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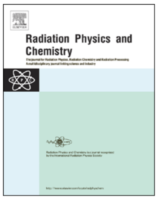

Tailoring the structural properties of macroporous electron-beam polymerized cryogels by pore forming agents and the monomer selection

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HIGHLIGHTS

- Electron-beam derived synthesis of tailor-made cryogels in water at subzero temperatures.
- Successful application of poly(ethylene glycol) as pore forming agent in cryogel synthesis.
- Lower molecular weight PEGs are more effective pore forming agents.

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ABSTRACT

In this study the influence of polyethylene glycol pore forming agents and the monomer selection on the conversion, the morphology and swelling properties of electron-beam derived macroporous cryogels was investigated. The cryogels were synthesized at subzero temperatures from aqueous solutions by applying a pulsed electron beam of a high-energy linear accelerator. The macroporous structure is templated by the ice crystals and the morphology and swelling characteristics depend on the type of monomers used. Pore forming agents introduce smaller pores in the naturally non-porous cryogel walls. The porous structure and swelling properties can be tailored by the choice of the monomer. The systems were thoroughly analyzed by scanning electron microscopy, X-ray photoelectron spectroscopy, thermogravimetrical analysis and mercury intrusion porosimetry.

1. Introduction

Macroporous cryogels (MPCs[1]) are highly crosslinked three-dimensional materials consisting of a large network of interconnected pores that range in size from 1–100 μm.(Plieva et al., 2007, 2008, 2011; Svec, 2010) They are synthesized from anorganic or organic precursors at temperatures below the crystallization temperature of the solvent/porogen. Mostly water is used as solvent and the growing ice crystals act as pore forming agent (also porogen). An approach to organic cryogels relies on the freezing of a monomer solution (i) (followed by a polymerization step) or of a preformed gel (ii) and later removal of the solvent by freeze-thawing (i) or freeze drying (ii). However, the freeze drying route is limited to hydrogels, whereas the large amount of monomers available for the freeze thawing approach allows the synthesis of a wide variety of MPCs with tailored properties. In this study the focus layed on the synthesis of freeze-thawed polymeric cryogels from frozen aqueous solutions. The common routes to MPCs are mainly based on thermally (Hwang et al., 2010) or ultraviolet (UV)-initiated (Petrov et al., 2011, 2009) reactions. Briefly, monomers containing double-bonds are mixed with an initiator and a porogen in a certain concentration. The system is cooled to subzero temperatures and the reaction is started by the initiator or by radiation. Some drawbacks in the case of thermally initiated polymerization are the lack of suitable initiator/activator systems which are still active at temperatures ⩽0 °C, the long reaction times up to 16 h and the immediate start of the reaction after adding the initiator which might lead to hydrogel formation instead of pores. Due to the low penetration depth of the UV photons, the UV-initiated synthesis is limited to transparent devices and allows only the formation of thin films (up to 300 μm). However both of them contain mostly toxic initiators which remain inside the polymeric network after polymerization, a drawback for several applications.

An environmentally benign approach based on electron beam irradiation that overcomes these negative aspects was developed. This new route for the synthesis of MPCs by electron beam irradiation was reported previously. (Reichelt et al., 2013) The

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[1] MPC—macroporous cryogel.

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major advantages of this technique are the absence of initiators, the wide range of sample sizes from capillaries to up to 7 cm thick devices (using two-sided irradiation, the reasonable thickness for electrons with 10 MeV and one-sided irradiation is approx. 3 cm) and the simple way to generate functional MPCs by radiation induced grafting or copolymerization. As previously reported the structural properties of a poly (ethylene glycol) methacrylate/tetra (ethylene glycol)diacrylate standard system depends on the influence of several reaction parameters like dose, temperature and monomer concentration. (Reichelt et al., 2013)

In the course of this study stood the modification of the pore walls by poly(ethylene glycol) (PEG) and the comparison of the morphology and swelling characteristics of cryogels with different chemical composition. The samples were analyzed by XPS, SEM and mercury intrusion porosimetry.

2. Experimental

2.1. Chemicals

Poly(ethylene glycol) methacrylate (PEGMA, Mn=360 g/mol, purity >99.0%), ethylene dimethacrlylate (EDMA, purity >98%), tetra(ethylene glycol) diacrylate (TEGDA, purity >99.5%) and poly (ethylene glycol) (Mw=6000; 20,000; 200,000; 400,000 g/mol) were purchased from Sigma-Aldrich. Poly(ethylenglycol (400)) diacrylate (SR 344), poly(ethylene glycol (400)) dimethacrylate (SR 603), ethoxylated trimethyolpropan triacrylate (SR 415), ethoxylated bisphenol A diacrylate (CD 9038) and poly(ethylene glycol) (300) methylethermethacrylate (PEGMEMA) were from Sartomer. All chemicals were used without purification. Bidestilled water (Milli-Q®-grade, resistivity=18.2 MΩ cm) was used as solvent and porogen.

2.2. Synthesis of the macroporous cryogels

The synthesis of the cryogels was performed as described recently. (Reichelt et al., 2013) In brief words, the acrylates and methacrylates were weighted in 10 wt% concentration (each monomer 5 wt%) and the PEGs in 1 or 2 wt% concentration in centrifuge tubes according to Table 1 and afterwards homogenized by simply vortexing. Due to the limited solubility of high molar mass PEGs the samples F and G were stored at 60 °C for 30 min. The mixtures were flushed with nitrogen for 5 min and sonificated for 5 min in order to remove air bubbles. The formulations were transferred to eppendorf ($V_{\mathrm{formulation}}=0.5$ ml) or centrifuge tubes ($V_{\mathrm{formulation}}=9$ ml). Then, the systems were frozen in a lab cryostat at $T=-20$ °C for 2 h and subsequently irradiated using a 10 MeV high energy linear accelerator (LINAC, Torjy Company, Russia) applying a dose of 12 kGy in 3 kGy dose steps. Dosimetry was conducted by a graphite calorimeter. The LINAC parameters were fixed as follows: repetition rate: 50 Hz; electron pulse length: 2 µs; irradiation time: <10 min, average dose rate: ~1.2 kGy/min. During irradiation the samples were stored in a home-built cooling chamber to keep the temperature constant at $T=-12$ to -15 °C. Finally, the cryogels were heated to room temperature, thoroughly rinsed with water and dried in vacuum at 40 °C over night.

Table 1
Feed composition for the preparation of macroporous cryogel in wt%.

#	Monomer 1 c=5 wt%	Monomer 2 c=5 wt%	PEG (M_w in g/mol)	final monomer concentration wt%	H_2O wt%
St	PEGMA	TEGDA		10	90
A	SR 415	PEGMEMA		10	90
B	SR 603	CD9038			
C	SR 344	EDMA			
D	PEGMA	TEGDA	6000	12	88
E			20,000	12	89
F			200,000	11	89
G			400,000	11	89

2.3. Characterization of MPCs

The morphology of the MPCs was imaged by SEM (Ultra 55, Carl Zeiss SMT, Germany) at an accelerating voltage of 5 kV. The pore size and pore size distribution (PSD) was studied by the means of mercury intrusion porosimetry (MIP[2], Poremaster 33, Quantachrome, Germany). A pore size range of ~3–250 µm was recorded at fixed values for the mercury density (13.5 g/cm^3) and for the contact angle ($\theta=140°$). (Skudas et al., 2009) The MIP examinations (PSD, intruded volume, d_{50} value) of three independent samples were performed repeatedly and the results were given as average values.

The chemical composition was examined by XPS (AXIS Ultra, Kratos Analytical, England). The kinetic energy of the electrons was analyzed with a pass energy of 160 eV for the survey spectra and 40 eV for the energy resolved spectra, respectively. The temperature stability of the MPCs up to 800 °C was determined by thermogravimetry (TGA 7, Perkin Elmer, USA). The yield of gelation was determined as follows: The freshly prepared and washed cryogels were dried in vacuum ($T=40$ °C) to constant mass. The gel content GC was calculated using Eq. (1):

$$GC = m_d/m_0 \times 100\% \quad (1)$$

where m_d is the mass of the dry cryogel and m_0 is the total mass of the monomers in the feed solution. The results were average values of three independent samples. Additional data were obtained by FT-IR (Vector 22, Bruker Optics) measurements of the double bond conversion at 810 cm^{-1} referenced to the pure acrylate formulations.

The swelling characteristics of dry cryogels after different swelling times were investigated in deionized water at room-temperature ($T=23$ °C). The samples were swollen in water and taken from the medium after 2, 5, 10 min, 1 and 24 h, wiped with tissue paper, weighted and returned to the swelling medium. The swelling ratio SR was calculated as:

$$SR = (m_s)/m_d \quad (2)$$

where m_s is the mass of the swollen and m_d the mass of the dried cryogel, respectively. All swelling experiments were average values of three or four independent samples.

3. Results and discussion

3.1. Structure modification by pore forming agents.

For several applications porous materials with both large and small pores are mandatory. One example might be the application of the cryogels in column enzyme reactors (reaction and separation in one column). Smaller pores especially inside the pore walls enhance the total surface area of the MPCs. This can improve the binding capacity for the catalysts or functional polymers and result in enzyme reactors with higher reactivity.

Four PEG molecules with different chain length were mixed with the standard cryogel formulation according to Table 1 using a vortexer. The properties of the standard PEGMA/TEGDA cryogels were thoroughly discussed in the reference (Reichelt et al., 2013). PEGs are well known pore forming agents and were already

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[2] MIP—mercury intrusion porosimetry.