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Radiation Physics and Chemistry 75 (2006) 1041–1046
Radiation Physics and Chemistry
www.elsevier.com/locate/radphyschem

Synthesis and electrical response of acrylic acid/vinyl sulfonic acid hydrogels prepared by γ-irradiation

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Received 19 April 2005; accepted 12 May 2005

Abstract

The electro-active acrylic acid/vinyl sulfonic acid copolymer (AAc/VS) was prepared using γ-radiation. The effect of preparation conditions such as comonomer composition and irradiation dose on copolymer gelation degree, and swelling property of the prepared copolymer in water and different electrolytes of various concentrations was studied. The degree of gelation decreases by increasing the VS content in the feed solution and increases by increasing the irradiation dose. The swelling degree decreases by increasing the irradiation dose and ionic strength. The electro-activity of the prepared AAc/VS copolymer was investigated to find out that it greatly affected by polymer composition and crosslinking density as well as the hydrogel counter ion. The electrical sensitivity increases by the increase of VS content and crosslinking density in the copolymer. AAc/VS copolymers showed various degrees of bending behavior depending on the counter ion. The presence of potassium as counter ion maximized the electrical response of the polymer.

Keywords: Vinyl sulfonic acid; Stimuli responsive; Hydrogel electroactive; Counterions; γ-rays

1. Introduction

Nowadays, much demand has been grown of systems that undergoes dramatic changes in shape, surface characteristics, solubility, formation of an intricate molecular self-assembly or a sol-to-gel transition and produces contractile force in response to environmental stimuli such as pH, solvent, composition, temperature, ionic concentration and electric field (Kim et al., 2004a,b; De and Aluru, 2004; Marsano et al., 2004; El-Hag Ali, 2005). Electro-responsive polymers, which change their shape under an electric field and have worm-like movement, are promising materials for the applications of biomechanical devices as well as artificial muscle actuator (gel robots) (Liu et al., 2002; Kim et al., 2004a,b). They may also have applications as, sensors, energy transducing devices and in separation techniques (Kim et al., 1999).

Hydrogels prepared from polyelectrolytes which containing relatively high concentrations of ionizable groups along the polymer backbone exhibit pH-responsive characteristics and are interesting for the design of electrically modulated systems (Kaetsu, 1995; Kaetsu et al., 1992). Crosslinked polyacrylic acid and its sodium or potassium salts, shows pH and electric-responsive properties. Among the mechanisms of the stimulus-sensitivity, the most important one is the volume change of polyelectrolyte due to the conformation change by ionic interaction between the polymeric ions or between the polymeric ion and the counter ion in the solvent (Kishi and Osada, 1989).

The stimuli-response mechanism of the hydrogels in direct current has been discussed frequently, but it is still

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doi:10.1016/j.radphyschem.2005.05.022

controversial. The most acceptable mechanism of such response is considered to result from the attraction of the hydrated mobile cation toward the negative electrode side due to the columbic force by the electric field, resulting in the swelling and shrink of the negative and positive electrode sides of the hydrogel, respectively (Kuhn et al., 1950; Kuhn, 1949; Katchalsky, 1949).

In this connection the research goal in the present study is to synthesize PAAc/VS copolymer hydrogel using γ rays as initiator. The sensitivity of the PAAc/VS copolymer hydrogel under an electric stimulus was investigated to assess its suitability in biomechanical devices.

2. Experimental

2.1. Materials

Acrylic acid, of purity 99.9% (Merck, Germany), vinyl sulfonic acid sodium salt, 25 wt% in water (Aldrich, Germany) were used as received. All salts used were reagent grade and were used without further purification.

2.2. Preparation of AAc/VS copolymer hydrogel

Mixtures of AAc and VS of different feed solution compositions in aqueous solution were exposed to ^{60}Co γ-irradiation at different irradiation doses (dose rate 4.8 kGy/h). The prepared gel was immersed in distilled water for 24 h to remove the un-reacted monomer.

2.3. Determination of copolymer composition

To determine the VS content in the copolymer, the copolymers were soaked for 24 h with 0.2 N HCl at 35°C. The copolymer removed and the mother solution was back titrated against 0.1 N Na_2CO_3 using phenolphethalin (ph. ph) as an indicator (Grodzinsky and Melcher, 1976; Yannas and Grodzinsky, 1973).

2.4. Preparation AAc/VS copolymer with different counter ions

To prepare AAc/VS with different counter ions the prepared hydrogel soaked in 0.2 N HCl for 24 h to remove all the Na ions and to get H form hydrogel. Thereafter, the H-form hydrogel soaked in 0.5 M of LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$ or $BaCl_2$ for 48 h.

2.5. Swelling studies

AAc/VS copolymers with different counter ions were allowed to swell in distilled water or different electrolytes. The degree of swelling at time intervals and equilibrium swelling was calculated as follow:

$$\text{swelling degree (\%)} = \frac{(W_s - W_o)}{W_o} \times 100,$$

where W_s and W_o are the weights of the swollen and the dry hydrogel, respectively.

2.6. Electro-responsive deformation

Fully swollen AAc/VS hydrogels (20 mm long, 5 mm wide, 2 mm thick) in absence and presence of different counter ions was held between the two carbon electrodes in the box of dimension (40 × 40 × 20 mm) connected to the DC source (12 V). The distance between the two-carbon electrodes is 30 mm (as shown in Fig. 1). The time needed for maximum displacement was considered as response time.

3. Results and discussion

3.1. Effect of preparation conditions on the copolymer gelation and actual molar composition

Fig. 2 shows the effect of the comonomer composition and irradiation dose on the copolymer gelation degree. The gelation degree increases by increasing AAc content in the comonomer feed solution. This is due to the high ability of AAc to copolymerize and to form crosslinking network and self-bridging. On the other hand, the concentration of the free radical formed during the irradiation process increased

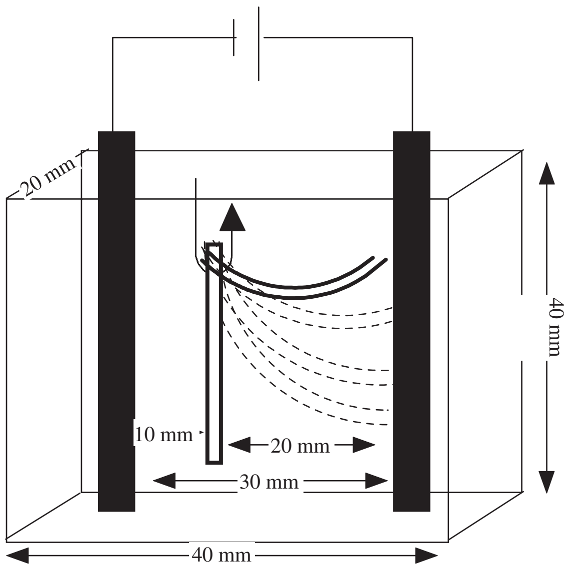

Fig. 1. Schematic diagram showing the AAc/VS specimen bending under an applied electric field.