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Synthesis and Swelling behavior of Poly(*N-tert*-amylacrylamide-*co*-Acrylamide/Maleic acid) Hydrogels

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Abstract: A series of ionic poly(N-tert-amylacrylamide -*co* –acrylamide / maleic acid) 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-tert-amylacrylamide (NTA) and Acrylamide (AM) monomers was fixed and the amount of Maleic acid (MA)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 Maleic acid. The surface morphology was studied by SEM analysis.
Keywords : Hydrogels, N-tert-amylacrylamide , Swelling behavior , SEM analysis.

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 [2-8].

The N-substituted acrylamides are used to prepare thermo sensitive polymers like poly(N-isopropylacrylamide)and copolymers of N-alkyl acrylamide and styrene [9]. Thermosensitive polymers have great potential in applications as drug delivery system [10] human gene vector [11] and biocatalysts [12].

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) andacrylamide in methanol. N,N[1]- 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 chains[13].

E.Turan et al., studied a Ionic poly(*N-t*-butylacrylamide-*co*-acrylamide) [P(TBA-*co*-AAm)] hydrogels were synthesized by the free-radical crosslinking copolymerization of *N-t*-butylacrylamide and acrylamide monomers in fixed amounts and the maleic acid (MA) comonomer in methanol in different amounts with *N,N*-methylene bis(acrylamide) as the crosslinker, ammonium persulfate as the initiator, and *N,N,N',N'*-tetramethylenediamine as the activator. The swelling behavior of these hydrogels was analyzed in buffer solutions at various pHs. The swelling studies in buffer solutions at various pHs and were related to the MA content[14].

These observations inspired us to synthesize the hydrogels based on N-tert-amylacrylamide (NTA) . The aim of this work was to prepare a series of poly(N-tert-amylacrylamide -*co* –acrylamide / maleic acid) Hydrogels , based on NTA , acrylamide and Maleic acid . Synthesis and swelling behavior of such copolymer gels have not been reported before. Hydrogels were prepared by free-radical crosslinking copolymerization of NTA, AM and MA 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 persulphate (APS) and Maleic acid (MA) 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 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%[15].

^{1}H-NMR($CDCl_3$),δ(ppm) :

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

^{13}C-NMR($CDCl_3$),δ(ppm) :

δ 163.90(CH_2 = C(H)-CO-NH..);
δ 132.93(CH_2 =C(H)-CO-NH…);
δ 123.87(CH_2=C(H)-CO-NH..) ;
δ 52.82(-CO-NH-C(CH_3)-CH2);
δ 31.87(-CO-NH-C(CH_3)2-CH_2-CH_3);
δ 26.19(-CO-NH-C(CH_3)2-CH_2-CH_3)
δ 8.26(-C(CH_3)$_2$-CH_2-CH_3).

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 , MA (,0.10, ,0.20, and 0.30 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.

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. 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.

EWC = (W_e-W_d/W_e) x 100 ---------- (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.

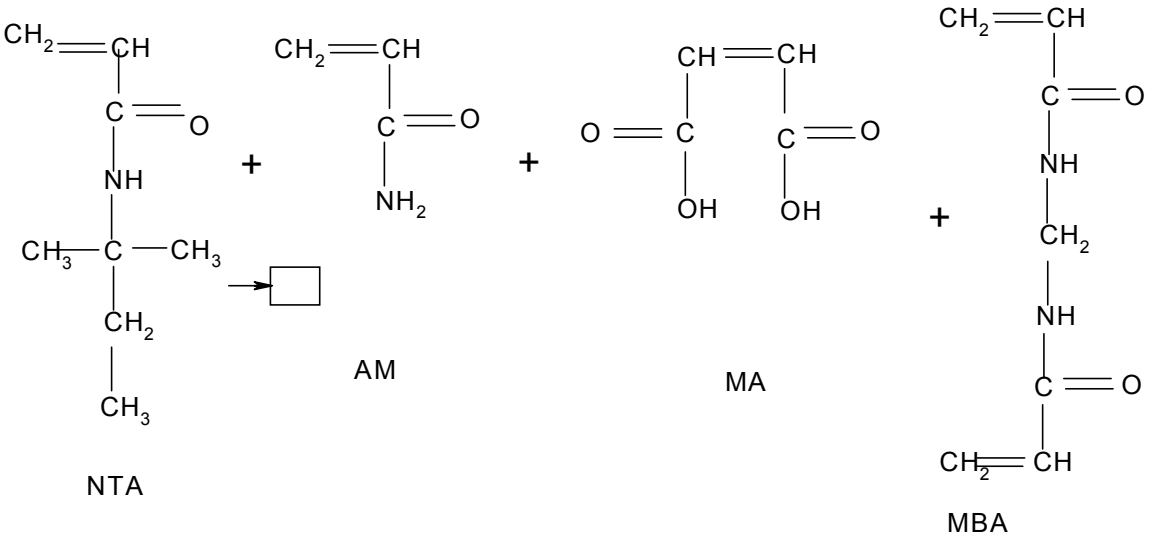
SEM Analysis

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

Preparation of Hydrogels

The Hydrogels were prepared by Free-radical copolymerization 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 , MA (,0.10, ,0.20, and 0.30 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. The schematic representation of hydrogel preparation is given below.



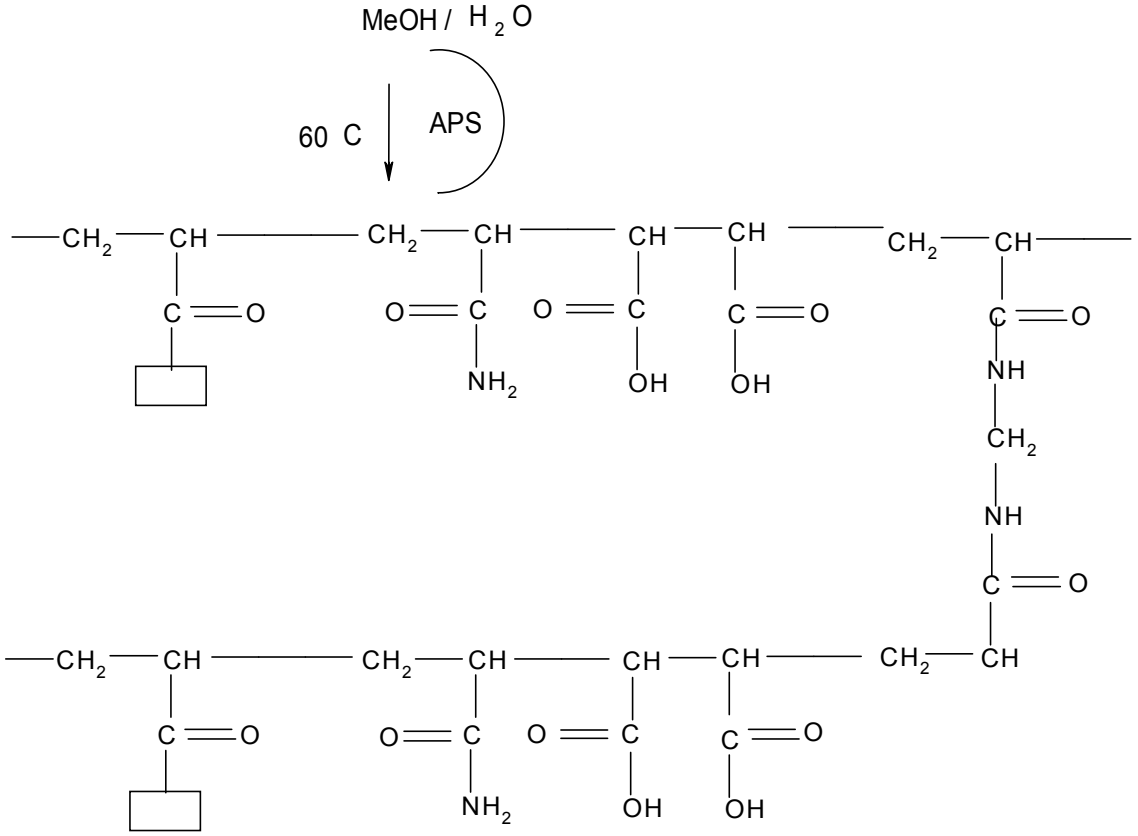


Figure 1. Poly (NTA-co- AM/ MA) Hydrogels

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 –COOH of maleic acid as well as NH stretching of acrylamide was observed around 3426 cm^{-1} . In addition to this, the peaks were also observed at 1662 cm^{-1} corresponding to C=O of NTAA unit and 1530 cm^{-1} corresponding to $C=ONH_2$ AAm unit. The above IR analysis indicate the presence of all monomeric units in the crosslinked hydrogels.

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.

Degree of swelling (Ds) = (W_s-W_d/W_d) ----- (1)

The equilibrium water content (EWC) is expressed in % on the weight of swollen gel at equilibrium, using the Eqn .2.

EWC = (W_e-W_d/W_e) x 100 --------- (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.

Dynamic swelling of some selected samples at different absorbing time in water was measured at room temperature as shown in Figure 2. 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 MA 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 60 minutes and gradually slows down until the equilibrium swelling is reached .The swelling rate and equilibrium swelling time varied from MA 0.1 g to MA 0.30 g. . In the hydrogel NTA-co-AM/MA(0.30g) the swelling rate is higher than the other hydrogels. As the content of MA is increases the swelling rate is increases rapidly. The incorporation of Maleic acid(MA) hydrophilic groups enhances the penetration of water[16] .

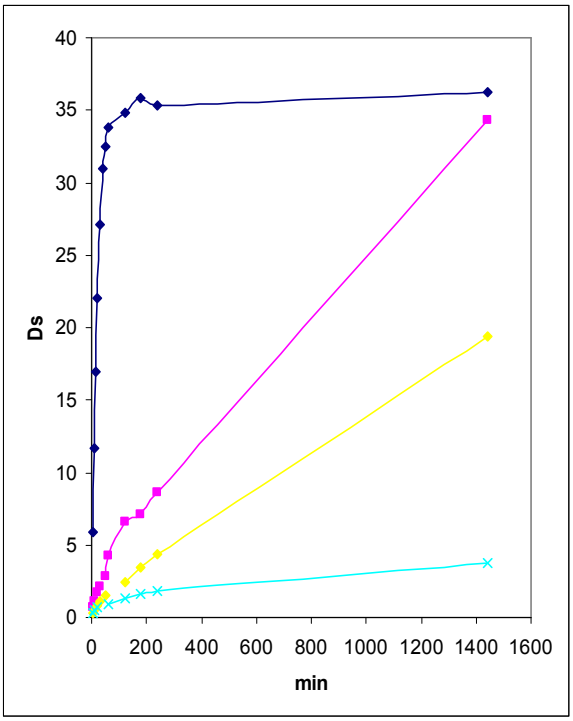
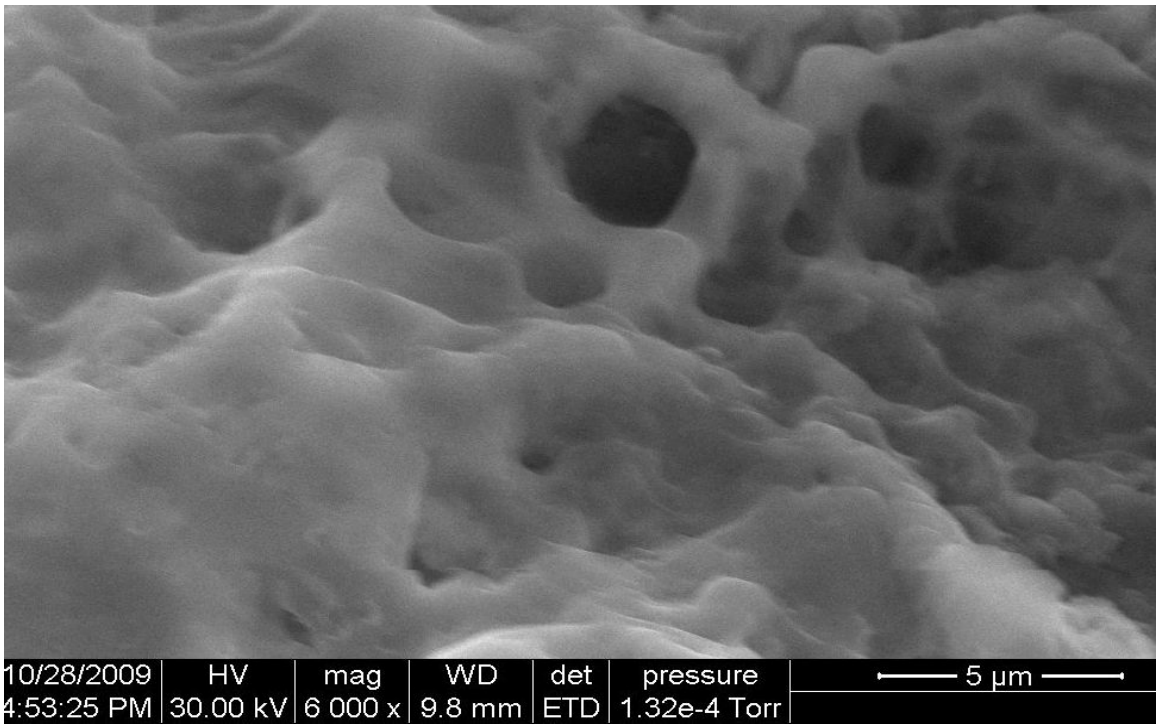


Figure 2. Swelling behavior of Poly(NTA-co- AM/MA) Hydrogels
MA: 0.0 g(×) , 0.10 g(■,yellow),0.20 g(■, pink) and 0.30 g (■, blue).



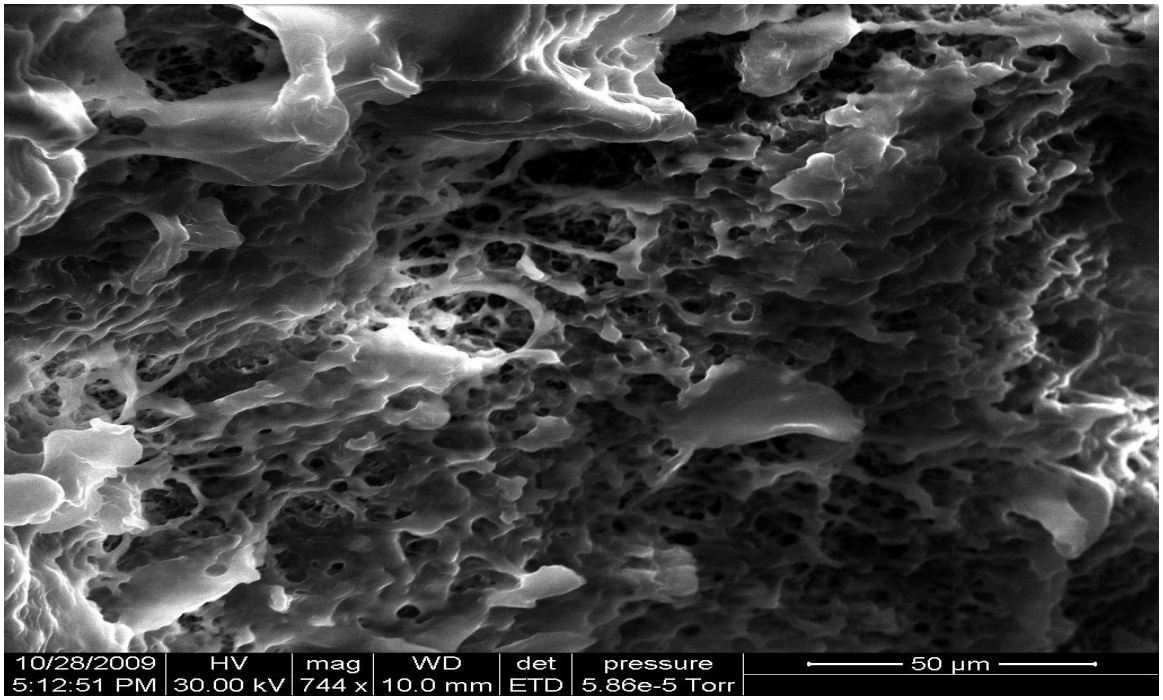


Figure 3. SEM picture of Hydrogel with different magnification

Morphological studies

Scanning electron Microscopy of hydrogels were performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. In Poly (NTA-co- AM/ MA) Hydrogel (Figure 3) micrographs have the morphology honeycomb like porous structure. So water molecules can be easily diffused in and out. Therefore the swelling or deswelling dynamics could be achieved [17].

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