



Physical-chemical behavior of novel copolymers composed of methacrylic acid and 2-acrylamido-2-methylpropane sulfonic acid



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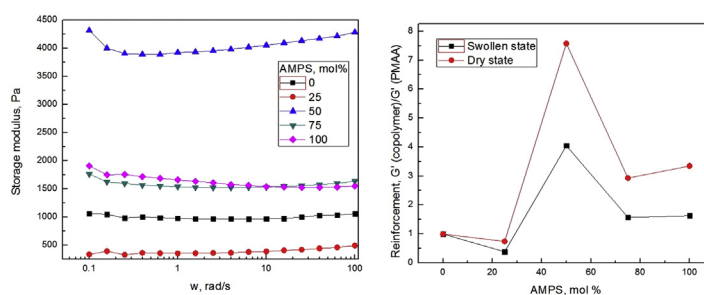
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HIGHLIGHTS

- The synthesis of copolymer hydrogels containing methacrylic acid and AMPS.
- Interactions elucidation by DSC, swelling degree and rheological measurements.
- The T_g values of obtained copolymer hydrogels were around 70 °C.
- The equal amount of monomers contributed to the highest strength of hydrogels.
- An increase in AMPS content in hydrogel led to higher swelling degree.

GRAPHICAL ABSTRACT



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ABSTRACT

This article described the synthesis and characterization of new copolymer hydrogels containing two hydrophilic units—methacrylic acid (MAA) and 2-Acrylamido-2-methylpropane sulfonic acid (AMPS). The resulting hydrogels were characterized by various techniques: FTIR, Elemental analysis, SEM, Dynamic-Molecular simulation, Dynamic-Mechanical analysis and DSC in order to confirm the structure of hydrogels and to predict the best ratio composition with enhanced physical–chemical properties. The swelling behavior in water was studied as a function of ratio of monomers and their concentration in medium. An increase in AMPS content led to expansion of network and increase in swelling degree capacity in water. An increase in AMPS content did not significantly influence the glass transition temperature of copolymers, indicated that the physical properties of initial components were preserved. The equal amount of monomers contributed to the highest strength of hydrogels. Meanwhile, the introduction of AMPS to the system was an effective method for improving the performances of the poly(methacrylic acid)- based hydrogels.

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1. Introduction

In recent years, a wide variety of hydrophilic monomers containing functional groups such as $-\text{COOH}$, $-\text{OH}$, $-\text{CONH}_2$, SO_3H ,

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¹ Dedicated to the memory of Dr Sava Velickovic.

amines or R_4N^+ have been investigated to synthesize hydrogels [1]. These materials have been utilized in numerous industrial fields such as medicine [2–4], pharmacy [5], foods [6,7], agriculture [8], sensors [9,10] and water purification [11,12] because of their high swelling capacity in water, biocompatibility, lack of toxicity and ability to respond to various changes of surrounding media like pH, temperature, electrical and magnetic field, ionic strength etc. One of the important types of synthetic hydrogels are those based on weak acids such as poly(methacrylic acid) (PMAA) due to the ability of the system to change strongly upon variations in the pH and ionic strength of the solution [13]. PMAA hydrogels swell extensively in high pH media (above the pKa value of PMAA), because of the ionization of pendant carboxylic groups and occurrence of intramolecular repulsions at those pHs. However, in pH solution below the pKa value of PMAA, PMAA chains resist expansion before a critical charge density is attained due to a hypercoiled conformation of PMAA in the unionized state [14]. The insufficient mechanical properties and ability to collapse under strong acidic conditions, restricts the wide application of PMAA hydrogels. The introduction of additional groups in the polymer chain may significantly enhance final material properties. Therefore, the disadvantages of PMAA hydrogels may be overcome by copolymerization with hydrophobic or rigid monomers; by formation of an interpenetrating network or by incorporation of inorganic ordered system.

2-Acrylamido-2-methylpropane sulfonic acid (AMPS) has been received attention in recent years due to its hydrolytic stability, nontoxicity and low price. It contains a hydrophilic sulfonic acid (SO_2) functional group and a nonionic amide group in its molecular structure and dissociate completely in the overall pH range. Therefore, the hydrogels based on AMPS exhibit pH independent swelling behavior [15]. AMPS has often been used as additive in synthesis of resins to improve their performances [16]. The characteristic high water absorbing capacity and electrical conductivity of PAMPS hydrogels make these materials ideally suited for medical application such as defibrillator pads, EKG electrodes, and similar medical equipment [17]. PAMPS-containing materials are also well-suited for unique applications such as drug delivery [18–20], wastewater treatments [21–25] and a variety of wound care applications [26–28].

Despite the large number of studies on PMAA or PAMPS hydrogels, there are no previous studies in which both components are involved in the same hydrogel. Combining the methacrylic acid with highly hydrophilic monomer such as AMPS could confer the water absorption of poly(methacrylic acid)-based hydrogels over wide range of pHs. Through controlling the ratio of monomers and their concentration, the new interpenetrating polymeric networks with excellent swelling ability and good mechanical properties, for potential use as multi-target carriers (drugs, metals, dyes) could be obtained. In this article, P(MAA-co-AMPS) copolymer hydrogels have been synthesized by free radical polymerization using potassium persulfate (KPS) as an initiator and N,N'-methylenebisacrylamide (MBA) as a crosslinker in an aqueous solution. The challenges to obtain a material for a specific application might be overcome by investigation of the structure-property relationships of a these two monomers that can allow a targeted design of material with the desired properties. Therefore, the synthesized hydrogels were characterized by FTIR, elemental analysis, SEM, dynamic-mechanical analysis and DSC analysis. The interactions between methacrylic acid and AMPS were elucidated by molecular-dynamic simulation. The effect of reaction conditions such as copolymer composition and copolymer concentration in the medium on swelling behavior in distilled water was investigated.

2. Experimental

2.1. Materials

Methacrylic (99.5%) and 2-acrylamido-2-methylpropane sulfonic acid were supplied from Merck KGaA, Darmstadt Germany. N,N'-methylenebisacrylamide (MBA) (p.a), dimethylethanolamine (DMEA) (p.a) and potassium persulfate (KPS) (p.a) were obtained from Aldrich Chemical Co., Milwaukee, USA. All chemicals were used as received.

2.2. Synthesis

2-acrylamido-2-methylpropane sulfonic acid was added in methacrylic acid solution prepared with given amount of distilled water (Table 1). The crosslinker (MBA) was subsequently added in the amount of 1.0 mol% with respect to monomers. In order to ensure homogeneity of the mixed solution it was stirred for approximately 20 min at room temperature before the initiator (KPS) was added. Stirring was continued in the next 10 min, and immediately after the addition of the activator (DMEA) reaction mixtures were poured into plate molds ($12 \times 12 \times 2$ mm) and placed into the oven at 70 °C, for 5 h to complete the reaction. Derived hydrogel sheets were taken out the molds, sliced to disks (10 mm in diameter, and ca. 2 mm thick) and immersed in distilled water. The water was changed in the next 7 days in order to remove sol fraction of copolymer and unreacted MAA and AMPS. The washed-out hydrogels were dried at room conditions until they reached constant weight and then stored in a desiccator before use.

2.3. Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra were recorded by Bomem MB100 FTIR spectrophotometer in the region between 4000 and 400 cm^{-1} . The samples were prepared in the form of pellets with KBr at room temperature and measured in the transmission mode.

2.4. Elemental analysis

Elemental analysis was used to estimate the chemical composition of all synthesized hydrogels. Elemental analysis was performed by Elemental Analyzer VARIO EL III.

2.5. Scanning electron microscopy (SEM)

In order to visually examine the surface and interior morphology of hydrogels a JEOL JSM-6610LV scanning electron microscope with an acceleration voltage of 20 kV was used. Before SEM observation, equilibrium swollen hydrogels were lyophilized to conserve the structure without pore collapse. Finally, the samples were covered with platinum vapor in LEICA SCD005 nebulizer.

2.6. Molecular-dynamic simulation (MDS)

Interactions between methacrylic acid and AMPS were simulated by using MDS module of Hyperchem 8.0 software (Hypercube Inc., Canada). This model of interaction was energetically optimized using the AMBER force field and imposing the limitation on a gradient of 0.01 Å mol. The obtained configuration was directly performed at a step size 0.001 ps under 300 K. The semi-empiric PM3 calculation method was employed for determination of charges of each atom in the structure. The optimized stable model was illustrated to analyze possible interactions between MAA and AMPS.

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