Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(7):302-306

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

N-cyclohexylacrylamide based hydrogels-II: Synthesis and characterization of poly(*N*-cyclohexylacrylamide-*co*-acrylamide/sodium acrylate) hydrogels

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ABSTRACT

In the present study ,a series of Poly(N-cyclohexylacrylamide -co –acrylamide / Sodium acrylate) 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^{0}C. The amount of N-cyclohexylacrylamide (NCA) and Acrylamide (AM) monomers was fixed and the amount of sodium acrylate(AcNa) was varied. The Hydrogels were characterized by IR spectroscopy. The swelling behavior of Hydrogels showed that the degree of swelling was increased with increasing the amount of Ac Na. The surface morphology indicated porous and well type structure.

Keywords: N-cyclohexylacrylamide, Hydrogels, Swelling behavior.

INTRODUCTION

Hydrogels are three-dimensional crosslinked hydrophilic polymer networks, which swell without dissolving when brought into water or biological fluids [1].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 others [2-4]. Hydrogels can swell to profitable rates when placed into an appropriate environment, which means a specific pH, temperature, electric field, light, pressure or specific molecule [5–11]. Several researchers have studied the swelling of pH-sensitive hydrogels and the influence of this parameter in chemical, biological and physiological systems [12]. Hydrogels exhibiting pH-sensitive swelling behavior have been usually swollen from ionic networks that can contain acidic or basic pendant groups. When these groups are ionized, a swelling osmotic pressure inside the material is built up, and fixed charges are trapped in the gel. As a result of the electrostatic repulsion, the uptake of solvent in the network is increased [13, 14]. In the previous paper [15], we reported the synthesis and swelling behavior of 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^{0}C. In this paper, we report the synthesis and characterization of poly(N-cyclohexylacrylamide -*co* –acrylamide / Sodium acrylate) Hydrogels .

EXPERIMENTAL SECTION

Materials

Acryiamide (AM, Merck) was crystallized from acetone/ethanol mixture .Ammonium persulphate (APS), Acrylic acid and Sodium hydroxide were supplied from Aldrich. The crosslinker N,N'-methylene-bis-acrylamide (MBA) was used as received.

Acrylonitrile

Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Orthophosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over andhydrous $CaCl_2$. The acrylonitrile was then distilled in an atmosphere of Nitrogen and reduced pressure. It was then collected in a clean dry amber colored bottle and kept in the refrigerator at 5° C.

Preparation of N-cyclohexylacrylamide (NCA)

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

^{1}H-NMR spectroscopy

The ^{1}H-NMR spectra of copolymers were recorded on the EM-390 NMR Spectrometer operating 90 MHz with $CDCl_3$ as solvent. The following peaks appear in NCHA spectrum; at 1.2-2.02 ppm for cyclohexyl CH_2 , at 3.72 ppm for cyclohexyl methane , at 5.38-6.28 ppm for vinyl protons and at 7.3 ppm for N-H proton.

Preparation of Hydrogels

Free-radical crosslinking copolymerization was carried out in methanol /water mixture as the polymerization solvent, at 60 ^{0}C in the presence of APS as initiator and MBA as crosslinker. Aqueous solution containing NCA (0.7g), AM (0.3g) , 0.045g MBA 0.005 g APS , Ac Na (,0.10, ,0.20 and 0.3) were prepared in methanol water mixture . After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 60 ^{0}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 ^{0}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 degree of swelling (Ds%) most commonly described as swelling ratio is expressed as increase in weight / gm of dried hydrogel after keeping in contact with water for selected period of time.

$$\text{Degree of swelling (Ds \%)} = [(W_s - W_d/W_d)\ ] \text{ X } 100 \quad \text{---------- (1)}$$

Where, W_s is the weight of the swollen gel at a given time and W_d is the weight of the dry gel. The equilibrium water content (EWC) is expressed in % on the weight of swollen gel at equilibrium, using the Eqn.2. Where, W_e is the weight of the swollen gel at equilibrium and W_d is the weight of the dry gel.

$$\text{EWC} = [(W_e - W_d/W_e)\ ] \text{ X } 100 \quad \text{---------- (2)}$$

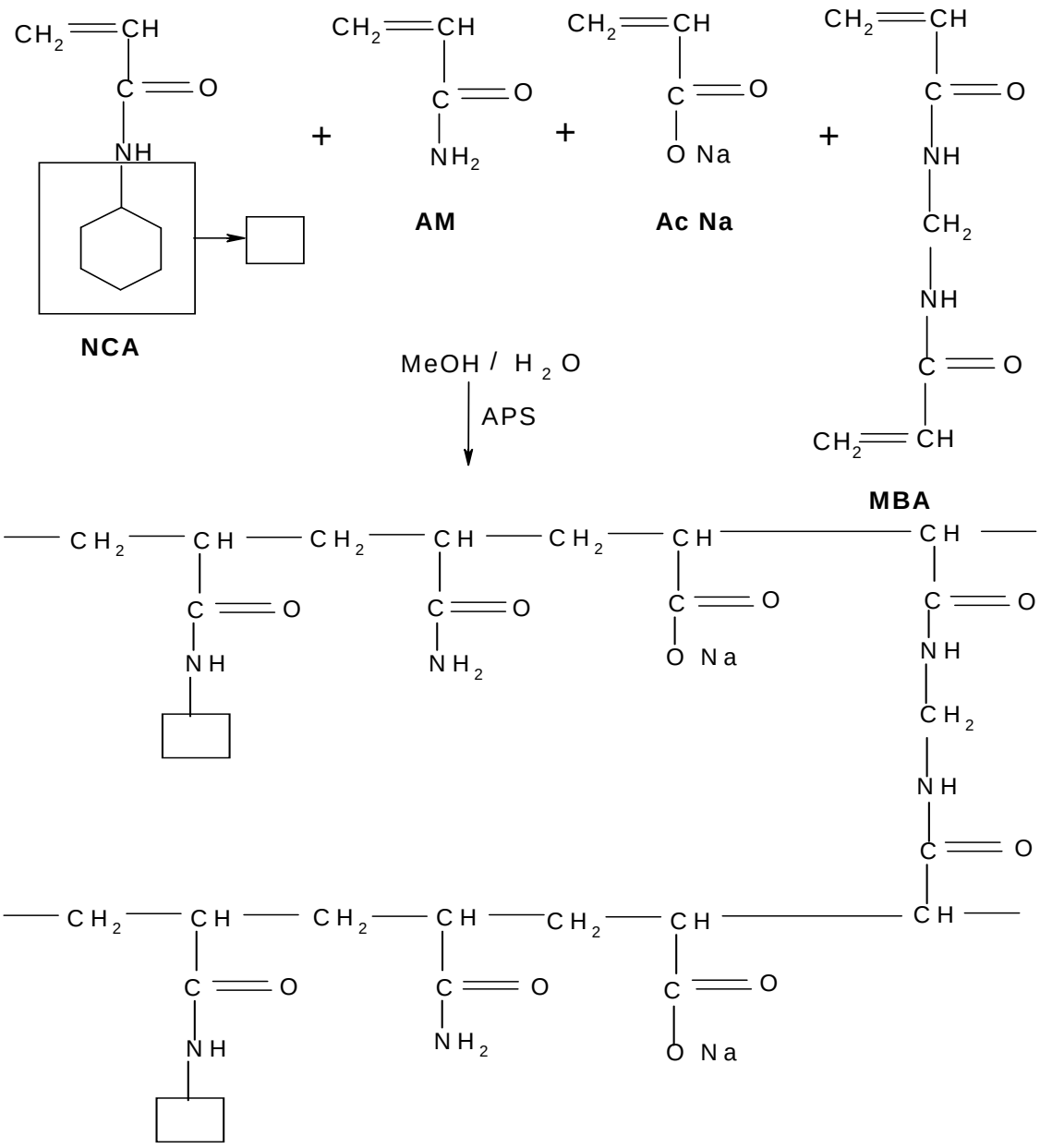
The swelling experiments were carried out as a function of time and the negligible change in weight of swollen gel is taken to be indicative of the equilibrium stage.

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

The schematic representation of the Hydrogels preparation is shown below:



Scheme 1: Poly (*N*-cyclohexylacrylamide-*co*-acrylamide/Sodium acrylate) Hydrogels

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 60^0C The amount of N-cyclohexylacrylamide (NCA) and Acrylamide (AM) monomers was fixed and the amount of sodium acrylate (AcNa) was varied from 0.1 to 0.3 g. In the other monomer feed ratios the formed hydrogels were soluble in water. So that , we fixed the amount of NCA and AM monomer as 70: 30 and the AcNa was varied from 0.1 to 0.3 g to study the effect of AcNa in the polymer network. The IR 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 typical spectrum of Poly(NCA-co- AM/AcNa) Hydrogel is shown in Figure 1. A broad peak corresponding to NH of NCA as well as NH stretching of acrylamide was observed around 3430 cm^{-1} . In addition to this, the peaks were also observed at 1665 cm^{-1} corresponding to C=O of NCA, C=O carboxyl unit and 1562 cm^{-1} corresponds to $C=ONH_2$ of AM unit. The above IR analysis indicates the presence of all monomeric units in the crosslinked hydrogels.

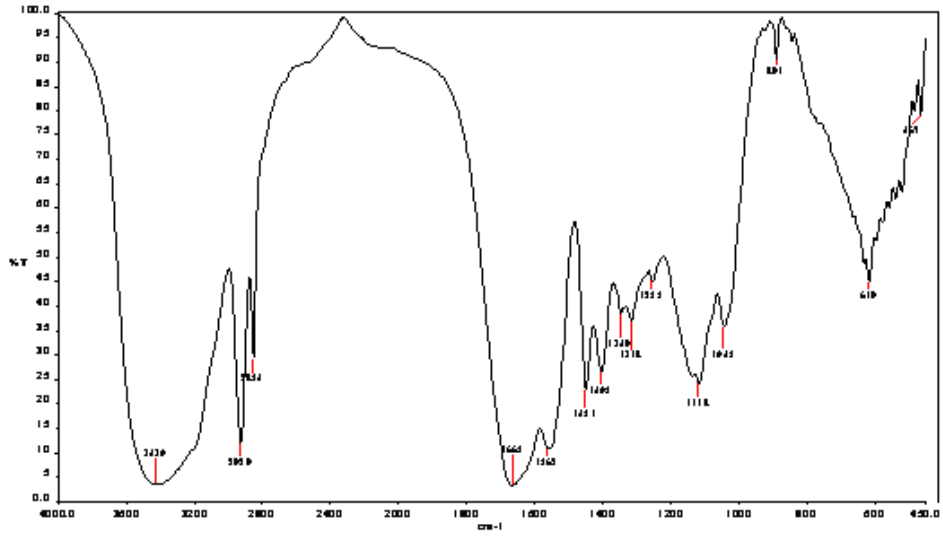


Figure 1: IR-Spectrum of Poly (N-cyclohexylacrylamide -*co* –acrylamide / Sodium Acrylate) Hydrogels

Dynamic swelling of some selected samples at different absorbing time in water was measured as shown in Figure 2. The swelling rate is slow during the first few 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 Ac Na and AM through formation of hydrogen bonds because of free NH_2 group available for hydrogen bonding [16]. 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 from 60 minutes and gradually increases until the equilibrium swelling is reached. The swelling rate observed for Ac Na 0.1 g to 0.30 g. As the content of AcNa is increases the swelling rate is increases rapidly. The incorporation of hydrophilic groups of Ac Na favorable for penetration of water.

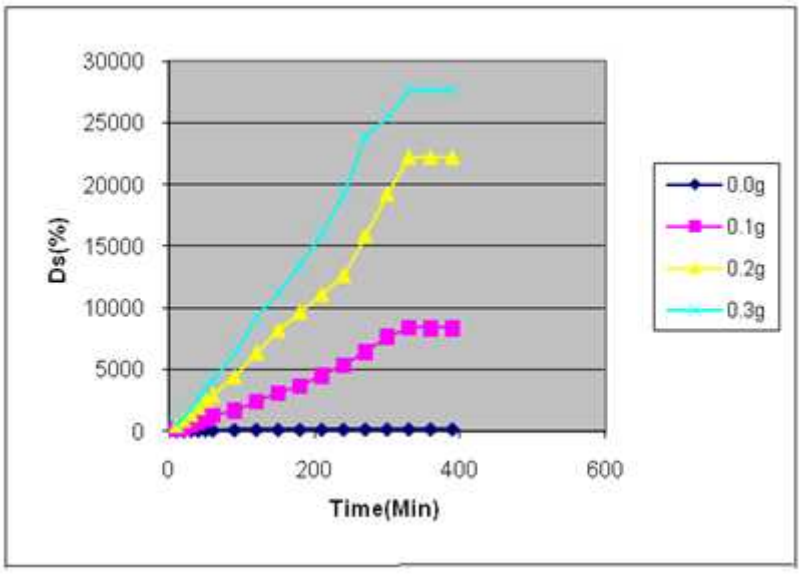


Figure 2: Swelling behavior of the Hydrogels

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. In Poly (NCA-co- AM/ Ac Na) Hydrogel(Figure 3&4) micrographs have the morphology of porous and well type structure and it conforms the presence of Ac Na in the whole gel surface. As the feeds of Ac Na increases the size of the porous also increases. The swelling behavior is also evident for the surface morphology.

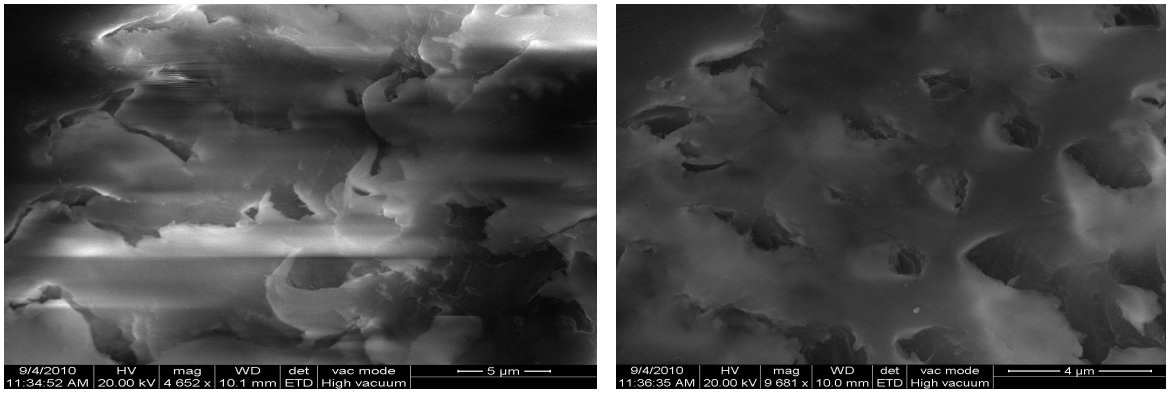


Figure 3: SEM image of Poly(N-cyclohexylacrylamide -*co* –acrylamide / Sodium Acrylate) Hydrogels (0.10g of Ac Na)

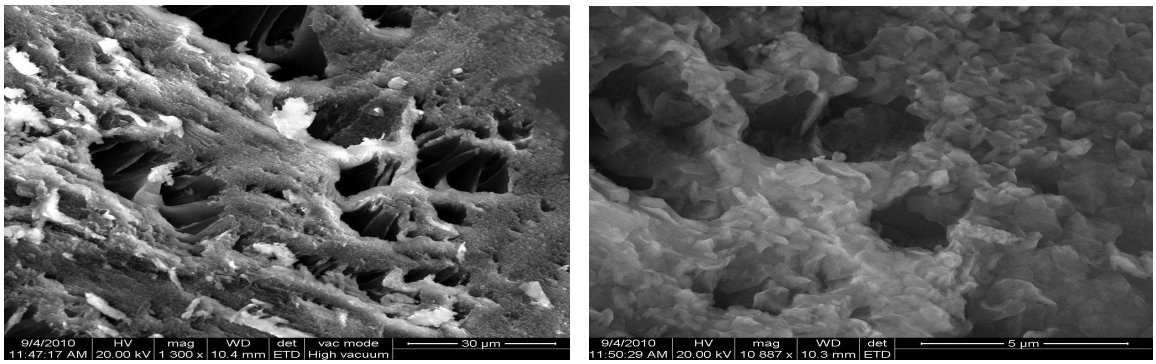


Figure 4: SEM image of Poly(N-cyclohexylacrylamide -*co* –acrylamide / Sodium Acrylate) Hydrogels (0.30g of AcNa)

Acknowledgements
The author S. Anbarasan thank the UGC, Hyderabad, for financial support (MRP-SERO, F.No.3714/11) towards the research work.

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