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# N-tert-amylacrylamide based copolymers–I : Synthesis and Swelling behavior of Poly(N-tert-amylacrylamide -*co* –acrylamide / AMPS Na) Hydrogels

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**Abstract:** Poly(N-tert-amylacrylamide -*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 The amount of N-tert-amylacrylamide (NTA) and Acrylamide (AM) monomers was fixed and the amount of 2-acrylamide-2-methylpropanesulfonic acid sodium salt was varied. The Hydrogels were characterized by IR spectroscopy. The swelling behavior of Hydrogels studied by Gravimetric method and degree of swelling was increased by increasing the amount of AMPS Na .The surface morphology was studied by SEM analysis.

**Keywords:** N-tert-amylacrylamide, AMPS Na , 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 [13-16].

The aim of this work was to prepare a series of poly(N-tert-amylacrylamide -*co* –acrylamide / AMPSNa) Hydrogels , based on NTA , acrylamide and 2-acrylamide-2-methylpropanesulfonic acid sodium salt and swelling behavior of such copolymer gels have not been reported before. Hydrogels were prepared by free-radical crosslinking copolymerization of NTA, AM and AMPSNa in the presence of N,N'-methylenebis(acrylamide) (MBA) as the crosslinker.

## Experimental

### Materials

Acrylamide (AM, Merck )was crystallized from acetone/ethanol mixture .Ammonium persulphate (APS) and 2-acrylamide-2-methylpropanesulfonic acid were supplied from Aldrich. AMPSNa was prepared by neutralizing the 2-acrylamide-2-methylpropanesulfonic acid using Sodium hydroxide. The crosslinker N,N'-methylene-bis-acrylamide (MBA) was used as received. Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Ortho phosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over anhydrous $CaCl_2$. 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-tert-amylacrylamide (NTA)

The monomer N-tert-amylacrylamide was prepared by the reaction of t-amyl alcohol with acrylonitrile. N-tert-amylacrylamide was recrystallized in warm dry benzene. The white crystals have amp.91° C (Lit.91-92° C) and the yield was - 87%[17 ].

### $^1$H-NMR($CDCl_3$),δ(ppm) :

The peaks observed at 0.78ppm for-$CH_3$ , at 1.2ppm for-$(CH_3)_2$, at 1.7 ppm for- $CH_2$, at5.49 ppm for =CH vinylic proton and at 6.1ppm for vinylic =$CH_2$ 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 NTA (0.5g), AM (0.5g) , 0.045g MBA 0.005 g APS , AMPS Na (0.1,0.2, ,0.30, and 0.40 g ) 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.

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### 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%. 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 / gm of dried hydrogel after keeping in contact with water for selected period of time.

Degree of swelling (Ds) = $(W_s-W_d/W_d)$ ------ (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.

### 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 $^1$H-NMR data of N-tert-amylacrylamide:** at 0.78ppm for-$CH_3$ , at 1.2ppm for-$(CH_3)_2$, at 1.7 ppm for- $CH_2$, at5.49 ppm for =CH vinyl proton and at 6.1ppm for vinyl =$CH_2$ proton .

### IR Spectral characterization of Hydrogel

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 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 NTA unit and 1535 cm$^{-1}$ corresponding to C=$ONH_2$ AM unit. The peak observed at 1449 cm$^{-1}$ corresponding to S=0 (Sym).
The schematic representation of the Hydrogel is shown below.

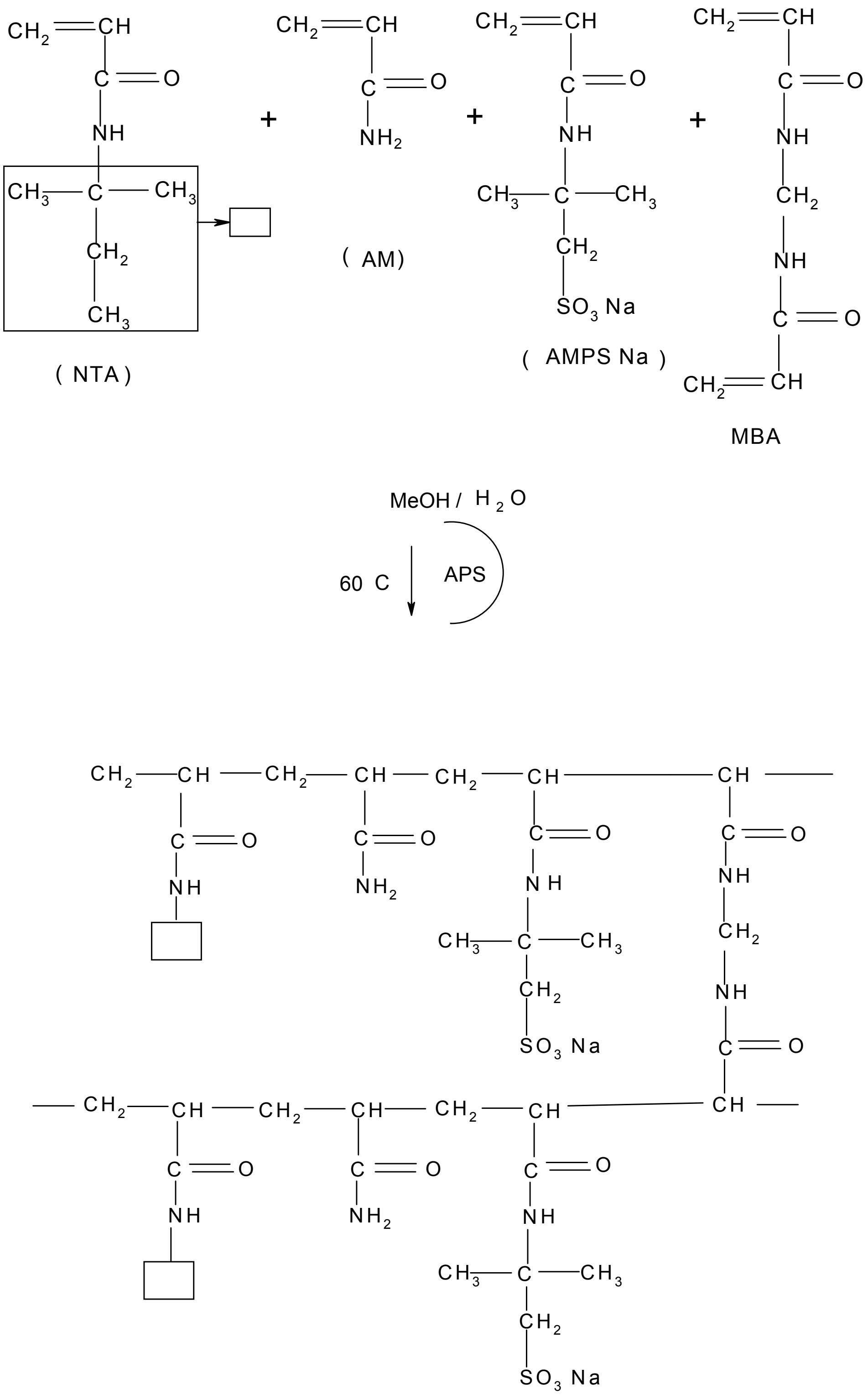


**Figure 1. Poly(N-tert-amylacrylamide -*co* –acrylamide / AMPS Na) Hydrogel**

## Swelling Behavior

Dynamic swelling of some selected samples at different absorbing time in water was measured as shown in Figure 2. The swelling rate was 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 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 gradually increases until the equilibrium swelling is reached. The swelling rate observed for AMPS Na 0.1 g to 0.40 g. As the content of AMPS Na is increases the swelling rate is increased rapidly. The incorporation of hydrophilic groups AMPS Na favorable to penetration of water [18].

## Morphological Studies

Scanning electron Microscopy of hydrogels were performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. InPoly (NTA-co- AM/ AMPSNa) Hydrogel (Figure 3) micrographs have the morphology sponge like porous structure. So water molecules can be easily diffused through in and out of the polymer matrix. Therefore the swelling or deswelling dynamics could be achieved [19].

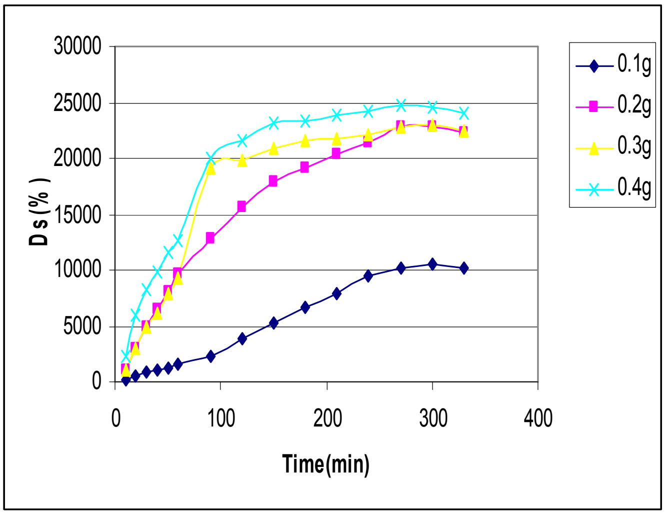
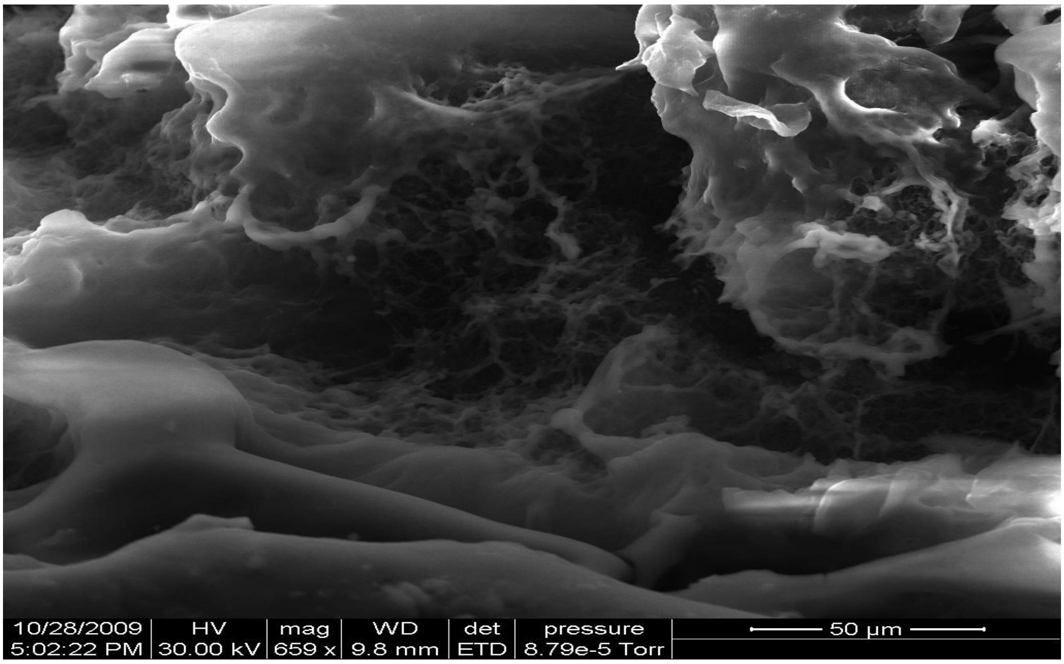


**Figure 2. Swelling behavior of Poly(NTA-co-AM/AMPSNa) Hydrogels**

**Fig 3-**



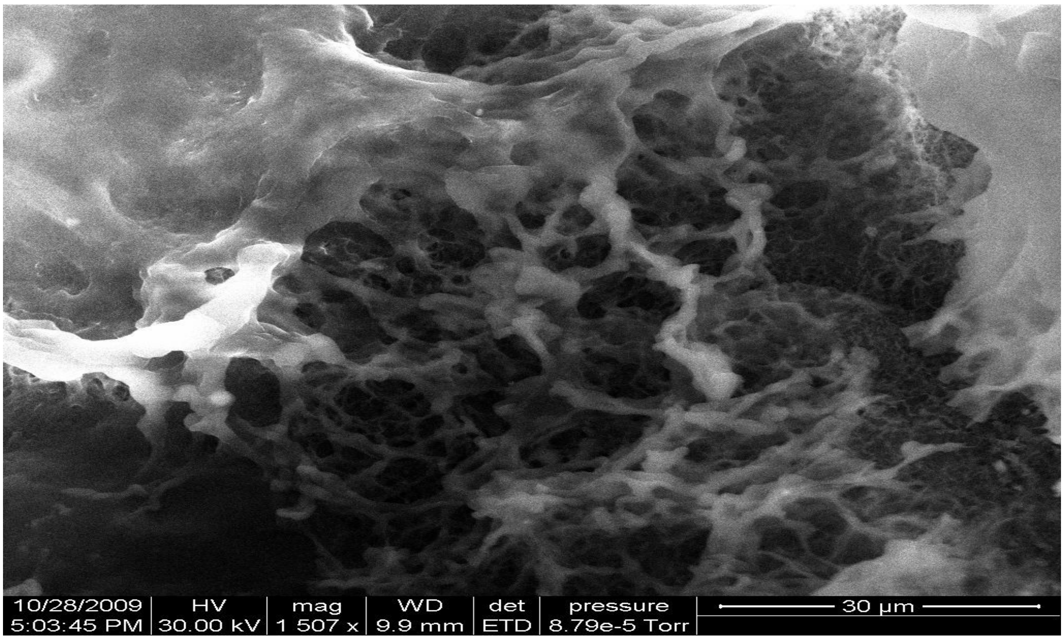


**Figure 3. SEM picture of Hydrogel with different magnification**

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