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Macroporous gels with fast response prepared by e-beam crosslinking of poly(*N*-isopropylacrylamide) solution

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Abstract

Macroporous temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) gels exhibiting fast response rates were obtained by electron beam irradiation of aqueous polymer solutions. The effect of polymer concentration, irradiation temperature and dose, as well as addition of crosslinker was studied. The gels synthesized above the critical temperature from 20 wt.% polymer solution without crosslinker exhibited the highest equilibrium swelling and fastest response rate measured by seconds. The gels show reversible response to cyclical changes in temperature and might be used as actuators or pulsed drug release.

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1. Introduction

Macroporous thermoreversible hydrogels are characterized by large pore size and high pore volume, therefore they are capable to respond to temperature changes much faster than conventional hydrogels. The deswelling rate of such gels is measured in minutes as opposed to conventional gels showing deswelling rates measured in hours or days. Therefore macroporous gels are of interest for numerous potential technological and biomedical applications, from rapid immunoassay and pulsed drug delivery to actuators, where short response rate of the order of minutes or seconds are required. Poly(*N*-isopropylacrylamide) (PNIPAAm) is a well-known and widely studied thermoresponsive polymer, which shows coil-globule transformation at a lower critical solution temperature (LCST) at around 32 ° C. When crosslinked, PNIPAAm gel shrinks above, and swells below the LCST. The formation of a porous structure has been shown to enhance the rate of gel shrinking,

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and several reports described ways for achieving this, including synthesis of gels above the LCST [1,2], by freezing polymerization [3], by two-step polymerization at two different temperatures [4,5], by polymerization in salt solution [6], by incorporation of silica particles [7], by grafting [8,9], and electron-beam initiated polymerization [10].

Common denominator of all those methods is that the gels were prepared by free radical polymerization from aqueous solutions of the monomer. When ionizing radiation is used to initiate the radical formation in aqueous NIPAAm solution, neither chemical initiator nor crosslinker is needed [10–12], allowing a simpler and cleaner preparation. Even more convenient method is the irradiation of the polymer solution, especially for hydrogels intended for biomedical use. PNIPAAm cannot be crosslinked by chemical methods, but irradiation of aqueous polymer solution produced insoluble, crosslinked gel [11]. We have shown, that when irradiating a PNIPAAm solution, the crosslinking most probably starts by combination of two isopropyl-centered radical [13]. However, when the hydrogel is synthesized from NIPAAm monomer solution, the α-carboxylalkyl radicals are first formed, and they are responsible for the onset of the polymerization. Since the equilibrium-swelling ratio and the response rate of the gels depend on the synthesis conditions, the properties of the gels prepared by these methods were also expected to differ.

We report here the swelling properties of gels obtained from polymer solutions of various concentrations irradiated with different doses at temperatures both below and above the critical temperature.

2. Experimental

2.1. Synthesis

Solutions of PNIPAAm (Monomer-Polymer & Dajac Labs. Inc., degree of polymerization = 220) were prepared in deionized water obtained by ELGA-4 purification system. Deaerated solutions of different polymer concentration were sealed and irradiated on a 4 MeV linear accelerator with pulse duration of 800 ns and dose/pulse of 100 Gy with doses up to 500 kGy. The temperature was kept constant during the irradiation either at around 5 °C or at around 40 °C. The gels so obtained were cut in circular discs, approx. 1 mm tick and 6 mm in diameter, washed for a week and lyophilized.

2.2. Swelling measurements

The gels were characterized by equilibrium swelling degree and by swelling/deswelling kinetics. The equilibrium swelling degree was calculated from gravimetric measurements of dry gels (W_0) and gels immersed in water for 24 h at different temperatures (W_T), as $S_E = (W_T - W_0)/W_0$.

To obtain the rate of shrinking, the gels were first allowed to swell to equilibrium at 5 °C in water, and then the swollen gels were transferred into 40 °C water, where they undergo deswelling. At designated times, the weight of the gel was recorded after blotting the excess surface water with moist filter paper. In reswelling kinetics measurements, the gels were first put in 40 °C water, and after equilibrium was obtained, they were transferred in 5 °C water. At designated times, the weight of the gel was measured. For all measurements, at least three different gels were used, with more samples when needed. The swelling degree at determined time was calculated as $S_t = (W_t - W_0)/W_0$.

To investigate the reversibility of swelling, the gels were first placed in water at 5 °C until equilibrium, then placed in water at 40 °C, and after 5 min they weight was measured. Then, the gels were placed back to 5 °C water for 5 min, and their weight was again measured, and this procedure was repeated several times.

2.3. Porous structure observation

Pictures of the gel surface and cross-section were taken on a JEOL JSM LV-5600 scanning electron microscope. The gels were either freeze-dried and sputter-coated with palladium/platinum on a JEOL JFC 1300 coater, or quick-frozen under liquid nitrogen and observed immediately without coating.