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Controlling of pore size and distribution of PDMAEMA hydrogels prepared by gamma rays

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Abstract

In this study, radiation synthesis and controlling of pore size and distribution of poly(*N*, *N*-dimethylaminoethyl methacrylate) (PDMAEMA) hydrogels have been investigated. Monomer mixtures containing various compositions of DMAEMA, water and ethylene glycol dimethacrylate (EGDMA) and poly(ethylene glycol) (PEG) have been prepared and irradiated. The molecular weight between cross-links of P(DMAEMA) hydrogels prepared in the presence of PEG increased with increasing amount of PEG in the initial mixture from 1% to 20%. Hydrogels with highest mesh size were obtained by using 20% PEG10 000. Upon PEG addition, an increase in the equilibrium degree of swelling (*Q*) was observed with increasing molecular weight of PEG until a molecular weight of 10 000. Maximum swelling was reached for systems containing 1% and 5% PEG10 000. SEM micrographs showed homogeneous pore structure of the hydrogels with open pores at lower pH.

Keywords: Hydrogels; Dimethylaminoethyl methacrylate; Radiation; Cross-linking; Pore size

1. Introduction

The preparation of poly(*N*, *N*-dimethylaminoethyl methacrylate) (PDMAEMA) and its copolymers has gained noticeable interest and a series of papers were published by Siegel and Firestone in the late eighties (Firestone and Siegel, 1988; Siegel and Firestone, 1988). They investigated the influence of comonomer *n*-alkyl methacrylate (*n*-AMA) and methyl methacrylate (MMA) on the pH dependent swelling properties and swelling kinetics. It was found that the extent of the transition from the collapsed hydrophobic state to the hydrophilic state changed depending on the comonomer composition. Generally, increasing of the proportion of *n*-AMA to MMA decreased the extent of the transition and shifted it to lower pH. It was also observed that longer *n*-AMA side chains also reduced the extent of the transition.

In recent years much more attention has been directed to PDMAEMA hydrogels that undergo controllable volume changes in response to small variations of pH and temperature changes in solution condition for use in a variety of novel applications including controlled drug delivery (Traitel et al., 2000; Hinrichs et al., 1999) and as a gene transfer agent (Rungsardthong et al., 2001; Takeda et al., 2004).

In our previous study, we proposed that a small amount of ethylene glycol dimethacrylate (EGDMA) can facilitate the cross-linking of DMAEMA effectively during low dose rate gamma irradiation and improve the cross-link efficiency approximately eightfold when only 0.05% concentration in the initial monomer mixtures was used (Uzun et al., 2003). We also reported that irradiation dose, comonomer VP and cross-linking agent EGDMA affect the gelation percentage and network structure of DMAEMA hydrogels. The effects of all these parameters on the pH and temperature response characteristics and enthalpy and entropy changes appearing in the χ parameter for the P(DMAEMA-co-VP)–water system were also determined in our previous study (Şen and Sarı, 2005).

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2. Experiments

For the preparation of PDMAEMA hydrogels (*DMAEMAxPEGy*) in the presence of poly ethylene glycol (PEG) 5 ml of DMAEMA was mixed with 1.5 ml 1.0%, 5.0%, 10.0%, 20.0% PEG solution and 0.05% by volume EGDMA (volume EGDMA/volume DMAEMA) was added into these solutions. The molecular weight of PEGs used as diluents in the polymerization medium were 2000, 10 000 and 20 000 g/mol. In the gel name x and y represent the % of PEG solution from which 1.5 ml was added into the initial mixture and the molecular weight of PEG as kD, respectively. Monomer solutions thus prepared were placed in PVC straws of 4 mm diameter and irradiated up to 4.0 kGy in Gammacell-220 type γ-irradiator at a fixed dose rate of 0.16 kGy/h. Hydrogels obtained in long cylindrical shapes were cut into pieces of 3−4 mm and stored.

Dried hydrogels were left to swell in various K_2HPO_4 and KH_2PO_4 phosphate buffer solutions at pH 3–8. Swollen gels were removed from the swelling medium at regular intervals, dried superficially with filter paper, weighed and placed back in the same medium. The measurements were continued until a constant weight was reached for each sample. This weight was used to calculate the volume fraction of polymer, v_{2m}, and the equilibrium degree of swelling (EDS), (Q), of the gel swollen to equilibrium in aqueous solution.

The mechanical properties were determined at room temperature by uniaxial compression experiments at a crosshead speed of 5 mm/s until failure, using a Zwick Z010 model Universal Testing Instrument and uniaxial compression module, equipped with a 1 kN compression load cell. The mechanical properties of the hydrogels were measured in their relaxed state (after preparation).

The pore structure of the gels was monitored by using Jeol JSM 5600 LV scanning electron microscope. For these studies the hydrogels were first swollen in pH 3 and pH 7 buffer solutions, then lyophilized, and sputter coated with platinum/palladium.

3. Results and discussion

3.1. Preparation of PDMAEMA hydrogels in the presence of PEG

In order to increase the pore size of hydrogels we added water soluble low molecular weight PEGS into the initial mixtures. The molecular weight of PEGs used as diluents in the polymerization medium was 2000, 10 000 and 20 000 g/mol. Percentage gelation i.e. percentage conversion of monomer (DMAEMA), cross-linking agent (EGDMA) into insoluble networks, was based on the total weight of these two monomers in the initial mixture. % gelation of DMAEMA decreased from 99% to 95% with decrease of molecular weight of PEG and with increasing PEG content in the initial mixture (Aguş, 2005).

After preparation of hydrogels, FTIR spectra were taken (spectra not given in the text). Two characteristic peaks of PEG at 1140 and 845 cm^{-1} were observed for non-washed DMAEMA20PEG20 hydrogel as a sharp and shoulder peak, respectively. Both peaks disappeared from the spectra after washing, indicating that PEG can easily be removed from the hydrogels.

On the other hand, these two characteristic peaks of PEG stayed in the FTIR spectra of washed DMAEMA5-PEG20, DMAEMA10PEG20 and DMAEMA20PEG20 hydrogels indicating that PEG20 000 probably formed inter-penetrating network with DMAEMA monomer. The higher gelation percentage of hydrogels with PEG 20 000 in the initial mixture when compared to mixtures containing PEG2000 and PEG 10 000 was also attributed to this inter-penetrating network and/or grafted PEG molecules.

3.2. Characterization of network structure of PDMAEMA-PEG hydrogels

For the characterization of the network structure and determination of the molecular weight between cross-links, $\overline{M}_c$, of DMAEMA hydrogels, the swelling properties at non-ionized state (pH 7) were first investigated. After swelling experiments the uniaxial compression was applied on the gels swollen at pH 7. During the determination of the shear modulus, the experiment was stopped before the complete deformation of the hydrogel system, in order to obtain the initial deformation. Shear modulus values were calculated by using the elastic deformation theory and the following equation (Mark and Erman, 1988):

$$f = G(\lambda - \lambda^{-2}). \tag{1}$$

When the equation is applied to the initial stages of deformation, plots of f vs. $(\lambda - \lambda^{-2})$ yield straight lines. The G value was calculated from the slope of the lines, and listed in Table 1. $\overline{M}_c$ values were calculated by using Eq. (2) and shown in Table 1 (Okay and Durmaz, 2002).

$$G = \frac{\rho}{\overline{M}_c} RT v_{2r}^{2/3} v_{2m}^{1/3}, \tag{2}$$

$$\xi = v_{2m}^{1/3} \left[C_n \left(\frac{2\overline{M}_c}{M_r} \right) \right]^{1/2} l. \tag{3}$$

The mesh size of PDMAEMA hydrogels were calculated by using Eq. (3) (Peppas and Mikos, 1986; Aguş, 2005) and plotted in Fig. 1. As seen from Fig. 1, addition of PEG during the preparation of DMAEMA hydrogels caused a decrease in the cross-link density and an increase in the mesh size. The highest mesh size was reached with 20% of PEG10 000. The smaller pores of the hydrogels containing PEG20 000 was probably due to the formation of inter-penetrating network structure, or