Chapter 2
Preparation and Characterization of Hydrogels

2.1 Materials and Methods

2.1.1 Materials

2-Acrylamido-2-methylpropane sulfonic acid (AMPS) was obtained from Vinati Organic Ltd. Acrylamide (AM), gelatin and Potassium peroxodisulfate (KPS) were obtained from Merck India Ltd. 1-vinyl-2-pyrrolidone (VP) and polyvinylalcohol (PVA) were obtained from Himedia Laboratories Pvt. Ltd. Acrylonitrile (AN) was obtained from Loba Chemie Pvt. Ltd. N,N'-methylene bisacrylamide (MBA) was obtained from Central Drug House Pvt. Ltd. Hydrochloric acid and NaOH were purchased from RFCL and Merck, India Ltd.

The AMPS was very hygroscopic in nature, therefore Na- salt of AMPS was prepared by reacting 1 mole of AMPS and 1 mole NaOH in double distilled water. 14.5 g of NaOH was dissolved in 76.8 g of double distilled water. To this solution 75.3 g of AMPS was added slowly under stirring and compressed air was purged to prevent auto-polymerization. The temperature of the exothermic reaction was controlled between 24-40°C. The solution should not be allowed to become acidic and the pH was maintained at 9. A slight excess of NaOH was required. The prepared solution was filtered using polystyrene cloth under vacuum, to remove precipitated iron and other insoluble. The concentration of AMPS-Na in the aqueous solution was determined by UV spectroscopic method. AM, KPS and MBA were purified twice by recrystallising with ethanol. Acrylonitrile was purified by washing it sequentially with 2N NaOH, 1M H2SO4 and finally with double distilled water.
The monomers used in the preparation of hydrogels are given below:

![Chemical structures of monomers](image)

**Fig. 2.1** Monomers used in the preparation of hydrogel

### 2.1.2 Preparation of Hydrogels

The hydrogels are prepared by free radical polymerization method. The monomers are dissolved in 5 ml of double distilled water and prepared a homogeneous solution by mixing thoroughly. To this solution 0.073 mM KPS as a reaction initiator and 0.129 mM MBA as a reaction cross-linker are added and mixed with continuous stirring. The solution is then transferred into PVC straw and polymerization is carried
out at 60-80°C for 15-30 minutes. After complete polymerization the hydrogels are dried at 50°C for 7-8 hours.

2.1.3 Purification of Hydrogels

The end polymers obtained as above are equilibrated with double distilled water for 7 days so that any unreactants are leached out from the swollen hydrogel. The swelling medium is then analyzed for any unreacted monomers using UV-visible spectrophotometer. The swollen hydrogels are taken out from the swelling medium, dried in the air and store in an airtight container for further experiments.

2.1.4 Characterization of Hydrogels

The structural feature of the prepared hydrogel is investigated by recording IR spectra of the hydrogel on Shimadzu-8400 FT-IR spectrometer in KBr. The morphology of the hydrogel is studied by taking SEM micrograph of the prepared hydrogel on CARLZEISS LEO 1430VP scanning electronic microscope. Thermal properties of the prepared hydrogel are evaluated by thermogravimetric analysis (TGA). Samples are heated from 0 to 700°C under N₂ atmosphere and at a heating rate of 10°C/ minute on METTLER TOLEDO, STAR® SW 9.10.

2.2 Preparation and Characterization of Hydrogel of AMPS-Na, AM, VP and AN (Hydrogel I)

2.2.1 Preparation of Hydrogel(I)

Using the above method, 2- acrylamido-2-methyl propane sulfonic acid (AMPS) based hydrogel is prepared and labelled as Hydrogel(I). The hydrogel contains 3.51 mM AMPS-Na, 7.03 mM acrylamide (AM), 8.9 mM vinyl pyrrolidone (VP), 30.34 acrylonitrile (AN), 0.073mM potassium peroxodisulfate (KPS), and 0.129 mM N,N'-
Methyline bisacrylamide (MBA). The polymerization temperature is maintained at 80°C and the time taken for complete polymerization is 30 minutes.

The end polymers obtained as above are equilibrated with double distilled water for 7 days so that any unreactants are leached out of the swollen hydrogel. The swelling medium is analyzed for any unreacted monomers using UV-visible spectrophotometer. It is found that almost no monomer is left as unpolymerized, and almost no homopolyers could be detected in the outer swelling medium. The swollen hydrogel are taken out from the swelling medium and dried in air then stored in airtight containers for further experiments.

2.2.2 Characterization of Hydrogel(I)

2.2.2.1 FT-IR Analysis Hydrogel(I)

To understand the cross-linking structure of the hydrogel, the FT-IR-spectra of AMPS-Na, AM, VP, AN and gel are recorded and their overlap spectra are given in the fig.2.2(a-e). In case of native VP in fig.2.2(a) the absorption bands at 3648 cm\(^{-1}\) and 2891-2966 cm\(^{-1}\) are characterized for N-H and C-H stretching respectively. The band at 1631 cm\(^{-1}\) is for C=O stretching. In case of native AN in fig2.2(b) the bands at 3624 cm\(^{-1}\) is due to N-H stretching of the amino group. The absorption band for N≡C is observed at 2244 cm\(^{-1}\). The IR spectra of AM (fig.2.2 c) show broad band in the region 2812-3161 cm\(^{-1}\) due to the CH stretching and banding. The absorption band at 1676 cm\(^{-1}\) is characterized for C=O stretching. In case of native AMPS-Na (fig2.2.d) the absorption bands at 3662 cm\(^{-1}\) and 2933 cm\(^{-1}\) are due to the N-H and C-H stretching respectively. The characteristic band of AMPS is observed at 1043 cm\(^{-1}\) for SO group\(^{253}\). The C=O stretching and the secondary amide N-H deformation peak of AMPS units are observed at 1668 cm\(^{-1}\) and 1535 cm\(^{-1}\) respectively.

The IR spectra of the prepared hydrogel(I) fig.2.2 (e) show a combined spectral feature of different functional groups of monomers. The N-H stretching of polyacrylamide, MBA and AMPS is observed at 3652 cm\(^{-1}\). Similarly band at 1687 cm\(^{-1}\) may be assigned to C=O stretching of acrylamide and MBA. The spectra also mark the presence of methylene (CH\(_2\)) twisting at 1288 cm\(^{-1}\). Band at 2243 cm\(^{-1}\) implies the
presence of N≡C from acrylonitrile. Bands around 2943-3166 cm\(^{-1}\) are due to C–H stretching of –CH = CH- groups present in vinyl pyrolidone, acrylamide, and AMPS. The evidence of the cross-linker in the prepared hydrogel(I) blend is confirmed by the peak at 671 cm\(^{-1}\) (secondary amide). The bands 1043 (SO stretching) and 1539 cm\(^{-1}\) (secondary amide N-H deformation) confirm the presence of APMS. The IR spectrum of the hydrogel is much sharper than those of the components. This may be due to the fact that because of the grafting of crosslinked AM and AMPS chains into AN and VP. This forms a loose matrix.

Fig. 2.2 IR spectra of VP(a), AN(b), AM(c), AMPS(d) and hydrogel(I) (e).
2.2.2.2 Scanning Electronic Microscope (SEM) of Hydrogel(I)

The SEM micrograph of AMPS, AM and gel are given in fig.2.3(a-c). From the fig.2.3a it is observed that the morphological surface of AMPS is rough and heterogeneous but AM has smooth surface (fig.2.3b). The SEM image of gel shows that the morphological surface of hydrogel is heterogeneous in nature having some hydrophobic microdomains. These hydrophobic microdomains of polyacrylonitrile provide mechanical strength to the gel by acting as reinforcement fillers and regulate the swelling behaviour of the gel.

Fig2.3 SEM of AMPS(a), AM(b) and hydrogel I(c)
2.2.2.3 Thermo gravimetric Analysis (TGA) of Hydrogel (I)

The thermo gravimetric analysis (TGA) of hydrogel(I) is depicted in fig.2.4. The thermogram shows four step weight loss. The first step of degradation due to dehydration is observed at 130\(^0\)C with 8.92\% weight loss. Second step of degradation is observed from 140-270\(^0\)C with 11.97\% weight loss and third step from 270-325\(^0\) C with 12.64\% weight loss due to degradation of functional groups of hydrogel. The final degradation of hydrogel is observed at 325-600\(^0\)C with highest \% of weight loss 43\%.

![Graph of thermo gravimetric analysis of hydrogel(I)](#/media/ND_C,05.03.2010_12_38_21.png)

**Fig 2.4 TGA of hydrogel(I)**
2.3. Preparation and Characterization of Hydrogel of AMPS, AM and gelatin (Hydrogel II)

2.3.1 Preparation of Hydrogel(II)

AMPS based second hydrogel is prepared using the same procedure as in hydrogel(I) and labelled as Hydrogel(II). The hydrogel contains 4.68 mM AMPS-Na, 14.06 mM AM, 0.25 g gelatin, 0.073 mM potassium peroxodisulfate (KPS), and 0.129 mM N,N'-methyline bisacrylamide (MBA). The polymerization temperature is maintained at 60°C and the time taken for complete polymerization is 20 minutes.

The prepared hydrogel is then equilibrated with double distilled water for 7 days. The swollen hydrogel is taken out from the swelling medium, dried in the air and stored in air tight container. UV-visible spectrophotometer analysis for any unreacted monomer is done similar to hydrogel(I). It is found that there is no noticeable monomer left after polymerization.

2.3.2 Characterization of Hydrogel (II)

2.3.2.1 FT-IR Analysis of Hydrogel (II)

The IR spectra of pure AM, Na-AMPS, gelatin and prepared hydrogel(II) are depicted in fig.2.5 (a-d). The IR spectra of AM (fig.2.5 a) show broad band in the region 2812-3161 cm⁻¹ due to the CH stretching and banding. The absorption band at 1676 cm⁻¹ is characterized for C=O stretching. In case of native AMPS-Na (fig.2.5 b) the absorption bands at 3662 cm⁻¹ and 2933 cm⁻¹ are due to the N-H and C-H stretching respectively. The characteristic band of AMPS is observed at 1047 cm⁻¹ for SO₂ group. The C=O stretching is observed at 1668 cm⁻¹. The N-H stretching of gelatin is observed at around 3587-3643 cm⁻¹. The IR spectra of the hydrogel(II) in fig.2.5(d) show a combined spectral feature of various functional groups of AM, Na-AMPS, and gelatin. The peak at 3652 cm⁻¹ is due to N-H stretching of AM, Na-AMPS gelatin and MBA. The peaks from 2788 to 3271 cm⁻¹ for C-H (symmetric and asymmetric) stretching confirms the presence of AM, Na-AMPS in the polymer network. The N-H
bending and N-C stretching is observed at 1525 cm\(^{-1}\) and 1222 cm\(^{-1}\) respectively. The C=O stretching for AM, Na-AMPS and MBA is observed at 1695 cm\(^{-1}\). The characteristic peak of Na-AMPS units can be seen at 1041 cm\(^{-1}\) due to SO group. The present of crosslinker in the hydrogel is confirmed by the peak at 678 cm\(^{-1}\) (secondary amide) for MBA.

Fig. 2.5 IR spectra of AM (a), Na-AMPS (b), gelatin (c) and prepared hydrogel (II) (d)
2.3.2.2 Scanning Electronic Microscope (SEM) of Hydrogel(II)

The SEM micrograph of AMPS, AM, gelatin and hydrogel(II) are depicted in fig.2.6(a-d). From the fig.2.6 (a) it is observed that the morphological surface of AMPS is rough and heterogeneous but AM and gelatin has a smooth surface (b and c). From the micrograph (d) it is clear that the surface of the hydrogel(II) is heterogeneous in nature.

![Fig.2.6 SEM of AMPS(a), AM(b), gelatin (c) and hydrogel(II) (d)](image)

2.3.2.3 TGA of Hydrogel(II)

The thermo gravimetric analysis (TGA) of hydrogel(II) is depicted in fig.2.8. The
thermogram shows three step weight loss. The first weight loss occurs between 20°C to 130°C with 9.365% weight loss, second at 200°C to 340°C with 28.713% weight loss and third at 360°C to 520°C with 33.849% weight loss. The first weight loss is due to the dehydration of polymer which is observed up to 130°C. The second weight loss is observed due to degradation of functional groups such as amide, sulfonic, amine of the macromolecular chain by dehydration and generation more stable group. The third weight loss is due to final degradation of hydrogel(II). But the degradation behaviour of monomers is different. The monomers are degraded in different stage fig.2.7. This difference in degradation stages in monomer and hydrogel may due to grafted polymer.

Fig.2.7 TGA of AM(a), AMPS(b) and gelatin(c).
2.4 Preparation and Characterization of Hydrogel of AMPS, AM and PVA (Hydrogel III)

2.4.1 Preparation of Hydrogel (III)

The third hydrogel containing 4.68 mM AMPS-Na, 7.03 mM AM, 0.025 g PVA, 0.073 mM KPS and 0.129 mM MBA is prepared and purified using the same method as in hydrogel(II).

The UV-visible spectrophotometer analysis for any unreacted monomer is found that there is no noticeable monomer is left after polymerization.
2.4.2 Characterization of hydrogel (III)

2.4.2.1 FT-IR analysis of Hydrogel(III)

The cross-linked structure of the hydrogel(III) can be understood by comparing the IR spectra of PVA, AM, AMPS and hydrogel in fig.2.9(a-d). In case of native PVA (fig.2.9 a), the absorption band around 3716 cm\(^{-1}\) is due to stretching vibration of O-H bond and 2918 cm\(^{-1}\) is due to C-H stretching. The characteristic absorption band for AM (fig.2.9 b) is observed in 3723 (N-H stretching), 3161 (C-H stretching), 1676 (C=O stretching) and 1595 cm\(^{-1}\) (for –CH=CH\(_2\) group). In case of native AMPS (fig.2.9 c) the characteristic absorption bands for N-H, C-H, C=O stretching, -CH=CH\(_2\), SO group are observed at 3662, 2933, 1668, 1525 and 1047 cm\(^{-1}\) respectively. The IR spectra of the polymer (fig.2.9d) shows the combined spectral feature of various functional groups of monomers. The absorption band around 3633 cm\(^{-1}\) is due to the stretching vibration of O-H and N-H. The C-H stretching for AM, AMPS-Na, PVA is observed at 2781 cm\(^{-1}\) to 3164 cm\(^{-1}\) and the N-H bending and C-N stretching is at 1541 cm\(^{-1}\) and 1211 cm\(^{-1}\) respectively. The C=O stretching for AM, AMPS-Na and MBA is observed in 1687 cm\(^{-1}\). The characteristic absorption peak of AMPS-Na units can be seen at 1043 cm\(^{-1}\) due to the SO group. This observation suggested for the formation of cross-linked structure of the gel.
2.4.2.2 Scanning Electronic Microscope (SEM) of Hydrogel(III)

The SEM micrograph of AMPS, AM, PVA and hydrogel(III) are depicted in fig.2.10(a-e). From the fig.2.10 (a) and (c) it is observed that the morphological surface of AMPS and PVA are rough, heterogeneous but AM has a smooth surface (b). The scanning electron micrograph of prepared hydrogel(III) is shown in fig.2.10 (d and e) at different magnification. From the micrograph it is observed that the morphological
surface of the hydrogel is heterogeneous in nature having some pores. The porosity nature of hydrogel may be due to grafting of PVA on AM-AMPS chain.

Fig. 2.10 SEM of AMPS (a), AM(b), PVA(c) and hydrogel(III) (d,e)
2.4.2.3 Thermo Gravimetric Analysis of Hydrogel

The thermo gravimetric analysis (TGA) of hydrogel(III) is depicted in fig.2.12. The thermogram shows four step weight loss. 9.49% weight loss is observed between 10 to 210^0C which may be due loss of water molecules. Second weight loss at 220^0 to 260^0 C (4.59 % weight loss) and third at 260^0 to 340^0 C (23.1212 % weight loss) are observed may be due to degradation of functional groups such as amide, sulfonic, amine of the macromolecular chain by dehydration and generation more stable group. The fourth weight loss is due to final degradation of hydrogel is and it is observed from 340^0-500^0C. But the degradation behaviour of monomers is different. The monomers are degraded in different stages as shown in fig.2.11. These different degradation stages may indicate that the back of the AM - AMPS chain is grafted to PVA.

Fig.2.11 TG of PVA(a), AMPS(b) and AM(c)
Fig. 2.12 TG of hydrogel(III)