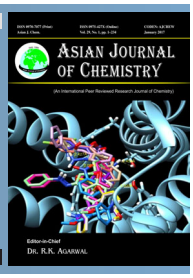
Asian Journal of Chemistry; Vol. 29, No. 3 (2017), 576-580

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20262



Synthesis, Structure and Swelling Properties of Hydrogels Based on Polyacrylic Acid

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Received: 22 August 2016; *Accepted*: 9 November 2016; *Published online*: 30 December 2016; AJC-18203

In polar environment, net shaped polymers with ability of high swelling rate have been synthesized from crosslinking of 5, 10, 15 and 20 % ratio (by weight) of polyacrylic acid having an average molecular weight of 230 kDa with N,N-methylene-*bis*-acrylamide by using ultraviolet ray. The structure of gel has been studied and explained mechanism of the crosslinking process using infrared spectrometer, scanning electron microscopy and X-ray phase analysis methods. The swelling rate of crosslinked polymer, in polar, non-polar, acidic, neutral and alkali environments, as well as in different concentrations of sugar and physiological (0.9 % NaCl) solutions were also studied. It was determined that obtained polymer hydrogel, in the presence of 10 % (by weight) crosslink reagent in pH = 9-10, has maximum 680 % swelling rate within 4-5 days.

Keywords: Polyacrylic acid, Methylen-*bis*-acrylamide, Cross-linking, Hydrogel, Swelling rate.

INTRODUCTION

Hydrogels are popular materials for biological applications since they exhibit properties like that of natural soft tissue and have tunable properties. Biodegradable hydrogels provide an added advantage in that they degrade in an aqueous environment thereby avoiding the need for removal after the useful lifetime. Hydrogels are three dimensional hydrophilic polymer networks that swell, but do not dissolve, when brought into contact with water [1-3]. Hydrogels have been actively studied, particularly those experiencing reversible volume changes in response to external stimulus, such as pH, temperature and ionic concentration. These "smart" hydrogels have found applications in biomedicine and bio-technology [4] including soft contact lenses [5], immobilization of enzymes and proteins [6], antibodies and antigens [7] and matrices for drug delivery systems [8-12]. The ability of these hydrogels to respond to their environment increase drug loading and provide protection from environmental conditions such as those found in the gastrointestinal tract [13]. In this regard, stimuli responsive hydrogels can be useful for the design of site-specific drug delivery devices; for instance, colon-specific drug delivery systems. Another important advantage of these hydrogels is that the active ingredient remains on the organ or tissue for longer times than conventional ones [14-18].

Intelligent hydrogels have also been prepared from interpenetrated polymer networks and it has been found that they combine high swelling capacity with increased mechanical properties [19,20]. Superabsorbent hydrogels of poly(acrylamide-co-acrylic acid) characterized mainly by fast swelling and pH swelling dependence, ionic strength and composition have been prepared by a number of authors [21-23].

Hydrogels due to their unique biocompatibility, flexible methods of synthesis, range of constituents and desirable physical characteristics are widely used in different biomedical fields. They can serve as scaffolds, which provide structural integrity to tissue constructs, control drug and protein delivery to tissues and serve as adhesives or barriers between tissue and material surfaces [24-27]. Among these properties one must evaluate the swelling, mechanical and biocompatible properties before the hydrogel biomaterials are applied.

EXPERIMENTAL

Polyacrylic acid purity 90 %, with M_w = 230 kDa was purchased from Fluca and used without further purification. Methylene-*bis*-acrylamide was supplied by Sigma Aldrich (St. Louis, MO, USA) and also used without further purification. Glucose (Glc) $C_6H_{12}O_6$ and sodium chloride was purchased from Primex (Iceland). All other reagents (NH_4OH, CH_3COONH_4, HCl, KOH, C_2H_5OH) were of analytical grade and used as received. Double distilled water was used through this work.

Preparation of hydrogels: 100 mg polyacrylic acid is fully solved in 50 mL deionized water or ethanol. Crosslink reagent-methylene-*bis*-acrylamide is added as 5, 10, 15, 20 %

quantity of polymer mass to the solution and mixing is continued until complete solution. The solution is poured into petri dish after forming a homogeneous system. After releasing the solution from the solvent at normal atmospheric pressure, thin film is continuously influenced with UV radiation within 6 h. The distance between the lamp and the sample is to be 30 cm and distance is regulated by controlling temperature (303 K) using thermometer. After irradiation, by washing two-three times first with deionized water, then 0,01N HCl and ethanol, samples are cleaned off from parts which don't participate in cross-linking process of polymer and crosslink reagent. In normal atmospheric pressure at 313-323 K samples are dried and set to a constant weight [28,29].

Structural analysis: Functional group confirmations were assessed by SHIMADZU IR-affinity Fourier transform infrared (FTIR) spectrometer. FTIR spectra were obtained with KBr discs and recorded in the spectral range from 4000 to 400 cm^{-1}. A film of the nanofluid was dried on the glass plate for X-ray diffraction analysis. The decomposition of cross-linking polyacrylic acid was studied with scanning electron microscopy (SEM) and the crystallization process was studied with X-ray phase analysis methods (XRD). XRD measurement was done by Advance A-8 (with Cu K_α radiation $\lambda = 1.5406$ Å) operating at room temperature.

Determination of Swelling: The discs were cut into fragments of about 30 mg and weighed accurately. These fragments were placed into flasks with 10 mL solution of a given pH and kept in a thermostated bath at 310 K. Solutions with pH 1 and 2 prepared with different concentrations of HCl, pH = 3-10 ammonium acetate buffered saline and pH 11 and 12 were prepared with different concentrations of KOH by double distilled water. The water uptake (W), was calculated by measuring the weight gain of the sample at different times after carefully wiping the surface with a filter paper. The dried hydrogels, which were punched into discs, were weighed and allowed to swell in distilled water. The rate of swelling (W) at equilibrium swelling was calculated as follows [30]:

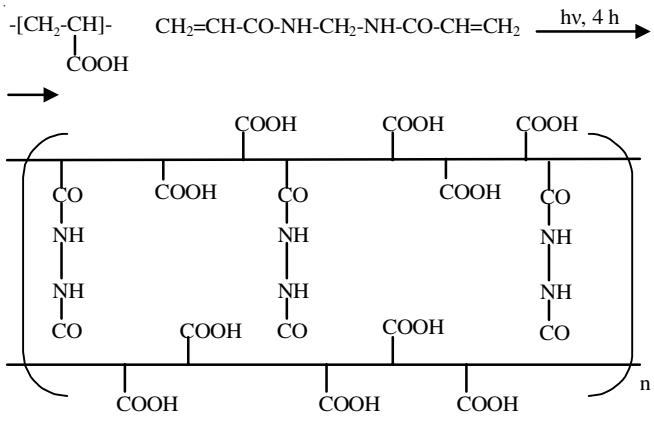
$$W = \frac{W_w - W_d}{W_d} \times 100\ \%$$

where W_d and W_s represent the weight of dry and wet hydrogel, respectively.

RESULTS AND DISCUSSION

Initial substances and crosslinked polymers were investigated with FTIR-spectroscopy method to determine the mechanism of crosslinking process of polyacrylic acid with methylene-*bis*-acrylamide. Supposed mechanism of crosslinking process is determined according to the changes in the value of the absorption strips of functional groups in polyacrylic acid macromolecule. And so absorption bonds with frequency 3345, 1638, 1430 and 1230 cm^{-1}, corresponding $>CH_2$, CH, >C=O, –OH functional groups in the FTIR spectra of polyacrylic acid are observed in accordance (Fig. 1).

There are 1650, 1645, 1445 cm^{-1} absorption strips characteristic of CH_2=CH–, $>CH_2$, >C=O and –NH groups, respectively in the crosslink reagent. Decreasing intensity of the absorption band of the $>CH_2$ groups in spectrum of crosslinked polymer and observation intensity characteristic of $–CH_3$ groups, in spectrum show the crosslinking process of the homopolymer on given below mechanism:



It was determined from analyzing of absorption bands belonging to functional groups in polyacrylic acid, methylene-*bis*-acrylamide and hydrogels with IR- and UV-spectroscopic methods that the crosslinking of polymer occurs as a result of nearing double carbon in main chain of polymer with triple carbon in the methylene-*bis*-acrylamide and recombination of radicals got during the process [31].

When hydrogels are used as a carrier, one of the main factors is pH causing hydrogels structure, ionization rate and in which environment immobilized biologically active substance affects. In this regard, dependence of swelling rate (SR) of polyacrylic acid based gels from environment pH was investigated (Fig. 2). It was determined that maximum swelling rate of gels, which obtained by crosslinking polyacrylic acid with 5-10 % methylene-*bis*-acrylamide, is at pH = 10 and make ~ 600-700 %. It is shown that, in the alkaline environment (pH = 10), gels obtained from crosslinking polyacrylic acid of quantity 5, 10, 15 and 20 % (by weight) naturally having acid-base properties with methylene-*bis*-acrylamide, perform maximal swelling rate.

As it is shown from Fig. 2, diffusion of water molecules inside is getting complicated accordingly to increasing of cross-link reagent's quantity and decreasing of nets' area in formed hydrogels. It is determined that at the low pH, protonization of functional group forms hydrogel collapse as it prevents forming hydrogen bonds between water molecules and >C=O group [32]. Moving to alkaline environment occurring deprotonization causes gradual increasing of hydrogel swelling rate.

Beside investigation of hydrogels swelling rate, investigation of process in water and physiological solutions (NaCl 0.9 % solution) depending on time are also important issues. For this purpose, dependence on time of hydrogels obtained from cross-linking polyacrylic acid with 10 % methylene-*bis*-acrylamide and dependence on time of swelling rates in physiological solutions were investigated (Table-1).

It was determined that swelling rate of gel changes when ion power of environment changes. In comparison with free water molecules, low rate (t = 24 h, %) of gel swelling rate in physiological solutions is related with penetration of Na^+ and Cl^- hydrates formed as a result of dissociation of salt in water.

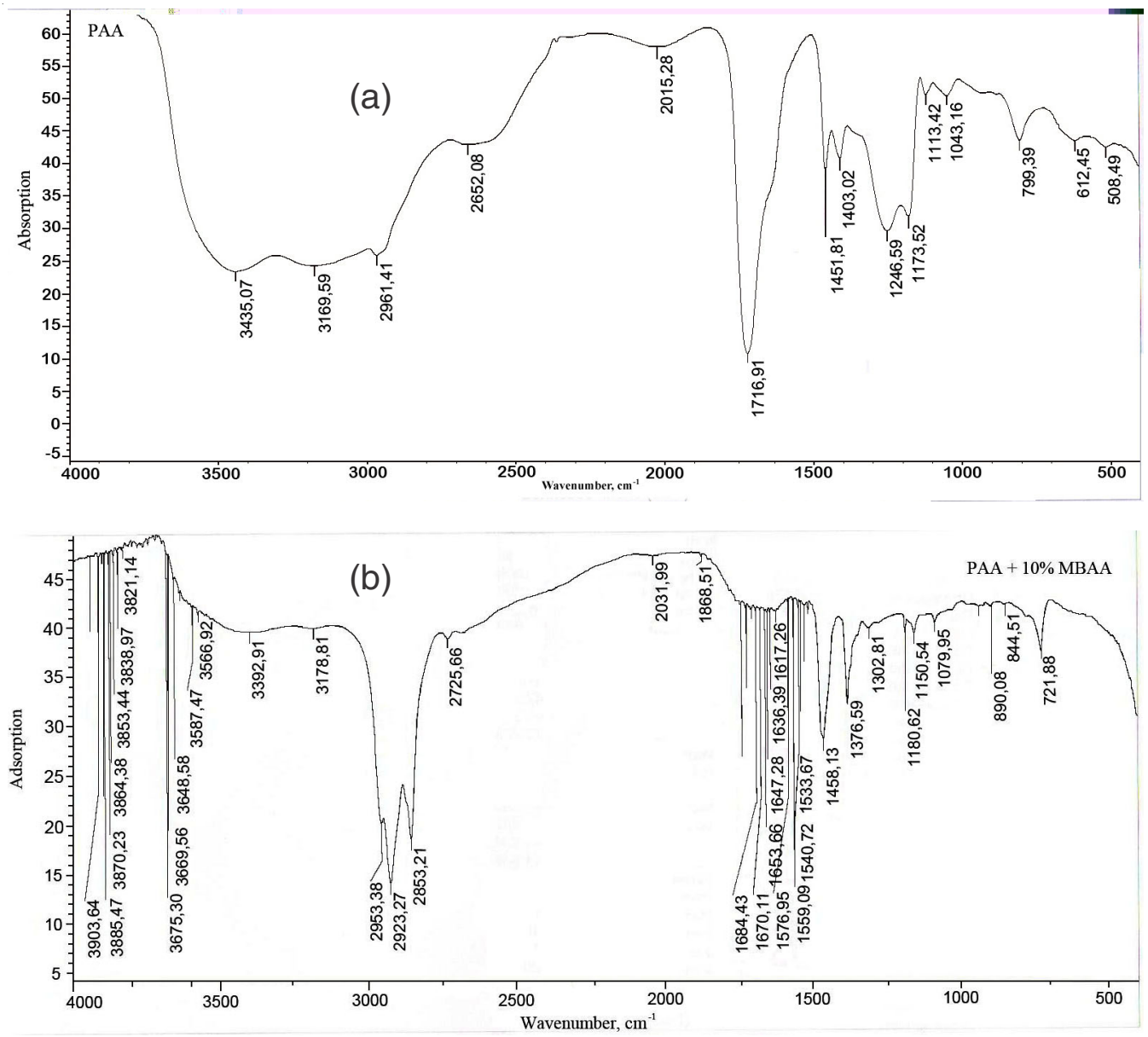


Fig. 1. IR spectrums of polyacrylic acid (a) and hydrogel based on poly-acrylic acid crosslinked with 10 % methylene-*bis*-acrylamide (b)

TABLE-1
DEPENDENCE OF CROSSLINK REAGENT PERCENTAGE QUANTITY WITH SWELLING RATE OF POLYACRYLIC ACID BASED GEL IN PHYSIOLOGICAL AND GLUCOSE SOLUTIONS WITH DIFFERENT CONCENTRATION

Crosslink agent, mass %	Swelling degree			
	0.9 % NaCl	0.1 % $C_6H_{12}O_6$	1 % $C_6H_{12}O_6$	10 % $C_6H_{12}O_6$
5 % Methylene-*bis*-acrylamide	128	145	234	208
10 % Methylene-*bis*-acrylamide	172	199	267	212
15 % Methylene-*bis*-acrylamide	185	298	364	314
20 % Methylene-*bis*-acrylamide	219	238	294	275

As it seems in Table-1, when quantity of reagent increases from 5 to 20 %, hydrogel swelling rate increases from 128 to 219 % in 0.9 % NaCl solution. It is known that as a result of dissociation of NaCl in water, Na^+ and Cl^- ions surrounded by water dipoles create hydrates. From this point of view when quantity of methylene-*bis*-acrylamide increases, appearance of 80-90 % difference in swelling rate and increasing of functional groups quantity like >C=O and –NH– belonging to crosslink reagent in hydrogel occurs and eventually mutual attraction between functional groups and hydrated Na^+ and Cl^- ions increases. This is related to the nature of functional groups in polymer matrix [33].

Beside this, comparing swelling rates in glucose solutions with different percentage concentration, it is determined that the same mass quantities of hydrogels, which formed from increasing quantity of crosslink reagent in crosslinking poly-acrylic acid with methylene-*bis*-acrylamide, have high swelling rate in 1 % of $C_6H_{12}O_6$ solution. But, this rate is 2-3 times

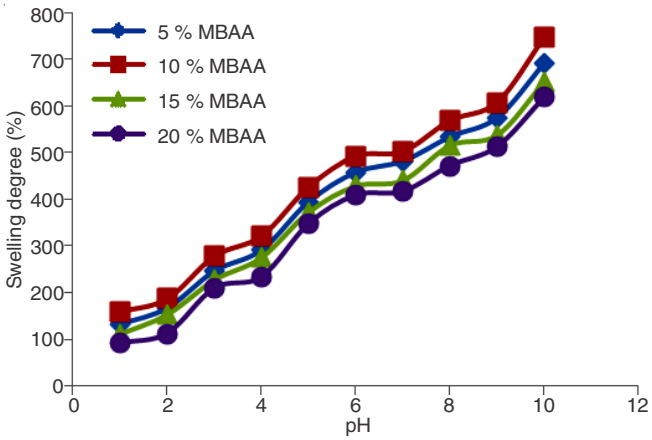


Fig. 2. Dependence curves with swelling rate of crosslinked polyacrylic acid in different ratio pH of environment

less than rate of swelling rates in water and pH buffers. The reason, why swelling rate of glucose with high concentration is low, is non-electrolyte of it. Because, electrostatic interaction between environment and functional groups of polyelectrolyte hydrogel does not occur in this case. Also, because the sizes of crystal hydrates formed in water in molecular shape by glucose are much more than sizes of hydrogel pores, diffusion process is complicated. Increasing the swelling rate accordingly to increasing of quantity of methylene-*bis*-acrylamide is related to increasing the quantity of functional groups which is able to create absorption in gel.

In addition to this, comparing swelling rates in physiological and glucose solutions, high swelling rate is shown in presence of organic substance. It can be related with nature and structure of those substances. High swelling rate can be explained by emergence of more hydrogen bonds with >C=O, –NH–, –COOH groups in hydrogel, considering glucose consisting of five –OH (hydroxyl) and one –CHO (aldehyde) functional groups [34,35].

It has been investigated with X-ray phase method that gives slight change in structure after crosslinking amorphous structured polyacrylic acid with methylene-*bis*-acrylamide (Fig. 3).

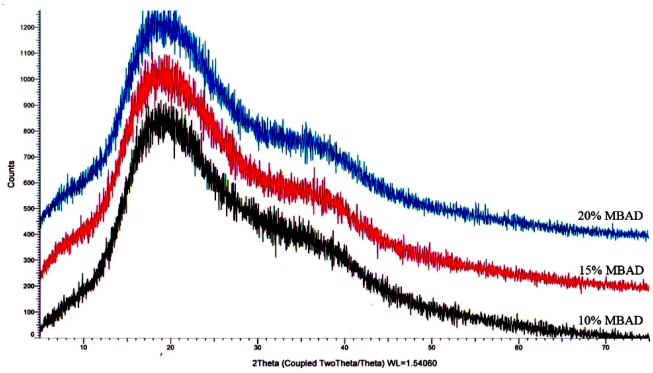


Fig. 3. X-ray phase spectrums of polyacrylic acid crosslinked with methylene-*bis*-acrylamide in different % ratios

Thus, crystallization rate of formed hydrogels increases to 8-12 % accordingly to increasing of methylene-*bis*-acrylamide quantity. It can be explained by formation of polymer net and more systematic structural crosslinked polymer.

The structure of the polyacrylic acid, polyacrylic acid crosslinked with methylene-*bis*-acrylamide at 10 % ratio have been studied by SEM (Figs. 4 and 5).

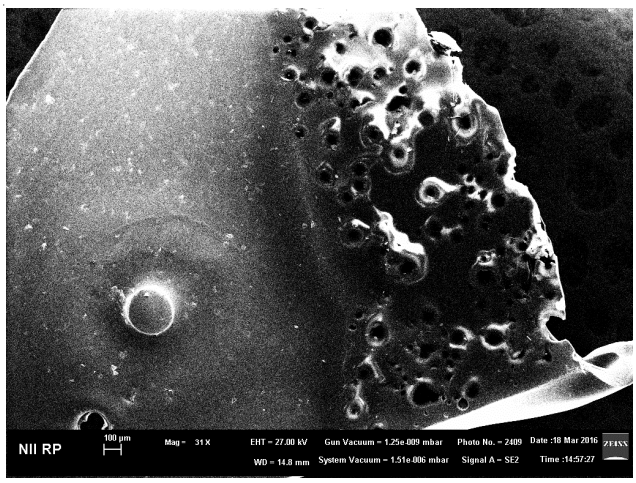


Fig. 4. Scanning electron microscopy of uncrosslinked polyacrylic acid

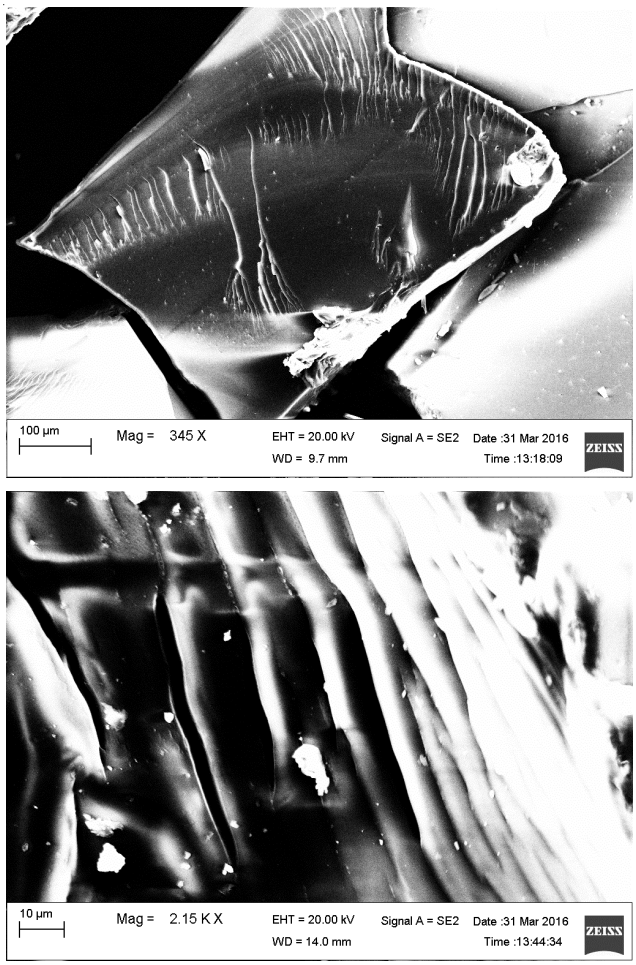


Fig. 5. Scanning electron microscopy of polyacrylic acid crosslinked with methylene-*bis*-acrylamide

It have been determined that there are white spots with various non-homogeneous phase and pores in the structure of uncrosslinked polyacrylic acid.

These porosities disappeared after crosslinking of polymer and smoothing is observed in polymer. Grained structure is

formed in crosslinked polyacrylic acid and thus as if polymer is separated into parts and non-homogeneous surface is observed in crosslinked polymer.

There are a number of layers, layer-shaped lines in the cross-linked polymer and it shows the generation of cross-linking (Fig. 5).

Conclusion

Hydrogels, which are swellable in water, physiological and glucose solutions with different concentrations, have been synthesized from crosslinking of 5:20 ratio (by weight) of poly-acrylic acid, having an average molecular weight of 230 kDa, with methylene-*bis*-acrylamide in ultraviolet ray presence. Structures of formed hydrogels have been investigated with physical investigation methods and it was indicated that poly-acrylic acid based hydrogels can be used in immobilization of biological active compounds and complex compounds having long lasting effect.

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