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Enhancement of copolymerization of itaconic acid with *N*-vinyl 2-pyrrolidone by radiation in the presence of cross-linking agent

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Abstract

Enhancement of copolymerization of itaconic acid (IA) with *N*-vinyl 2-pyrrolidone (VP) by radiation in the presence of cross-linking agent was investigated. Hydrogels with varying IA content were prepared from the ternary systems *N*-vinyl 2-pyrrolidone/itaconic acid/water by irradiating with gamma-rays in the presence of a chemical cross-linker, ethylene glycol dimethacrylate (EGDMA) at ambient temperature. The incorporation of EGDMA into the ternary mixtures caused an increase in the amount of IA in the gel system up to a mole fraction of 13.7%. Hydrogels showed a typical pH response such as high pH swelling and low pH deswelling. Equilibrium volume swelling ratio at pH 7 was varied from 15–40 with changing the IA content in the gel system and irradiation dose. The equation recently modified by the authors for the determination of $\overline{M}_c$ is observed to describe the swelling behaviour of P(VP/IA/EGDMA) networks containing relatively higher amount of charged units very well. In addition to the evaluation of $\overline{M}_c$ from swelling data, the measurement of polymer solvent interaction parameter and the determination of the reaction yield of cross-links of the systems were examined.

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Keywords: Hydrogel; Gamma-rays; Copolymerization; *N*-vinyl 2-pyrrolidone; Itaconic acid; Cross-link

1. Introduction

Poly-electrolytes are polymers which contain relatively ionizable groups at levels ranging from a few mole% to 100% of the repeating unit. Poly-electrolytes may be anionic, cationic or

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amphophilic and may be synthetic or naturally occurring.

As early as 1950 attempts were made for the development of environmental sensitive materials in biomedical and biotechnological applications and as a result of these studies the past 25 years has shown that different type of hydrogel systems can be used as biomaterials [1,2].

Environmental sensitivity or control of swelling ability of poly-electrolyte hydrogels under a variety of external conditions make them ideal adsorbents for removal, adsorption on enrichment of some water soluble agents such as proteins, biomolecules, metallic impurities, dyes, etc. Novel applications of hydrogels in bioseparation or as intelligent artificial systems have been widely presented in the recent literature by Ottonbrite et al. [3]. The hydrogels based on poly-electrolyte structure and synthesized via irradiation of aqueous solutions of acrylamide and *N*-vinyl 2-pyrrolidone with small quantities of maleic or itaconic acids are regarded as systems with potential immobilization, chelating and adsorptive properties for various bioapplications. The capacity of those gels to adsorb bovine serum albumin (BSA) was investigated by using gels with varying compositions of maleic acid [4] and itaconic acid moieties [5]. An increase in the content of diprotic acids has lead to an increase of adsorption of BSA. It has also been determined that by controlling external conditions, the BSA uptake of these hydrogels were enhanced [6].

Recently Şen and Yakar [7] also investigated the delivery of a positively charged antifungal drug terbinafine hydrochloride (TER-HCl) from itaconic acid containing vinyl pyrrolidone hydrogels. TER-HCl is a topically and orally active allylamine antifungal agent which appears to act by preventing fungal ergesterol biosynthesis via specific and selective inhibition of fungal squale oxidase. They investigated the usability of the hydrogels for the controlled release of TER-HCl and the influence of IA content and pH of the medium on the release properties of VP/IA hydrogels. They observed that TER-HCl adsorption capacity of hydrogels can be increased from 6 to 82 mg TER-HCl per gram dry gel with increasing the amount of IA in the gel system. In order to evaluate biocompatibility of acrylamide/maleic acid hydrogels, they were incubated in human serum and their biocompatibility with some biochemical parameters were controlled [8,9]. Recently, biocompatibility of P(VP/IA) hydrogels have been investigated as in vivo and some biochemical parameters of mice serum and histology of their tissues have been examined by Özdemir et al. [10].

Radiation synthesis of P(VP/IA) hydrogels, the effect of external stimuli on the swelling behaviour of these hydrogels and determination of the molecular weight between cross-links were explained in details in our previous studies [11]. In this study, radiation synthesis of VP/IA/EGDMA hydrogels, characterization of their network structure and the effect of EGDMA on the copolymerization of IA with VP have been investigated.

2. Experimental

2.1. Chemicals

The two monomers used in this study, namely *N*-vinyl 2-pyrrolidone (VP) and itaconic acid (IA) were obtained from Aldrich. Cross-linking agent namely ethylene glychol dimethacrylate (EGDMA) was obtained from BDH.

2.2. Preparation of hydrogels

Mixtures of 2 mL VP and 60, 120, 180 and 240 mg IA and 0.25%, 0.50%, 1.0% and 2.5% EGDMA (W_{EGDMA}/W_{VP}) were prepared in 1 mL of distilled water. Monomer solutions thus prepared were placed in PVC straws of 4 mm diameter and irradiated to different doses in air at ambient temperature in Gamma cell 220 type γ irradiator at a fixed dose rate of 0.16 kGy/h.

2.3. Composition of gels

Irradiated mixtures were dried in a vacuum oven at 315 K to constant weight and subjected to Soxhlet extraction by using water as solvent. Uncross-linked polymer and/or residual monomer was removed with this extraction from the gel structure. Extracted gels were dried again in