



SYNTHESIS AND SWELLING BEHAVIOR OF POLY (NCA-co-AM/AMPS Na) HYDROGELS

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ABSTRACT

Poly(N-cyclohexylacrylamide -co -acrylamide / AMPS Na) Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N,N'-methylenebisacrylamide (MBA) as a crosslinker at 60°C. The amount of N-cyclohexylacrylamide (NCA) and Acrylamide (AM) monomers was fixed and the amount of AMPS Na was varied. The Hydrogels were characterized by IR spectroscopy. The swelling behavior of Hydrogels studied by Gravimetric method and the degree of swelling was increased when increasing the amount of AMPS Na. The surface morphology was studied by SEM analysis.

Keywords: N-cyclohexylacrylamide ; AMPS Na ; Hydrogels; Swelling behavior.

INTRODUCTION

Hydrogels are three-dimensional crosslinked hydrophilic polymer networks, which swell without dissolving when brought into water or biological fluids¹. These crosslinked polymers have been used widely in various types of applications such as controlled drug delivery, immobilization of enzymes, dewatering of protein solution, solute separation, baby diapers, soil for agriculture and horticulture, water-blocking tape, absorbent pads, and others²⁻⁸. The N-substituted acrylamides are used to prepare thermo sensitive polymers like poly(N-isopropylacrylamide) and copolymers of N-alkyl acrylamide and styrene⁹. Thermosensitive polymers have great potential in applications as drug delivery system¹⁰ human gene vector¹¹ and biocatalysts¹². Vildan Ozturk, and Oguz Okay reported that a series of temperature sensitive hydrogels was prepared by free-radical crosslinking copolymerization of N-t-butylacrylamide (TBA) and acrylamide in methanol. N,N'-methylenebis(acrylamide) was used as the crosslinker. It was shown that the swelling behavior of the hydrogels can be controlled by changing the amount of TBA units in the network chains¹³. The crosslinked copolymers and terpolymers of N-isopropyl acrylamide (NIPAm) with sodium-2-acrylamido-2-methyl propane sulfonate (NaAMPS) and glycidyl methacrylate (GMA) were prepared by E.Serkan et al. The results indicated that the higher the NaAMPS content in NIPAm/NaAMPS copolymer, the higher water uptake rate, but less the water release rate¹⁴. These observations inspired us to synthesize the hydrogels based on N-cyclohexylacrylamide (NCA). The aim of this work was to prepare a series of poly(N-cyclohexylacrylamide -co -acrylamide / AMPS Na) Hydrogels, based on NCA, acrylamide and AMPS Na. Synthesis and swelling behavior of such copolymer gels have not been reported before. Hydrogels were prepared by free-radical crosslinking copolymerization of NCA, AM and AMPS Na in the presence of N,N'-methylenebis(acrylamide) (MBA) as the crosslinker. By preliminary experiments, methanol/water was found to be the most suitable solvent for the copolymerization.

EXPERIMENTAL

Materials

Acrylamide (AM, Merck) was crystallized from acetone/ethanol mixture. Ammonium persulfate (APS) and 2-acrylamido-2-methyl-1-propanesulphonate acid (AMPS) and Sodium hydroxide were supplied from Aldrich. The crosslinker N,N'-methylenebisacrylamide (MBA) was used as received.

Preparation of N-cyclohexylacrylamide (NCA)

The monomer N-cyclohexylacrylamide was prepared by the reaction of Cyclohexanol with acrylonitrile¹⁵. N-cyclohexylacrylamide was recrystallized in warm dry benzene. The white crystals have a m.p. 115 °C and the yield was 87%.

Preparation of Hydrogels

Free-radical crosslinking copolymerization was carried out in methanol water mixture as the polymerization solvent, at 60 °C in the presence of APS as initiator and MBA as crosslinker. Aqueous solution containing NCA (0.7g), AM (0.3g), 0.045g MBA, 0.05 g APS, AMPS Na (0.10, 0.20, 0.30, 0.4, and 0.5g) were prepared in methanol water mixture. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 60 °C and the polymerization was conducted for 1 day. After the reaction, the hydrogels were cut into pieces 3-4 mm long. The extracted hydrogels were dried in vacuum oven at 50 °C to constant weight for further use.

Swelling characteristics

The swelling characteristics were measured by immersing weighed samples of dry hydrogels in double distilled water. The excess surface water in the swollen gel was removed by blotting and then the swollen gel was weighed. The swollen gel was blotted several times till three consecutive weights are same within limits of experimental error of 1 percent. All measurements were performed thrice and the reported values are average of at least three individual measurements. The degree of swelling (Ds) most commonly described as swelling ratio is expressed as increase in weight per gram of dried hydrogel (W_d) after keeping in contact with water for selected period of time.

$$\text{Degree of swelling (Ds)} = (W_s - W_d / W_d) \quad (1)$$

SEM Analysis

The Micro structure of Hydrogels were studied by Scanning electron Microscopy hydrogels were performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification.

RESULTS AND DISCUSSION

Hydrogels were prepared by Free-radical crosslinking copolymerization (Scheme-1). The contents of NCA and AM monomer was fixed and the AMPS Na monomer feed was varied from 0.10, 0.20, 0.30, 0.4 to 0.50g. The IR spectral analysis of the hydrogels showed that the presence of peaks corresponding to the functional groups of monomeric units present in the copolymeric hydrogel chain. A broad peak corresponding to NH of AMPS Na as well as NH stretching of acrylamide was observed around 3432 cm^{-1} . In addition to this, the peaks were also observed at 1634 cm^{-1} corresponding to C=O of NCA unit and 1535 cm^{-1} corresponding to C=O(NH₂) AM unit. The peak observed at 1449 cm^{-1} corresponding to S=O (Sym).

Dynamic swelling of some selected samples at different absorbing time in water was measured as shown in Fig. 1. The swelling rate is slow during the first two minutes; it indicates that the initial swelling is due primarily to the water penetrating into the polymeric gel through capillary and diffusion. Then the penetrated water is absorbed by hydrophilic groups such as AMPS Na and AM through formation of hydrogen bonds. The swelling is driven by repulsion of hydrophilic groups inside the network and osmotic pressure difference between the gels and the external solution. The swelling rate is fast during the first 210 minutes and gradually increases until the equilibrium swelling is reached. The swelling rate observed for AMPS Na 0.1 g to 0.50 g. As the content of AMPS Na is increases the swelling rate is increases rapidly. The incorporation of hydrophilic groups AMPS Na in the hydrogel favored for penetration of water in the polymer matrix¹⁶.

Morphological studies

Scanning electron Microscopy of hydrogels was performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. In Poly (NCA-co- AM/ AMPS Na) Hydrogel(Fig.2) micrographs have the morphology layered structure and it conforms the presence of AMPS Na in the whole gel surface¹⁷. The wet SEM picture shows the absorption of water on the surface of the Hydrogels.

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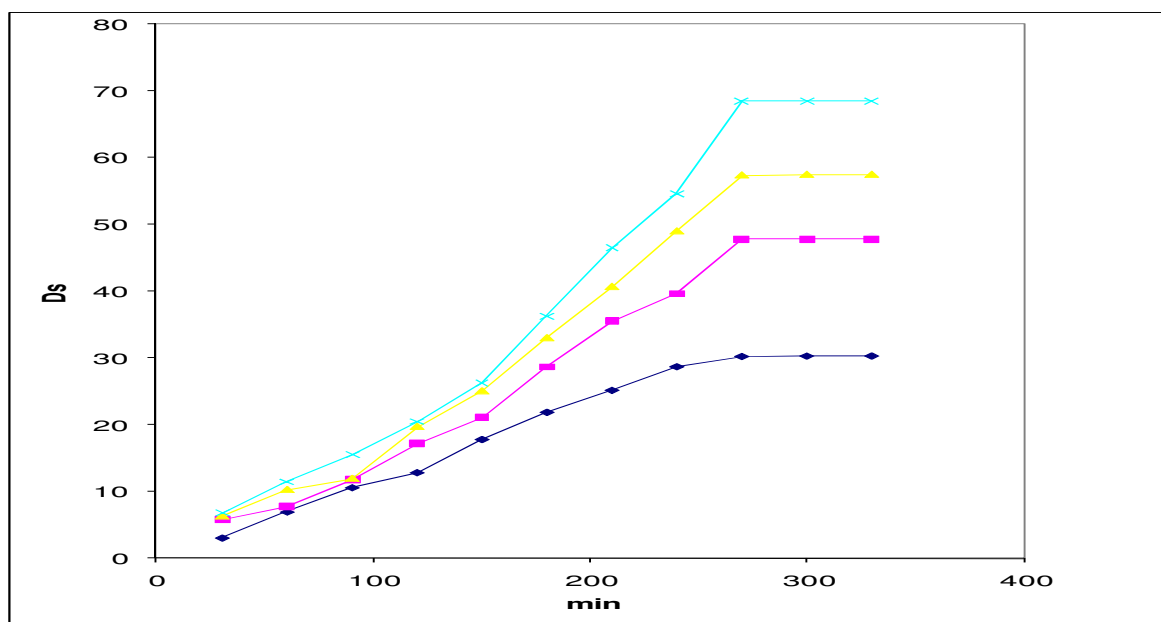
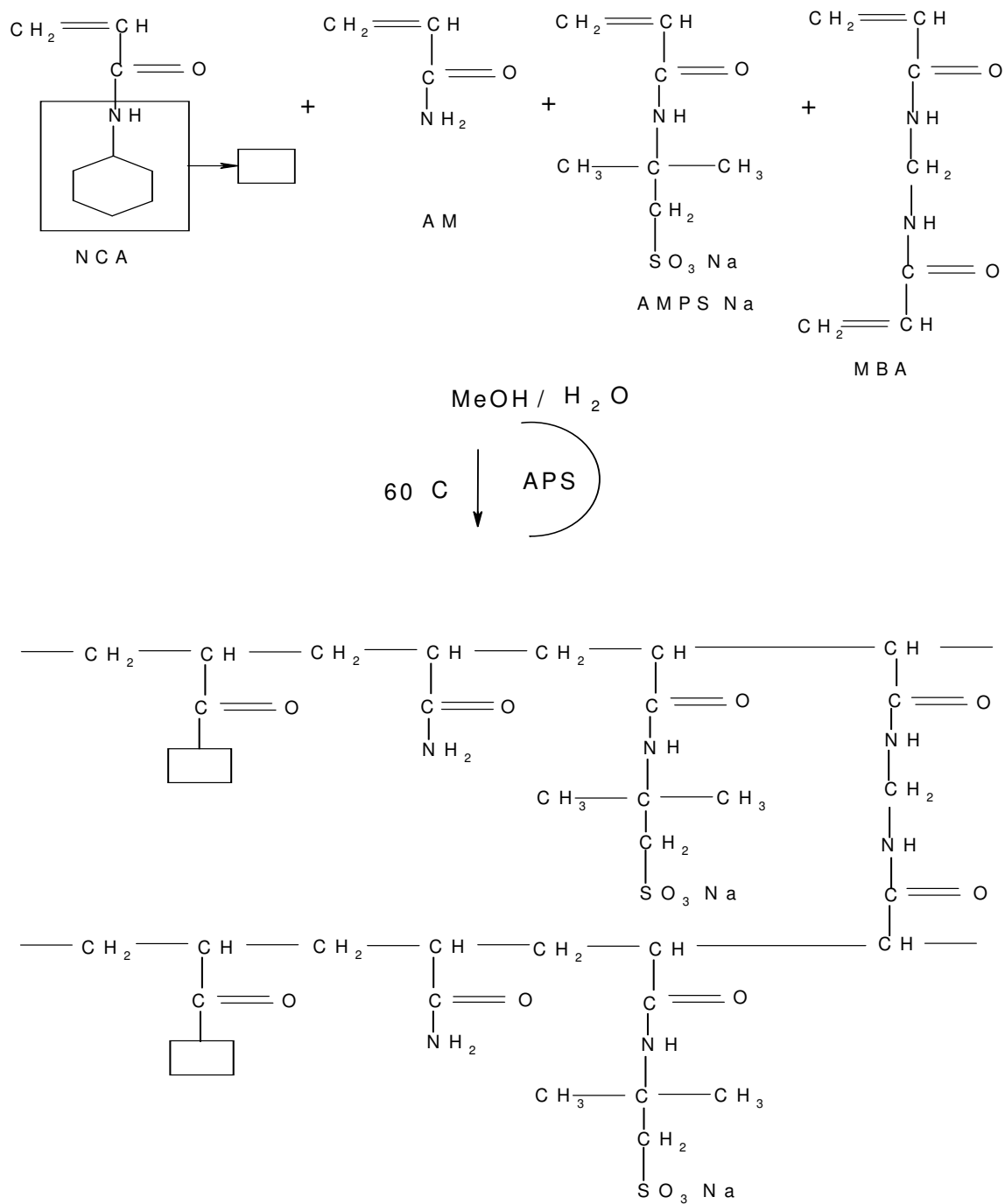


Fig.-1: Swelling behavior of Poly(NCA-co-AM/AMPS Na) Hydrogels
AMPS Na: 0.1 g(♦) ; 0.20 g(■) ; 0.30 g(▲) ; 0.40 g(x).



Scheme-1: Poly (NCA-co- AM/ AMPS Na) Hydrogel

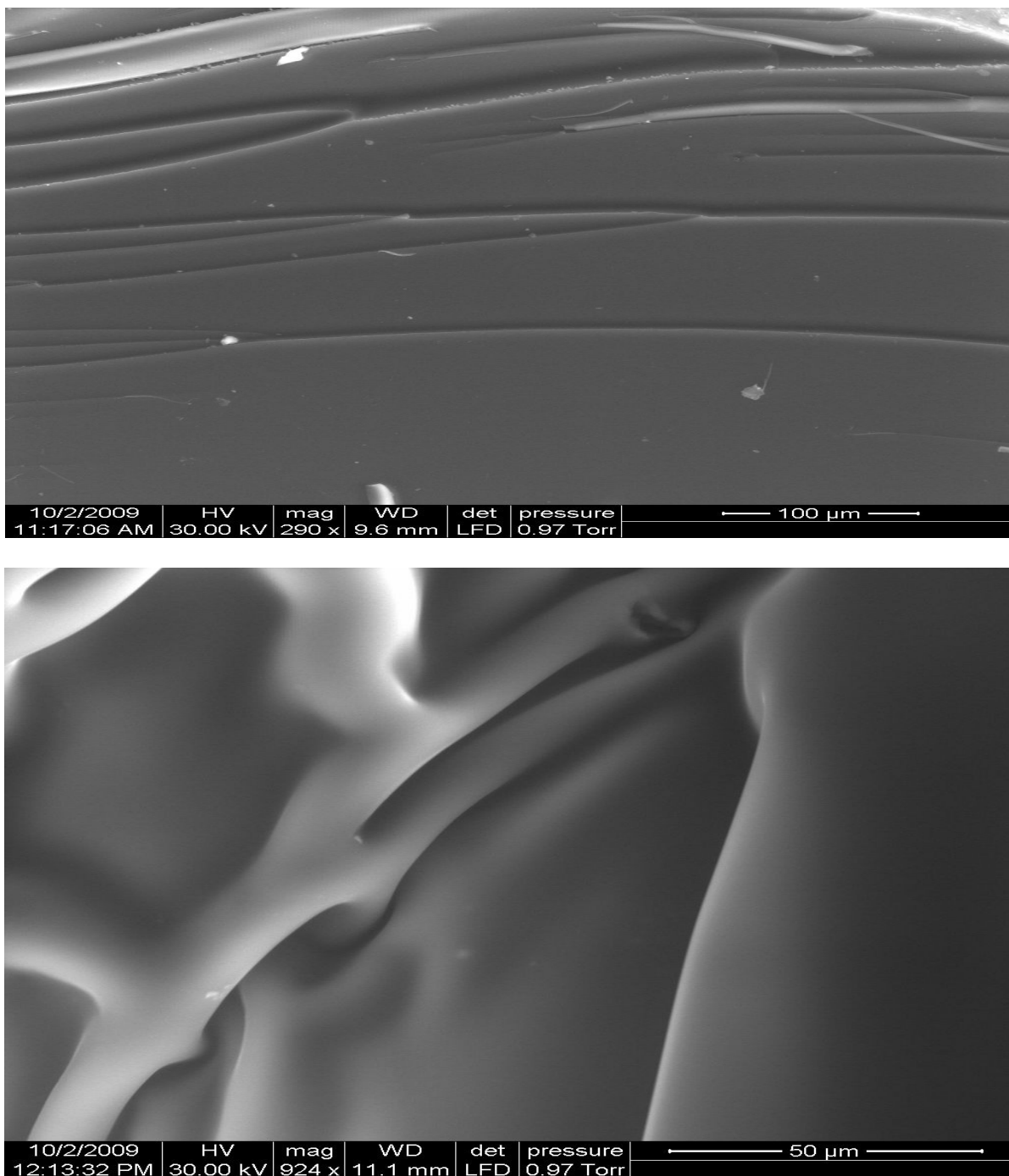


Fig. -2: SEM image of Poly(NCA-co- AM/AMPS Na) Hydrogel
Dry gel (above); Wet gel (below)

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