypropyl)-phthalimide and further modification [19]. Cleavage of the N-phthalimide protecting groups, yielded functionalized dendritic polyglycerol sulfates that could be used as multivalent anti-inflammatory compounds. Phthalimide functional groups were also introduced to the HBPG structure by post-polymerization modification with N-hydroxy phthalimide [20].

While most of the literature reports considering amine containing HBPGs concentrate on biomedical applications, the same macromolecules may be used to develop polymeric materials capable of the capture of carbon dioxide from atmospheric gases. Several review articles dealing with CO<sub>2</sub> capture specifically over the general solid adsorbents [21], nonporous materials [22], MOFs [23], ionic liquids [24] and chemisorbents [25] have appeared in the literature. According to the reviews, amine-functionalization has been universal concept applied to just about all different classes of materials for CO<sub>2</sub> capture over the last decades.

However, the area of amine functionalized polymers as CO<sub>2</sub> adsorbents is still not well recognized. Chen et al. [26] prepared an amine-containing porous polymer by the condensation of melamine with several aromatic aldehydes through Schiff base chemistry. This melamine based porous polymer exhibited a CO<sub>2</sub> capture capacity of 59 mg per gram of adsorbent (25 °C, 1 atm). Gebald et al. [27] synthesized an amine-functionalized nonporous material by freeze-drying an aqueous suspension of nanofibrillated cellulose and N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane. The resulting materials achieved a CO<sub>2</sub> capture capacity of 61 mg per gram of adsorbent in 12 h at the CO<sub>2</sub> concentration of 506 ppm in air and a relative humidity of 40% at 25 °C. Guillerme et al. [28] synthesized a porous organic polymer with free aldehyde moieties, which allowed a deliberate amine grafting (aldehyde conversion to imine) via a mild one-step post-synthetic modification procedure. Amine-functionalization led to ca. 20% increase in CO<sub>2</sub> capture capacity.

The only example of the use of polyglycerols in reversible capture of carbon dioxide was reported by Azzouz et al. [29]. Three polyglycerol dendrimers with average molecular masses of 500, 1100, and 1700 were used for intercalation of Na-montmorillonite producing effective

organo-Mt adsorbents. Such adsorbents released CO<sub>2</sub> at much lower temperatures as compared to amines. However, the reported CO<sub>2</sub> capture capacities of those materials were only on a μmol/g level compared to mmol/g level for most of the contemporary solid carbon dioxide adsorbents.

The preparation of effective CO<sub>2</sub> adsorbents is still a challenge. Therefore, in this work we concentrated on the synthesis of amine-containing HBPGs and their characterization considering the capability of CO<sub>2</sub> adsorption from the ambient air.

## 2. Experimental

### 2.1. Materials

All the reagents were purchased from Sigma-Aldrich (Poznań, Poland) and used as received. Solvents were purchased from POCh (Gliwice, Poland) and used as received except of tetrahydrofuran that was used immediately after distillation over potassium benzophenone ketyl (distillation to the reaction flask over argon).

### 2.2. Instrumentation

FTIR spectra were recorded on a Nicolet iS5 Mid Infrared FT-IR Spectrometer equipped with iD7 ATR Optical Base. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian VXR 400 MHz or Bruker AVANCE 500 MHz spectrometers using tetramethylsilane as an internal standard and deuterated solvents (CDCl<sub>3</sub>, DMSO-d<sub>6</sub>). The average molecular masses of polymers were determined based on <sup>1</sup>H NMR spectra. The integral of the CH<sub>3</sub> group signal coming from the core trimethylolpropane (TMP) molecule was used as a reference. MALDI-TOF spectra were measured on a Bruker UltraFlex (Bremen, Germany) spectrometer using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as a matrix. Carbon dioxide concentration was measured using HORIBA APCA-370 air pollution monitor. High carbon dioxide concentrations (100 to 10,000 ppm), temperature and humidity were measured with a modified AZ-77535 multimeter. Rheological measurements were performed with Malvern Kinexus Pro rheometer in the parallel plate geometry (φ20 mm, spacing gap 0.5 mm) within the shear rate 0.1–100 1/s. Elemental analysis was performed with Elementar Vario EL III CHNS analyzer. Nitrogen physisorption measurements using ASAP 2020 (Micromeritics Instrument Co.) were used to determine textural properties of the prepared materials. The specific surface area (S<sub>BET</sub>) was determined by the multipoint Brunauer-Emmett-Teller (BET) method. Whereas, the results of multipoint measurements in the range p/p<sub>0</sub> = 0.01–1 were approximated by the Barret-Joyner-Halenda adsorption isotherm (BJH), on the basis of which the pore volume distribution of the tested materials was determined. The values of total pore volume were estimated at p/p<sub>0</sub> ~ 1.

### 2.3. Syntheses

#### 2.3.1. N-(2,3-epoxypropyl)-phthalimide (1)

Monomer **1** was synthesized according to modified literature procedures. [30,31], 354 g (3.83 mol, 300 ml) of epichlorohydrin was placed in a 1 L round bottom flask equipped with a reflux condenser, magnetic stirrer and an oil heating bath. Subsequently, 100 g (0.49 mol) of potassium phthalimide was added and the reaction flask flushed with argon and closed with a balloon. The reaction mixture was stirred at reflux overnight. The resulting slurry was placed on a rotary evaporator and the excess of epichlorohydrin removed *in vacuo*. The solid residue was dissolved in chloroform and inorganic salt was removed by filtration. The solution was evaporated to dryness and the product was crystallized from hot methanol. The product was obtained as white crystals.

Yield 93.2 g (93.7%), mp = 98–99 °C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz); δ (ppm) = 7.85–7.78 (m, 2H, H<sub>Ar</sub>), 7.73–7.65 (m, 2H, H<sub>Ar</sub>), 3.91 (dd, 1H,

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