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Radiation synthesis and characterization of poly(*N*,*N*-dimethylaminoethyl methacrylate-co-*N*-vinyl 2-pyrrolidone) hydrogels

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Abstract

In this study, radiation synthesis and characterization of swelling behavior and network structure of poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA), and poly(*N*,*N*-dimethylaminoethyl methacrylate-co-*N*-vinyl 2-pyrrolidone) (P(DMAEMA-co-VP)), hydrogels were investigated. PDMAEMA and P(DMAEMA-co-VP) hydrogels in the rod forms were prepared by irradiating the ternary mixtures of DMAEMA/VP/cross-linking agent, ethyleneglycol dimethacrylate (EGDMA), by gamma rays at ambient temperature. In composition ranges where the three components were completely miscible, water was also added to the ternary mixture to provide the formation of homogeneous polymerization and gelation. The influence of irradiation dose, comonomer, VP, and cross-linking agent, EGDMA, content on the total percentage gelation and monomer conversion were investigated. The effect of pH and temperature on the swelling behavior of hydrogels have also been examined. Hydrogels showed typical pH response and temperature responses, such as low-pH and low temperature swelling and high-pH and high temperature deswelling. Polymer–solvent interaction parameter (χ) and enthalpy and entropy changes appearing in the χ parameter for the P(DMAEMA-co-VP)–water system were determined by using Flory–Rehner theory of swelling equilibrium. The negative values for ΔH and ΔS indicate that prepared pure PDMAEMA and P(DMAEMA-co-VP) hydrogels have lower critical solution temperature (LCST) and Flory–Rehner theory of swelling equilibrium provides a satisfactory agreement to the experimental swelling data of the hydrogels.

Keywords: *N*,*N*-Dimethylaminoethyl methacrylate; *N*-vinyl 2-pyrrolidone; Hydrogel; Radiation synthesis

1. Introduction

Poly-electrolytes are polymers which contain relatively ionizable groups at levels ranging from a few mole percentage to 100% of the repeating units. Poly-electrolytes may be anionic, cationic or amphophilic and may be synthetic or naturally occurring.

The preparation of poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) and it's copolymers has gained noticeable interest and a series of paper published by Siegel and Firestone in the late eighties [1–3]. They investigated the influence of comonomer *n*-alkyl (*n*-AMA) and methyl methacrylate (DMA) on the pH-dependent swelling properties and swelling kinetics. It

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was found that the extent of the transition from the collapsed hydrophobic state to the hydrophilic state changed depending on the comonomer composition and as the proportion of *n*-AMA to DMA is increased generally the extent of the transition is reduced and shifted to lower pH. It was also observed that increasing the length of the *n*-AMA side chain was also caused a reduction in 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 variation of pH and temperature changes in solution condition for use in a variety of novel application including controlled drug delivery [4,5] and gene transfer agent [6–8].

Traitel et al. [4] synthesized glucose-responsive insulin controlled release system based on the hydrogel, poly(2-hydroxy ethyl methacrylate-co-*N*,*N*-dimethylaminoethyl methacrylate), with entrapped glucose oxidase, catalase and insulin. It was found that pH sensitive poly(HEMA-co-DMAEMA) hydrogels can be used as glucose-responsive insulin release systems for the reducing blood glucose level.

Recently, Kim et al. [9] studied the PDMAEMA and polyethyl acrylamide microspheres. The release of hydrocortisone was studied in various pH and temperatures. It was found that the release of hydrocortisone in response to pulsatile pH changes and release rate increased drastically due to dissociation of polymer complex at acidic conditions. However, decrease of pH increased the LCST of polymer complex of microsphere led to the dissociation of aggregate polymer complex and released of hydrocortisone in stepwise manner. As a result of these studies, authors proposed that based on the pH/response sensitivity of hydrogen bond in the microsphere, pH/temperature release of hydrocortisone can be controlled in an on-off manner without considerable log time.

Yanfeng and Min [10] synthesized P(DMAEMA) hydrogels by UV irradiation and investigated swelling kinetics and responsive properties of these gels. It was found that PDMAEMA hydrogel proved to be pH-sensitive at about pH 3 and equilibrium swelling ratio decreased with increasing ionic strength. It was also observed that PDMAEMA hydrogels have thermosensitive character and lower critical solution temperature in water about 40 °C.

More recent study for the preparation and characterization of environmental responsive poly(dimethylaminoethyl methacrylate)/polyethylene oxide (PEO) semi-interpenetrating network was published by Liu et al. [11]. They used radiation technology for the preparation of semi-IPNs. It was found that the temperature-induced phase transitions of semi-IPNs retained up to 5% PEO content and LCST of PDMAEMA shifted to a lower value from 40 to 27 °C. Semi-IPNs containing more than 5% PEO retained the pH sensitivity but the pH shifted slightly to lower values with increasing PEO content in the semi-IPNs.

In our previous study, we proposed that a small amount of EGDMA can facilitate the cross-linking of DMAEMA effectively during low dose rate gamma irradiation and improve the cross-link efficiency approximately eightfold when used only 0.05% concentration in the initial monomer mixtures [12].

In this study we reported the effect of irradiation dose, comonomer VP and cross-linking agent EGDMA, on the total percentage gelation and network structure of hydrogel. The effect 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.

2. Experimental

2.1. Chemicals

The two monomer used in this study, namely *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) and *N*-vinyl 2-pyrrolidone (VP) were obtained from Aldrich. The cross-linking agent EGDMA was obtained from BDH.

2.2. Preparation of hydrogels

Four components were used in the preparation of poly(*N*,*N*-dimethylaminoethyl methacrylate-co-*N*-vinyl 2-pyrrolidone) P(DMAEMA-co-VP) hydrogels, namely *N*,*N*-dimethylaminoethyl methacrylate, *N*-vinyl 2-pyrrolidone, cross-linking agent, ethylene glycol dimethacrylate and water. Various compositions were prepared where the four components showed complete miscibility. For the preparation of aqueous solutions, 2 ml of 100% DMAEMA, 90% DMAEMA and 10% VP, 70% DMAEMA and 30% VP (as volume ratio) containing mixtures were mixed 1 ml water and 0.1%, 0.5% and 1.0% by volume EGDMA were added into these solutions. The volume percentages of monomers in the initial mixtures are summarized in Table 1. In the notation used for the identification of samples, the numbers preceding the abbreviations denote the percentage composition by volume. Since the densities of the monomers are close to each other and the conversion is almost 100% we can assume that volume composition can be taken as the same as the weight composition. Thus, the prepared monomer solutions were placed in PVC straws of 3 mm diameter and irradiated up to 8.0 kGy in Gammacell-220 type γ-irradiator at a fixed dose rate of 0.16 kGy/h. Hydrogel obtained in long cylindrical shapes were cut into pieces of 2–3 mm and stored for later evaluations.