ANNEXURE

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

S. Anbarasan 1, B.A. Brundha 2 and P. Pazhanisamy 2*

1 Research and Development Centre, Bharathiar University, Coimbatore, India.
2 Department of Chemistry, Sir Theagaraya College, Chennai-600 021, India
*E-mail: p_pazhanisamy@yahoo.com

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-methylethylenbisacrylamide (MBA) as a crosslinked 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 fluids. 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. The N-substituted acrylamides are used to prepare thermo-sensitive polymers like poly(N-isopropylacrylamide) and copolymers of N-alkyl acrylamide and styrene. Thermosensitive polymers have great potential in applications as drug delivery system and human gene vector and biocatalysts. Vildan Ozturk and Oguz Okay reported that a series of temperature sensitive hydrogels was prepared by free-radical crosslinking copolymerization of N-4-butylacrylamide (TBA) andacrylamide in methanol, N,N'-methylethylenbis(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. The crosslinked copolymers and terpolymers of N-isopropyl acrylamide (NIPAm) with sodium-2-acrylamido-2-methyl propane sulfonate (NaAMPS) and glycylid 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 rate. These observations inspired us to synthesize the hydrogels based on N-cyclohexylacrylamide (NCA) and acrylamide (AM). 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'-methylethylenbis(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 2-acrylamido-2-methyl-1-propanesulphonate acid (AMPS) and Sodium hydroxide were supplied from Aldrich. The crosslinker N,N'-methylethylenbisacrylamide (MBA) was used as received.
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 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 (Wd) after keeping in contact with water for selected period of time.

\[ \text{Degree of swelling (Ds) = } \frac{(W_s-W_d)}{W_d} \] (1)

SEM Analysis
The Micro structure of Hydrogels were studied by Scanning electron Microscopy hydrogels were performed using Hitachi, 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 0.50. 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 2432 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(NH₃⁺) 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 was 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 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 matrix.

Morphological studies
Scanning electron Microscopy of hydrogels was performed using Hitachi, 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 layer ed structure and it conforms the presence of AMPS Na in the whole gel surface. The wet SEM picture shows the absorption of water on the surface of the Hydrogels.
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REFERENCES

![Fig.-1: Swelling behavior of Poly(NCA-co- AM/AMPS Na) Hydrogels](image)

AMPS Na: 0.1 g(●); 0.20 g(■); 0.30 g(▲); 0.40 g(x).
CH₂=CH
C=O

NH

NCA

+ CH₂=CH
C=O
NH₂
AM

+ CH₂=CH
C=O
NH
CH₃-C-CH₃
H₂O
AMPS Na

+ CH₂=CH
C=O
NH
CH₂
SO₃ Na
MBA

MeOH / H₂O

60 °C → APS

CH₂
C=O
NH₂

CH₂
C=O
NH
CH₃-C-CH₃

CH₂
C=O
NH
CH₂
SO₃ Na

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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Swelling behavior of Poly (N-cyclohexylacrylamide-co-acrylamide/ AMPS Ionic Liquid) Hydrogels

KEYWORDS

S. Anbarasan  
Research and Development Centre, Bharathiar University, Coimbatore, India.

B.A. Brundha  
Department of Chemistry, Sir Theagaraya College, Chennai-600 021, India.

P. Pazhanisamy  
Department of Chemistry, Sir Theagaraya College, Chennai-600 021, India.

ABSTRACT

Ionic Hydrogels were synthesized using N-cyclohexylacrylamide, acrylamide and AMPS Ionic Liquid by free radical polymerization at 60°C. The swelling behavior increased with increasing amount of AMPS IL. The SEM analysis showed that the hydrogels are in rod like shape. XRD pattern exhibits more amorphous in nature.

Introduction

Hydrogels are three-dimensional polymer networks that are capable of absorbing large amount of water or aqueous solution. They are insoluble because of the presence of crosslinks, entanglements or crystalline regions. [1] There are a wide variety of natural and synthetic hydrogels. Their ability to absorb water is due to the presence of hydrophilic groups such as -OH, CONH, CONH₂, COOH, SO₂H etc. [2] Hydrogels can classify into non-ionic and ionic materials. The ionic types comprise anionic (-CO₂-) and cationic pendant (-NR₃⁺). The presence of these ionic groups in the hydrogels opens potential area of application that is related to remove pollutants from wastewater [3]. Hydrogels may be chemically stable or may degrade and eventually disintegrate and dissolve. To avoid this dissolution/degradation, controlled crosslinking is introduced within the hydrogels. Depending on the nature of side groups along the polymer chains, hydrogels have the ability to respond to their environmental changes such as pH, ionic strength or temperature. In recent years, these stimuli sensitive hydrogels have proved to be important carriers for the development of drug devices. [4]. In the present study we described the preparation and swelling behavior of Poly (N-cyclohexylacrylamide-co-acrylamide/ AMPS Ionic Liquid) Hydrogels.

Experimental Preparation of Hydrogels

Free-radical cross linking 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 0.005 g APS, AMPSIL (0.00, 0.10, 0.20 and 0.50) 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 24 h. 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 (Scheme-1).

Swelling behavior

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.

\[(D_s\%) = \frac{(W_s - W_d)}{W_d} \times 100\]

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 Hitachi, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification.

XRD Study

X-ray powder diffraction (XRD) patterns were collected using a Philips X-Pert automatic diffractometer operating at 40 kV and 40 mA in theta-theta configuration, secondary monochromator with Cu Ka radiation (\(\lambda = 1.5418 \, \text{Å}\)) and a PIXcel solid state detector. The samples were mounted on a zero background silicon wafer fixed in a generic sample holder.

Results and Discussion

The schematic representation of hydrogel preparation is as follows

![Scheme 1](image)

\[\text{NCA} + \text{AM} \rightarrow \text{AMPSIL}\]

Scheme- 1. Poly (N-cyclohexylacrylamide-co-acrylamide/ AMPS Ionic Liquid) Hydrogels
The swelling behavior of the hydrogels was carried out in water at room temperature and is depicted in the Figure 1. The swelling is driven by repulsion of hydrophilic groups such as \( \text{NH}_2, \text{C}=\text{O} \), \( \text{NH} \), \( \text{SO}_4^- \) inside the network and osmotic pressure difference between the gels and the external solution. As the concentration of AMPS II increases, the swelling behavior also increases and it is due additional osmotic pressure develops that expands the gel network further [5, 6].

The Surface morphology of hydrogels was studied under a scanning electron microscope (SEM). The rods like structure are seen in the matrix (Figure 2a). In the XRD study, broad peaks are obtained, which confirms more amorphous region and less crystallinity. It showed that the more the amorphous region in the matrix more will be the swelling.

Figure 1. Swelling behavior of poly (N-cyclohexylacrylamide-co-acrylamide/ AMPS Ionic Liquid) Hydrogels

Figure 2. SEM image (a), XRD pattern (b)

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

S. Anbarasan¹, B. A. Brundha² and P. Pazhanisamy²*¹

¹Research and Development Centre, Bharathiar University, Coimbatore, India
²Department of Chemistry, Sir Theagaraya College, Chennai, India

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°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°C. In this paper, we report the synthesis and characterization of poly(N-cyclohexylacrylamide-co-acrylamide/Sodium acrylate) Hydrogels.

EXPERIMENTAL SECTION

Materials
Acrylamide (AM, Merek) 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 anhydrous CaCl₂. 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%.

³¹H-NMR spectroscopy

The ³¹H-NMR spectra of copolymers were recorded on the EM-390 NMR Spectrometer operating 90 MHz with CDCl₃ as solvent. The following peaks appear in NCHA spectrum; at 1.2-2.02 ppm for cyclohexyl CH₂, 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°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 (.10, .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°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 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.

\[
\text{Degree of swelling (Ds %)} = \left[ \frac{W_t - W_d}{W_d} \right] \times 100
\]

Where, \(W_t\) 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.

\[
\text{EWC} = \left[ \frac{W_e - W_d}{W_d} \right] \times 100
\]

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°C. 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=ONH₂ of AM unit. The above IR analysis indicates the presence of all monomeric units in the crosslinked 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 NH₂ 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.

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.
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