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Swelling behaviour of crosslinked hydrogels based on (2-hydroxyethyl methacrylate) with a zwitterionic comonomer (1-3-sulfopropyl-2-vinyl-pyridinium-betaine)

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Abstract

Copolymeric hydrogels were prepared by the chemically initiated free radical copolymerization in aqueous solution of mixtures of [1-(3-sulfopropyl)-2-vinyl-pyridinium-betaine] (SPV) and (2-hydroxyethyl methacrylate) (HEMA) in the presence of a crosslinking agent *N*,*N*′-methylene-bis-acrylamide (MBA). The hydrogels were swollen to equilibrium in water and aqueous KSCN at 298 K and their swelling behaviour has been investigated using gravimetric measurements. The effects of the concentration of KSCN and the mole fraction of SPV in the feed (F_s) have been noted and discussed. The main findings are:

(a) In water, the water content (W_1) of copolymeric hydrogels is insensitive to SPV content at $F_s \geqslant 0.45$. In contrast, W_1 decreases sharply with decreasing F_s within the range of $0 < F_s < 0.45$. (b) In aq. KSCN, the degree of total swelling (W) exceeds the value in pure water, the enhancement in swelling being most marked at low values of [KSCN]. The content of water within the hydrogel increases with KSCN concentration in the swelling medium for low values of [KSCN], but thereafter falls with further increase in salt concentration. In contrast, the salt content within the swollen hydrogel displays a continuous increase with increasing [KSCN]. All these results of item (b) are for copolymeric hydrogels within the full range of F_s ($0 < F_s < 1$). (c) at a fixed aq. KSCN concentration, both W and W_1 increase sharply with increasing F_s over the entire range of copolymer composition.

Keywords: Poly [1-(3-sulfopropyl)-2-vinyl-pyridinium-betaine]; Poly(2-hydroxyethyl methacrylate); Zwitterionic hydrogel; Swelling

1. Introduction

Hydrogels are crosslinked, three-dimensional hydrophilic polymer networks, which can swell but do not dissolve in water or aqueous solutions. Hydrogels containing zwitterionic monomer moieties extend the range of properties cf. those having

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neutral, anionic or cationic groups. Polycarbobetaines, recently found [1] to have application as components of thermally reversible gels, contain the COO^- anionic part at the zwitterions. They are less common than polysulfobetaines, which contain groups of the type

$$-\overset{|}{N}^+-R-SO_3^-$$

Zwitterionic polymers, whether in linear or crosslinked forms, display "anti-polyelectrolyte" behaviour. Thus, the presence of salts breaks intra-chain and intra-group association of the poly (sulfobetaines) and gives rise to chain expansion [1–3]. Several groups [2–7] investigated the solution behaviour of some polyzwitterions, and noted the difference from that of polyelectrolytes. Huglin and Rego investigated the influence of a salt on swelling properties of poly [*N*,*N*-dimethyl-*N*-[(methacryloyloxy)-ethyl]-*N*-(3-sulfopropyl) ammonium betaine] (PSPE) [8]. Recently, Zohuriaan-Merhr et al. [9] studied the swelling behaviour of poly [[3-(methacrylamido) propyl] dimethyl (3-sulfopropyl) ammonium hydroxide-co-(2-acrylamido-2-methylpropane sulfonic acid)] hydrogel. Published work discloses the following features of these materials in aqueous systems: (1) They are generally insoluble in water at room temperature and of only moderate swellability when crosslinked [3,8]. (2) Solubility (or swellability) is enhanced by dissolved salts [2–4,8]. (3) For systems exhibiting solubility at room temperature, the viscosity is higher in aq. salt solution than in pure water [2–4]. As an example of applied relevance [10], the major drawback in the use of high molecular weight hydrolysed polyacrylamides in enhanced oil recovery is the drastic decrease of the viscosity of their aq. solutions when increasing the ionic strength, especially in the case of divalent cations.

With regard to [1] the linear polymers of 2-vinylpyridiniumsulphobutyl-betaine and of 1-(3-sulfopropyl)-2-vinyl-pyridinium-betaine (SPV) are rather exceptional in the respect that they are soluble in water at and above 20 °C [3]. In our previous study [11,12], SPV displayed two unusual phenomena, viz. (a) gamma irradiation was unable to induce the polymerization [11]; (b) in aqueous media of high pH, the crosslinked form of PSPV develops a reddish-brown coloration followed by physical disintegration and dissolution; the linear form undergoes a reduction in molecular weight, solution viscosity and T_g [12].

Although the swelling behaviour of PSPV and its copolymeric hydrogels has been studied in our previous papers [11,13,14], so far we have not seen other reports relating to SPV hydrogel. Zwitterionic polymers contain the unique positive and negative charge and this kind of polymer is useful for such applications as polyacrylamide copolymer compounds for enhancing oil recovery [10], as functional monomers used in the preparation of synthetic copolymers [7] and utility in producing recyclable elastomers [15]. In these applications, both swelling behaviour and mechanical properties are essential important parameters, although the former has attracted greater attention over the last two decades, than the latter. The swelling degree of hydrogels depends not only on the nature of polymer and swelling medium, but also on the crosslink density.

Some studies have already been made on solutions and hydrogels of a common synthetic zwitterionic polymer (PSPE) [8] (linear PSPE is insoluble in water) and its copolymers [16], with 2-hydroxyethyl methacrylate (HEMA).

As far as the authors are aware only one corresponding study has been made on the swelling properties of the hydrogels of P (SPV-co-HEMA) by Lee and Chen [17], but these workers only investigated samples in a narrow range of the mole fraction (F_s) of SPV ($0 \leqslant F_s \leqslant 0.12$). The present work focuses on the synthesis of P (SPV-co-HEMA) hydrogels covering the full range of the mole fraction (F_s) of SPV ($0 \leqslant F_s \leqslant 1.0$), and subsequent attention to investigate the swelling behaviour of P (SPV-co-HEMA) hydrogels in water and in aq. salt. HEMA was chosen as comonomer in this work because of: (1) the earlier observation for poly (SPV-co-HEMA) and poly(SPE-co-HEMA) system by Lee and Chen [17] and by Huglin and Rego [16], respectively. (2) The wide studies and the variety and biomedical applications such as drug delivery and contact lenses [16,18–26]. This material was first studied by Wichterle [27] who suggested its use as soft contact lenses. PHEMA hydrogels have been shown to be a class of materials that have great versatility, with a broad range of possible uses in the biomedical area since these materials can be easily prepared in different forms and are sterilizable in boiling water [28]. (3) The moderate Young's modulus E exhibited by PHEMA hydrogels which ranges between 0.5 and 1.2 MN m^{-2} [16,18–26]. (4) The only moderate water uptake due to the presence of the hydrophilic hydroxyl group [16,18–26]