

The Swelling Behaviors of poly(2-acrylamido-2-methyl-1-propane sulfonic acid co-1-vinyl-2-pyrrolidone) Hydrogels

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In this study, poly(2-acrylamido-2-methyl-1-propane sulfonic acid-co-1-vinyl-2-pyrrolidone), P(AMPS-co-VP), hydrogels were prepared by free radical cross-linking polymerization method in deionized water at 60 °C for 24 hours with different molar percentages of AMPS and VP. In the preparation of hydrogels, ammonium persulphate (APS), N,N'-methylenebisacrylamide (NMBA) and N,N,N',N'-tetramethylethylenediamine (TEMED) were used as initiator, cross-linking agent and accelerator, respectively. NMBA was used in amounts of 5, 6 and 8% with respect to total monomer concentration in the feed. The equilibrium swelling value (ESV) of P(AMPS-co-VP) hydrogels was determined in deionized water and in buffers with different pH values. ESV of P(AMPS-co-VP) hydrogels prepared with 5% NMBA is higher than that of the counterparts with 6 and 8%. Swelling behavior of hydrogels was strongly dependent on AMPS content and ESV decreased with increase in AMPS amount. An evident pH-sensitivity was not observed for the P(AMPS-co-VP) hydrogels. The characterization study was performed using Fourier transform infrared spectroscopy and thermogravimetric analysis.

DOI: [10.12693/APhysPolA.134.129](https://doi.org/10.12693/APhysPolA.134.129)

PACS/topics: Hydrogels, sulfonic acid, 1-vinyl-2-pyrrolidone, swelling

1. Introduction

Hydrogels are environmentally responsive hydrophilic network systems containing various functional groups such as -OH, -NH₂, -CONH-, -CONH₂, -COOH and -SO₃H [1]. Response of the hydrogels depends on the temperature [1, 2], pH [1, 2], ionic strength [1, 3] and electrical field [1, 3] by showing remarkable changes in their swelling behavior.

The response to stimuli of hydrogels is one of the foremost parameters determining their applications in industrial [2], biomedical [1] and environmental [1] fields. Improvements in the synthesis of smart hydrogels substantially depend on the stimuli-responsive behavior [4]. 2-acrylamido-2-methylpropanesulfonic acid (AMPS) based hydrogels show pH independent swelling attitude since ionic monomer AMPS has strongly ionizable sulfonate group and it dissociates wholly in the overall pH range [1, 4]. 1-vinyl-2-pyrrolidone (VP) is a water soluble biocompatible monomer with nonionic nature [5]. However, homopolymer of VP (PVP) exhibits poor mechanical properties and low swelling capacity restricting the application of PVP hydrogels [4].

Studies on the swelling behaviors of hydrogels synthesized from AMPS and VP are limited to analysis of the effect of AMPS on the swelling characteristics and structure of the hydrogels. Thereby, the aim of this study was to prepare copolymer hydrogels based on 2-acrylamido-2-methyl-1-propane sulfonic acid and 1-vinyl-2-pyrrolidone

and to investigate their swelling behavior with respect to the monomer ratio and cross-linker concentration.

2. Experimental

2.1. Materials

AMPS and VP were provided by Merck Schuchardt OHG (Germany) and were used without any purification. Ammonium peroxydisulfate (APS) Merck KGaA Darmstadt (Germany), N,N'-methylenebisacrylamide (NMBA) Merck Schuchardt OHG (Germany) and N,N,N',N'-tetramethylethylenediamine (TEMED) Merck Schuchardt OHG (Germany) were also used as received. Buffer solutions [6] with different pHs and with constant ionic strength ($I = 0.08$ M) were prepared for swelling experiments. Potassium dihydrogen phosphate (Carlo Erba Reagenti), potassium hydrogen phthalate (Merck KGaA, Darmstadt, Germany), sodium hydrogen carbonate (Merck KGaA, Darmstadt, Germany), sodium hydroxide (BDH AnalaR, England), hydrochloric acid solution (Merck KGaA, Darmstadt, Germany), potassium chloride (Lachema, Czech Republic) and sodium chloride (Merck Schuchardt OHG, Germany) were used as received.

2.2. Preparation of P(AMPS-co-VP) hydrogels

In the previous study, P(AMPS-co-VP) hydrogel was prepared to determine its efficiency in the heavy metal removal. The molar ratio of AMPS to VP was 80/20 and the amount NMBA was 5 mol% of the total monomer concentration [7].

In the present study, P(AMPS-co-VP) hydrogels with various monomer feed ratios and different percentages

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of cross-linkers were prepared by free-radical cross-linking polymerization in deionized water at 60 °C for 24 hours using APS initiator, NMBA cross-linking agent and TEMED accelerator. Feed composition of hydrogels is given in Table I. Total initial monomer concentration is 1 mol/L.

TABLE I

Feed contents of the P(AMPS-co-VP) hydrogels

Hydrogel code*	AMPS [mol%]	VP [mol%]	APS [mol%]	NMBA [mol%]
AMPS90/VP10	90	10	1	5, 6, 8
AMPS80/VP20	80	20	1	5**, 6, 8
AMPS70/VP30	70	30	1	5, 6, 8

*Cross-linker content is shown in parenthesis within the paper. **Ref. [7]

2.3. Characterization studies and swelling behavior

Dried hydrogels were characterized by FTIR (Perkin-Elmer Spectrum One FTIR spectrometer) and TGA (Shimadzu, DTG 60). Thermogravimetric analysis was carried out under nitrogen atmosphere (flow rate of 20 mL/min) by heating from 25 to 500 °C at a rate of 20 °C/min. The equilibrium swelling value (ESV) of P(AMPS-co-VP) hydrogels was calculated as $ESV(g_{\text{water}}/g_{\text{gel}}) = (W_s - W_d)/W_d$ where W_d and W_s indicate the weights of the gels in dry and swollen forms (in equilibrium), respectively.

3. Results and discussion

3.1. Swelling of P(AMPS-co-VP) hydrogels

A series of P(AMPS-co-VP) hydrogels was prepared to investigate the effect of cross-linker and monomer concentration on the swelling behavior. The equilibrium swelling values of poly(AMPS-co-VP) hydrogels were determined in deionized water and in buffer solutions with constant ionic strength (pH = 2.8, 5.3, 7.0, 10, and 12.40) at room temperature.

Clara et al. [1] prepared copolymer hydrogels based on 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and methacrylic acid. They reported that high contents of the AMPS provided more transparent hydrogels. Water swollen P(AMPS-co-VP) hydrogels are transparent in appearance (Fig. 1) due to high AMPS content, confirming the previous results.

The equilibrium swelling value of P(AMPS-co-VP) hydrogels was investigated in deionized water as a function of monomer and cross-linker concentration. A lower swelling value was observed in the case of higher cross-linker content (Fig. 2). Swelling capacity of hydrogels decreases with the increase of the cross-linking degree [5] since more cross-linked form of polymeric chains is produced [8]. It was observed that the equilibrium swelling value of P(AMPS-co-VP) hydrogels both in deionized water (Fig. 2)

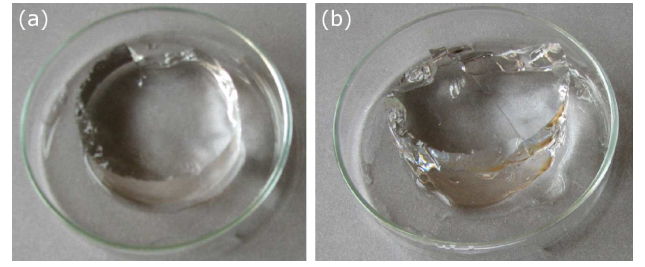


Fig. 1. The appearance of AMPS90/VP10 (5%) (a) and AMPS70/VP30 (5%) (b).

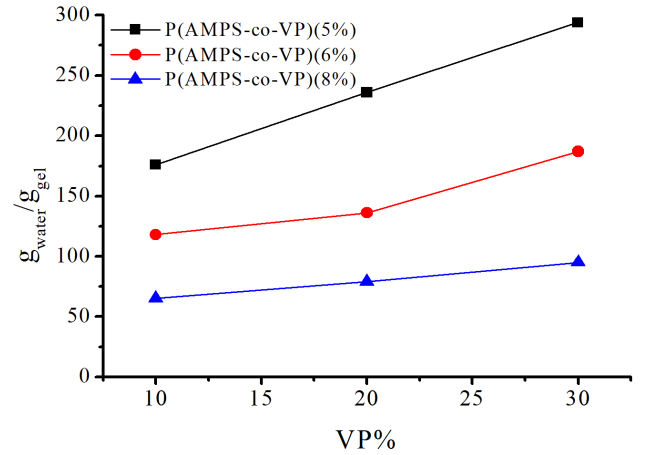


Fig. 2. The ESVs of P(AMPS-co-VP) hydrogels in deionized water at room temperature.

and in buffer solutions with different pHs (Fig. 3) increases while the concentration of AMPS decreases.

The presence/increase of ionic groups in the hydrogel structures results in improvement of swelling capacity [4, 8, 9]. Therefore, it is predicted that the swelling value of hydrogels increases with increase in AMPS content [4].

Unlike the previous studies, the reverse effect of AMPS was seen on the swelling of P(AMPS-co-VP) hydrogels. The swelling experiment results show that AMPS70/VP30 has the highest ESV. ESV of P(AMPS-co-VP) (5%) in deionized water increased from 176 to 294 $g_{\text{water}}/g_{\text{gel}}$ by increasing the VP from 10 to 30% (Fig. 2).

It was reported that high concentration (5–20 wt.%) of cross-linker is required to obtain VP-based hydrogels with good mechanical strength [5]. Since concentration of VP is the lowest in AMPS90/VP10, mechanical property of this hydrogel is better than those of the AMPS80/VP20 and AMPS70/VP30 (see Fig. 1). It can be concluded that cross-linker is more effective for P(AMPS-co-VP) hydrogels with high content of AMPS providing the rigid structure. High swelling value of hydrogels with high content of VP might also be attributed to the amphiphilic structure of VP and increased polymer-water interactions.

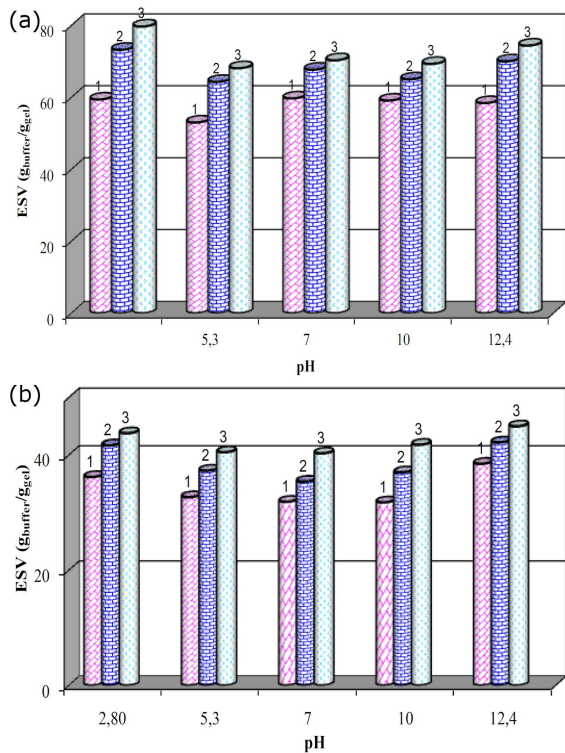


Fig. 3. Effect of pH on the swelling behavior of the P(AMPS-co-VP)(5%) (a) and P(AMPS-co-VP)(8%) (b) hydrogels (1, 2 and 3 denote AMPS90/VP10, AMPS80/VP20, and AMPS70/VP30, respectively).

The variation in pH did not considerably influence the ESVs of the hydrogels. P(AMPS-co-VP) hydrogels did not show an explicit pH-dependent swelling behavior (Fig. 3). ESVs are slightly higher in most acidic (pH = 2.8) and basic medium (pH = 12.40) because of dissociation of NH groups and probably ionization of SO_3H groups [9]. Decreasing effect of AMPS on the swelling value is also evident from Fig. 3.

3.2. FTIR characterization

The FTIR spectra of P(AMPS-co-VP) hydrogels are presented in Fig. 4. The bands at $1657/1656/1658/1662\text{ cm}^{-1}$ are attributed to the $\text{C}=\text{O}$ stretching vibration of the amide group [4, 5, 10, 11]. The bending vibration of the amide group can be seen at $1556/1557/1554/1559\text{ cm}^{-1}$ [4, 5]. Amide III band is present at $1460/1450/1460/1458\text{ cm}^{-1}$ [4]. While the bands at $1039/1038/1039/1040\text{ cm}^{-1}$ are assigned to the symmetric stretching vibrations of the SO_2 group, the bands at $1223/1225/1223/1220\text{ cm}^{-1}$ show asymmetric stretching vibrations of the SO_2 group [11, 12].

3.3. Thermal Behavior

The thermal properties of P(AMPS-co-VP) gels with different cross-linker content were investigated and the corresponding thermograms are presented in Fig. 5. The

change in the cross-linker concentration did not significantly affect the thermal stability. All TGA curves exhibit similar trend. The 2.5% mass loss at 120°C is attributed to loss of water. There is a mass loss of less than 7% at 180°C . Mass losses were approximately 20, 39 and 68% at 250, 300 and 350°C , respectively. It was reported that the degradation because of decomposition of the $-\text{SO}_3\text{H}$ groups can be seen between $250\text{--}300^\circ\text{C}$ [7, 13]. The mass loss from room temperature to 200°C is due to VP content [4].

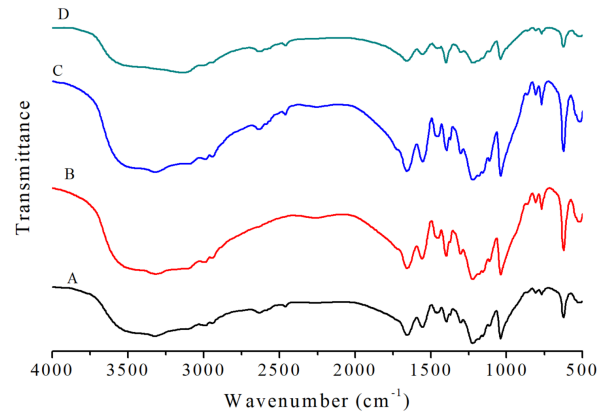


Fig. 4. FTIR spectra of gels (AMPS90/VP10 8% (A), AMPS90/VP10 5% (B), AMPS70/VP30 8% (C) and AMPS70/VP30 5% (D).

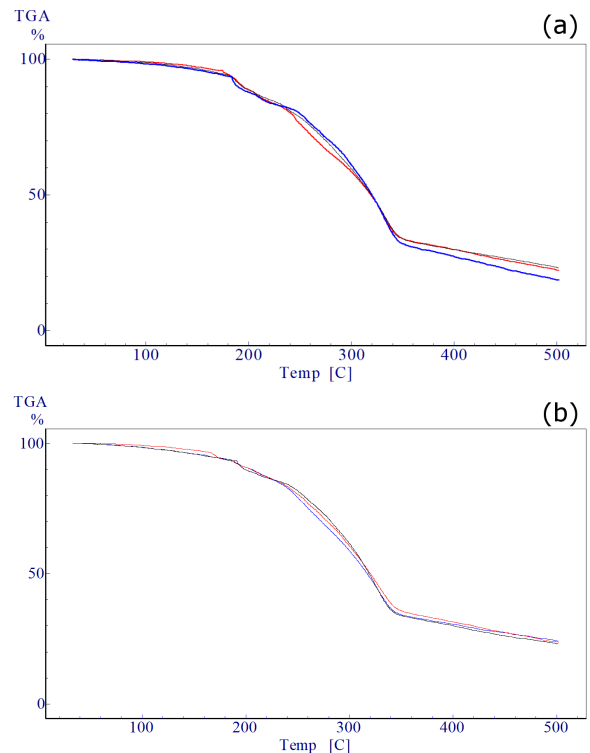


Fig. 5. Thermograms of the some of the P(AMPS-co-VP) hydrogels (AMPS90/VP10 (5, 6, 8%) (a) and AMPS70/VP30 (5, 6, 8%) (b)).

4. Conclusions

The equilibrium swelling value of hydrogel with 70% VP content is higher than those with 80 and 90% VP, which shows that the increase in VP concentration affects positively the ESV of hydrogels based on AMPS and VP. The change in monomer mol ratio and percentages of cross-linker did not evidently affect the pH-sensitive swelling behavior of P(AMPS-co-VP) hydrogels and their thermal stability. The ESV of the hydrogels increases with the decrease in NMBA concentration.

Acknowledgments

This work was supported by Scientific Research Project Coordination Unit of Istanbul University. Project number 2687.

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