

Preparation of fast response superabsorbent hydrogels by radiation polymerization and crosslinking of *N*-isopropylacrylamide in solution

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Abstract

Macroporous temperature-responsive poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogels with high equilibrium swelling and fast response rates were obtained by a ⁶⁰Co γ - and electron beam (EB) irradiation of aqueous *N*-isopropylacrylamide (NIPAAm) monomer solutions. The effect of irradiation temperatures, the dose, the addition of a pore-forming agent on the swelling ratio, and the kinetics of swelling and shrinking of the PNIPAAm gels was studied. The gels synthesized above the LCST exhibited the highest equilibrium swelling (300–400) and fastest response rate measured by minutes. Scanning electron microscope (SEM) pictures revealed that the gels synthesized above the LCST have larger pores than those prepared at temperatures below the LCST. The gels showed a reversible response to cyclical changes in temperature and might be used in a pulsed drug delivery device. The gels synthesized above the LCST exhibited the highest testosterone propionate release.

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1. Introduction

Radiation synthesis of stimuli-responsive membranes, hydrogels and adsorbents is a wide field of important applications of radiation technology. Stimuli-responsive hydrogels have emerged in recent years as a unique class of materials that can offer many advantages over the conventional materials, and have great potential in diverse applications, such as artificial muscles (Suzuki, 1991; Osada et al., 1992; Ueoka et al., 1997), chemical valves (Osada and Hasebe, 1985), immobilization of enzymes and cells (Dong and Hoffman, 1986; Hoffman, 1987) and concentrating dilute solutions in bioseparation (Feil et al., 1991; Gehrke et al., 1986; Freitas and Cussler, 1987). Many physical and chemical stimuli have been applied to induce responses of the smart hydrogel systems. Physical stimuli include temperature, electric field, solvent, light, pressure, sound and magnetic field, while chemical or biochemical

stimuli include pH, ions and specific molecular recognition temperature.

The most studied stimuli-responsive hydrogel is made from NIPAAm monomer. PNIPAAm is a thermo-responsive polymer, which shows coil–globule transformation at a lower critical solution temperature (LCST) at around 32 °C. Cross-linked PNIPAAm gel shrinks above, and swells below the LCST (Hirokawa et al., 1984). Since the LCST of PNIPAAm gels is close to the normal body temperature of human beings, they show attractive potentials in biomedical area (such as drug delivery, diagnostic agents, bioseparation, etc.). While slow swelling of a dried hydrogel is optimal for a number of applications, there are situations where a fast swelling or shrinking is desirable. The formation of a porous structure has been shown to enhance the rate of gel shrinking, and methods for achieving this include the synthesis of gels above the LCST (Bae, 1997; Safrany, 1999), by freeze-drying polymerization (Kato and Gehrke, 2004), by two-step polymerization at two different temperatures (Kabra and Gehrke, 1991), by polymerization in salt solution (Cheng et al., 2003), by incorporation of silica particles (Serizawa et al., 2002), by grafting (Yoshida et al., 1995), by addition of

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a blowing agent (Kabiri et al., 2003; Chen et al., 1999) and by electron-beam initiated crosslinking (Panda et al., 2000; Safrany, 2005).

Besides the fast swelling–shrinking rate, in some applications a high swelling capacity is also desirable. In this study, we report the synthesis of a PNIPAAm hydrogel by combining several methods to obtain a gel with fast response rate that also has improved absorbing capacity. These gels were obtained from aqueous monomer solutions irradiated with different doses on a ^{60}Co γ -source and an electron accelerator at temperatures below and above the critical temperature, in the presence of a pore-forming (blowing) agent. We also show the effect of the gel response to cyclical changes in temperature on the pulsed drug release.

2. Experimental

2.1. Synthesis

Solutions of NIPAAm (Scientific Polymer Products Inc.) were prepared in deionized water obtained by ELGA-4 purification system. Deaerated solutions containing 20 wt% NIPAAm monomer were sealed and irradiated on a ^{60}Co γ -source up to 50 kGy, and on a 4 MeV linear accelerator with pulse duration of 800 ns and dose/pulse of 100 Gy with doses up to 100 kGy. Diethyleneglycole dimethacrylate (DEGDMA) (0.1%) was added to the monomer solutions as crosslinker, pH was adjusted to 5.0% and 1% of pore forming sodium bicarbonate was added. The temperature was kept constant during the irradiation either at around 0 °C or at 50 °C. The gels so obtained were cut in circular discs (approximately 1 mm thick 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

$$\text{SE} = \frac{W_T - W_0}{W_0}.$$

To obtain the rate of shrinking, the gels were first allowed to swell to equilibrium at 8 °C in water, and then the swollen gels were transferred into 45 °C water. At designated times, the weight of the gel was recorded after blotting the excess surface water with moist filter paper. In swelling kinetics measurements, the gels were first put in 45 °C water, and after equilibrium was obtained, they were transferred in 8 °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

$$\text{St} = \frac{W_t - W}{W_0},$$

where W_0 and W_t are the dry gel weight and the weight after time t , respectively.

2.3. Porous structure observation

Pictures of the gel surface and cross-section were taken on a JEOL JSM LV-5600 scanning electron microscope (SEM). 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.

2.4. Modeling the pulsed drug release

Testosterone propionate (Fluka) was used as model drug. The gels were first allowed to swell in the drug solution at 8 °C, then taken out and lyophilized. They were placed in water at 45 °C for 5 min, then back to water at 8 °C, followed by placement of the gel in water at 45 °C; this was repeated many times. The release was monitored by absorbance measurement at 306 nm by using a Jasco V-550 UV–vis spectrometer.

3. Results and discussion

3.1. Gel synthesis

In this study, the macroporous thermo-responsive hydrogels were synthesized by crosslinking polymerization initiated by irradiating aqueous NIPAAm solutions. In this way, first reactive intermediates of the water radiolysis (hydrated electrons, hydroxyl radicals and hydrogen atoms) were formed, and they, by reacting with the monomer, produced α -carboxyalkyl type radicals (Nagaoka et al., 1997; Strauss et al., 1998; Safrany and Wojnarovits, 2003). These radicals then, depending on the synthesis conditions, start the polymerization. By further irradiations, these reactive species can also abstract hydrogen from the growing polymer chains, producing thus polymer radicals that may further react to form branched, and finally, crosslinked molecules. While in this way NIPAAm can be crosslinked by irradiation without addition of a crosslinker (Nagaoka et al., 1997; Safrany and Wojnarovits, 2004), the presence of a monomer with two double bonds improves the mechanical properties of the final gel. We have used small amounts of DEGDMA (1%) for that purpose. To introduce excess gas bubbles during the polymerization to form big pores, sodium bicarbonate was added and the pH was adjusted to 5. We used both ^{60}Co γ -source and electron beam (EB) irradiation, i.e. low and high dose rate. In the high dose rate case,

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