Diffusion Mechanism of Poly (N-cyclohexyl acrylamide -co-Acrylamide / [3- (Methacryloylamino) propyl] trimethylammonium chloride) Hydrogels

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Abstract

In the present study, 3-(Methacryloylaminopropyl) trimethylammonium chloride, acrylamide and N-cyclohexylacrylamide monomeric unit containing hydrogels were synthesized by free radical copolymerization using MBA as cross-linker APS as initiator in methanol/water medium at 60^0C. The synthesized hydrogel was confirmed by IR spectroscopy. The XRD analysis indicated that the hydrogel exhibited more amorphous and less crystalline in nature. SEM analysis showed sponge like morphology. TGA analysis showed double stage decomposition and stability up to 270^OC. The swelling behavior of hydrogels increased with increasing amount of MPTMACl content. At higher content of MPTMACl, the swelling rate decreased due to the extent of cross linking occurring during the synthesis of hydrogel. The effect of temperature on swelling increases with increasing temperature up to 30^OC and then decreased due to reduction in segmental mobility of polymeric chain at higher temperature.

Introduction

Hydrogels are three-dimensional polymer network containing hydrophilic groups which can absorb more amount of water. Also, they are very sensitive to pH, temperature, light and ionic strength. Due to presence of ionic groups [COO^- , NH_2, SO_3^- , $N^+(CH_3)_3$] in the polymer matrix, the equilibrium swelling is increased. The increase in equilibrium swelling is also due to the parameters such as hydrophilic/hydrophobic interaction, degree of crosslinking, degree of ionization and interaction of counterions. The swelling behavior of poly (N-cyclohexylacrylamide-co-Acrylamide/AMPSNa) gold nanocomposite hydrogels was increased with increasing amount of AMPSNa ionic content. 3-(Methacryloylaminopropyl) trimethylammonium chloride, cationic monomer is used to prepare superabsorbent hydrogels . Hydrophilic groups containing hydrogels are in more resemblance to natural living tissues than the synthetic biomaterials. MPTMA Cl based ionomers showed good corrosion inhibitor efficiency 99% of mild steel in NaCl solution [1].

In the present investigation, we report the synthesis of poly (N-cyclohexylacrylamide- co - Acrylamide / 3- (Methacryloylaminopropyl)trimethylammonium chloride) gold nano composite hydrogels via free radical polymerization using N-cyclohexylacrylamide, Acrylamide, 3-(Methacryloylamino propyl) trimethyl ammonium chloride (PMTMACl) monomers, MBA as cross-linker and APS as initiator in methanol/water medium at 60^0C. The synthesized gold nanocomposite hydrogel was characterized by IR spectroscopy. The swelling and swelling kinetics of hydrogels were evaluated.

Experimental

Preparation of N-cyclohexylacrylamide (NCA)

The monomer N-cyclohexylacrylamide was prepared by the reaction of Cyclohexanol with acrylonitrile [1]. N-cyclohexylacrylamide was recrystallized in warm dry benzene. The white crystals have a m.p.115^0C and the yield was 87%.

Synthesis of Poly (N-cyclohexyl acrylamide -co-acrylamide / [3- (Methacryloylamino) propyl] tri methyl ammonium chloride) Hydrogels

Free-radical crosslinking copolymerization was carried out in methanol /water mixture as the polymerization solvent, at 60^0C in the presence of AIBN as initiator and MBA as crosslinker.Aqueous solution containing NCA (0.5g), AM (0.5g), MBA (0.050g), AIBN (0.050g), MPTMACl (0.1, 0.3, 0.5 and 0.7g), were prepared in methanol/water mixture. After bubbling nitrogen for 30 min, the contents were placed in thermostatic water bath at 60^0C and the polymerization was conducted for 1 day. After the reaction, the resulting hydrogels were cut into pieces of 3-4mm long. The extracted hydrogels were dried in vacuum oven at 50^0C to constant weight for further use. Hydrogels feed compositions are shown in Table-1.

Table- 1: Preparation of Hydrogels with varying amount of MPTMACl

S. No	Wt. of NCA (g)	Wt. of AM (g)	Wt. of MPTMACl (g)	Wt. of AIBN (g)	Wt. of MBA (g)	Methanol/ water (3:1) (ml)
1	0.500	0.500	0.100	0.050	0.050	**20**
2	0.500	0.500	0.300	0.050	0.050	**20**
3	0.500	0.500	0.500	0.050	0.050	**20**
4	**0.500**	**0.500**	**0.700**	**0.050**	**0.050**	**20**

Characterization of Hydrogels

FT-IR Spectroscopy is an effective way to identify organic compounds or polymers with functional groups. For FT-IR measurements Nicolet Nexus-670 FTIR spectrophotometer was used. The hydrogels were dried in vacuum at 50^0C for 48 hrs till constant weight. The dried samples were embedded in KBr disks after being ground into powder. The scanning wave number ranged from 4000 to 500 $cm^{-1.}$ The surface morphology of the freeze-dried hydrogels was studied by Scanning Electron Microscopy. Hydrogels were performed using Hitach, model-JSM-5000 imaging mode at 30 kV with varying levels of magnification. To prepare samples for SEM, the swollen hydrogels were freeze-dried and then sputter coated with gold.

The X-ray diffraction studies of the hydrogels were carried out using a BRUKER diffractometer (Germany), model D8 Advance, employing rotting Cu anode. Thermo Gravimetric Analysis was used to investigate the thermal stability and crosslink densities of the prepared hydrogels. The TGA thermograms were recorded on a Perkin Elmer-7 at a heating rate of 10^0C/min under N_2 protection over a temperature range from room temperature to 800^0C.

Swelling behavior

Swelling experiments were carried out with a view of evaluation the swelling capacity of the hydrogels under investigation in double distilled water. When a hydrogel is brought into contact with water, water diffuses and the hydrogel swells. The swelling behavior of the hydrogels was determined by applying in the following equation

Ds % = [(Ws-Wd/Wd)] X 100 -------(1)

Where **(Ds%)** is the degree of swelling most commonly described as swelling ratio which is expressed as increase in weight / gm of dried hydrogel after keeping in contact with water for selected period of time. Ws is the weight of the swollen gel at a given time and Wd is the weight of the dry gel.

Effect of electrolytes

Different concentrations of NaCl and KCl have been used to see the effect of electrolyte concentration on swelling of hydrogel.The swelling decreased as the concentration of NaCl and KCl increased in the solution. It was due to the fact that an increase of the ionic strength of the solution leads to a decrease in the swelling ratio of the hydrogels. In water, the hydrogel has maximum osmotic pressure, hence the maximum swelling. But when the hydrogel was placed in NaCl and KCl solutions, the osmotic pressure of ionic hydrogel is lower due to Na^+ , K^+ and Cl^- ions.

Effect of Temperature

Temperature dependent swelling of hydrogels was studied from 10^0C to 60^0C. All hydrogels show a temperature responsive swelling behavior due to the association/dissociation of hydrogen bonding within the polymer network.

Diffusion studies

Analysis of the mechanisms of diffusion in swellable polymeric systems has received considerable attention in recent years because of important applications of swellable polymers in biomedical, pharmaceutical, and agricultural engineering. The following equation is used to determine the nature of diffusion of water into hydrogels.

$$F=M_t/M_\infty=kt^n \quad .... (2)$$

Results and Discussion

Synthesis of Poly (N-cyclohexyl acrylamide -co-acrylamide / [3-(Methacryloylamino)propyl] tri methyl ammonium chloride) Hydrogels

The Figure -1, shows the schematic representation of the Hydrogel

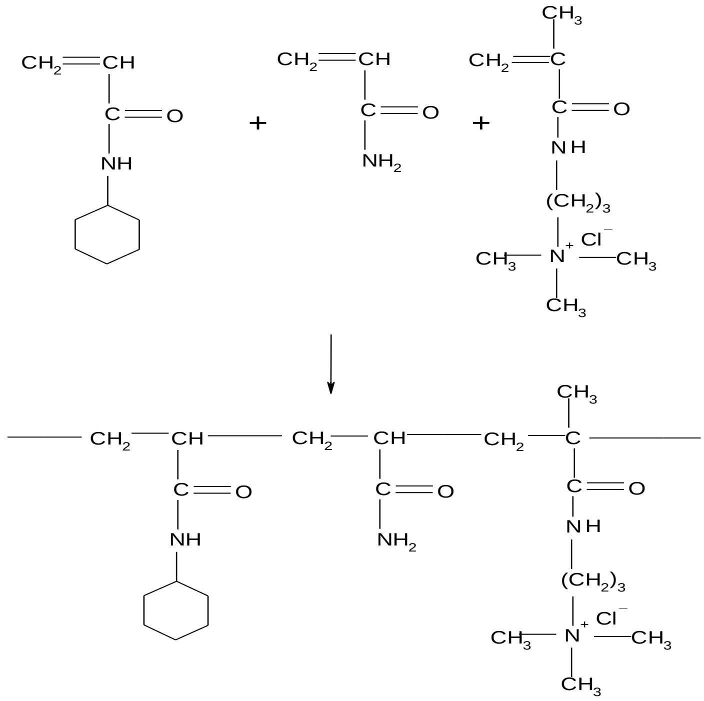


Figure-1: Poly (N-cyclohexyl acrylamide -co-acrylamide / [3- (Methacryloylamino) propyl] tri methyl ammonium chloride) Hydrogels

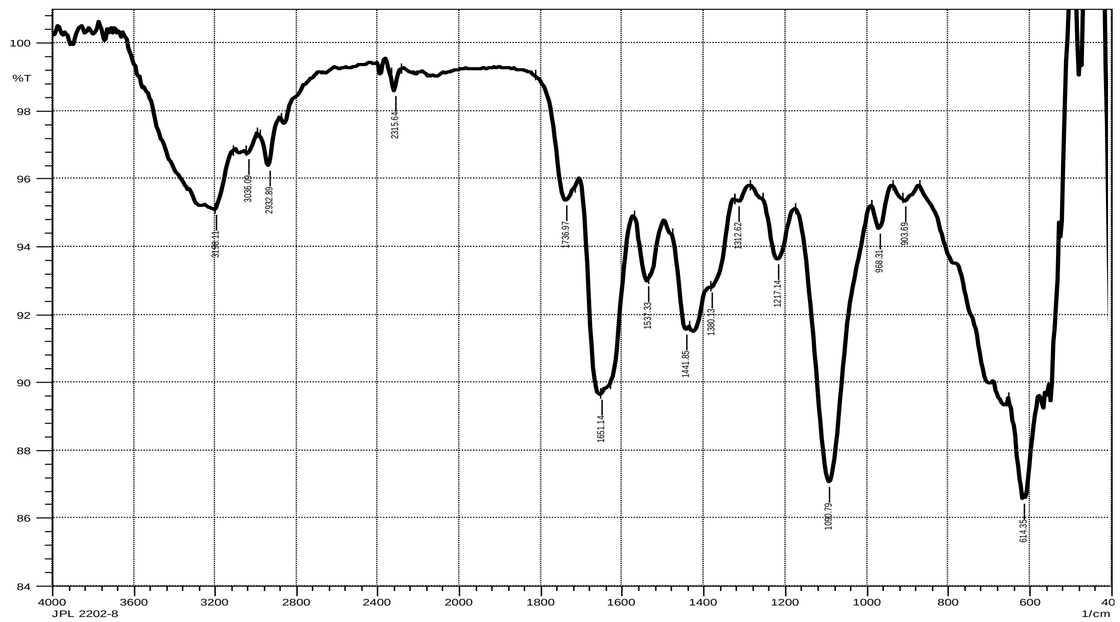


Figure-2: FT-IR spectrum of Poly (N-cyclohexyl acrylamide -co-acrylamide / [3(Methacryl oylamino) propyl] tri methyl ammonium chloride) Hydrogels

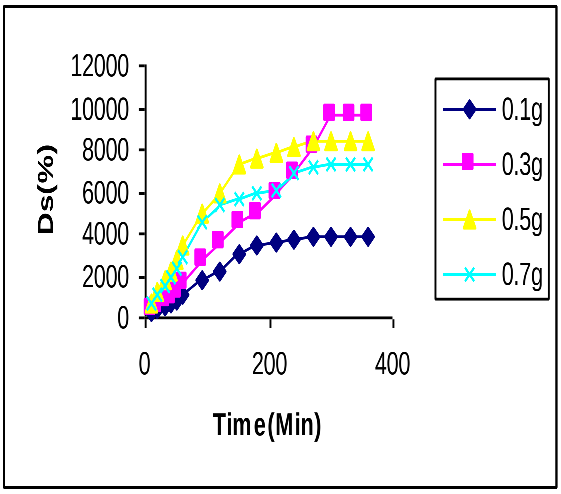
FT-IR Spectral Characterization:

The FT-IR spectrum of poly (NCA-co-AM/MPTMACl) Hydrogel is given in Figure -2. The IR analysis of the hydrogel showed that the presence of peaks corresponding to the functional groups of monomeric units present in the copolymeric hydrogel chain.

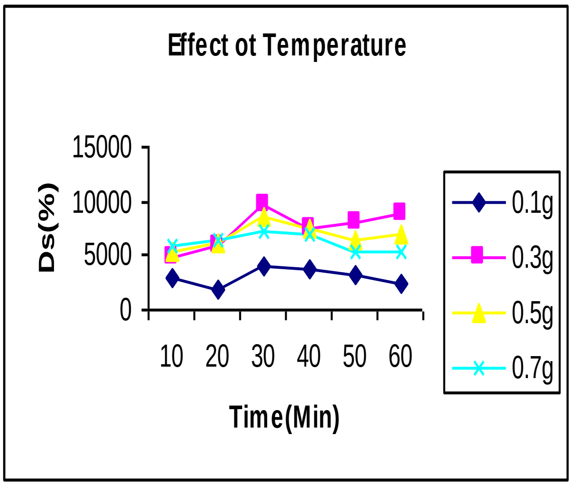
Swelling behavior of poly (NCA-co-AM/MPTMACl) Hydrogels at various temperatures

Equilibrium swelling ratio curves for Poly(NCA-co-AM/MPTMACl) with varying amount of MPTMACl (0.1,0.3 0.5 and 0.7g) in water at various temperatures are given in Figure-3 and 4.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 MPTMACl 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 [8,9].

From the Figure -3, it is noticed that the maximum swelling is 10023.5 for 0.1g, 18009.1 for 0.2g and 16902.2 for 0.3g of MPTMA Cl content at ambient temperature. The extent of swelling of nanocomposites at equilibrium increases with an increase in the concentration of functional ionizable groups in the network. The swelling rate increases up to 0.2g of MPTMA Cl and then decreases 0.3g; this may be due to the extent of crosslinking occurring during the synthesis process.

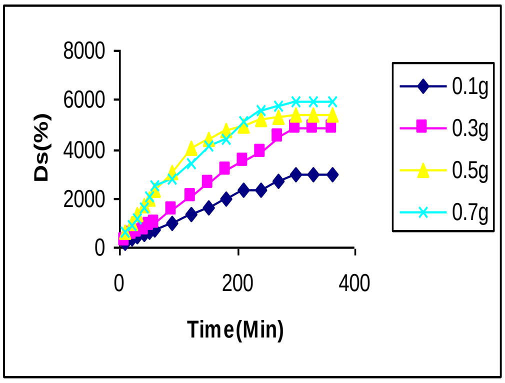


(a)

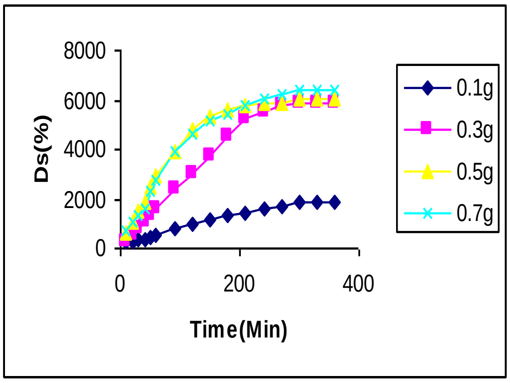


(b)

Figure -3: Poly (N-cyclohexyl acrylamide -co-acrylamide / [3- (Methacryloylamino) propyl] tri methyl ammonium chloride) Hydrogels . (a) Room Temperature (b) Effect of Temperature



(a)



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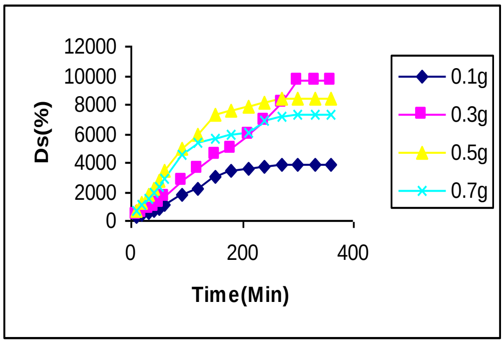

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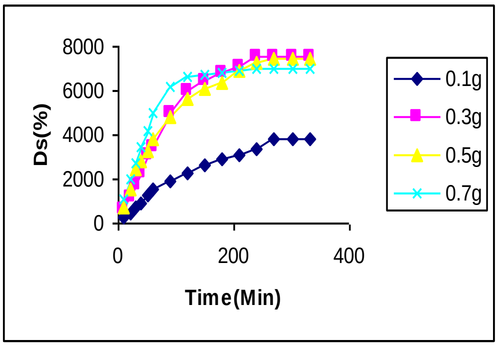

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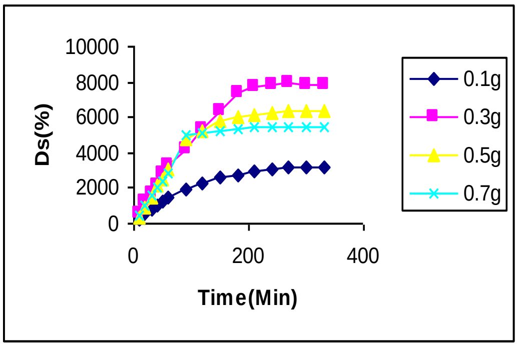

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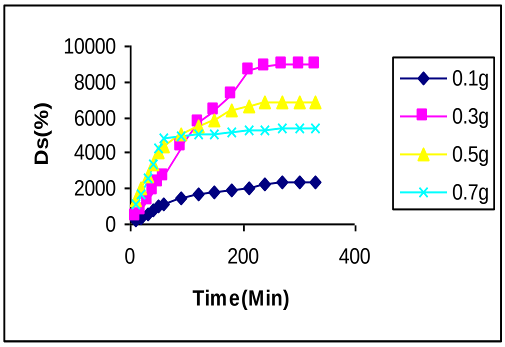


(f)

Figure -4: Poly (N-cyclohexyl acrylamide -co-acrylamide / [3-(Methacryloylamino) propyl] tri methyl ammonium chloride) Hydrogels in water at various temperature(0^{O} C) (a) 10;(b)20; (c)30;(d) 40; (e) 50 ;(f) 60.

Effect of Temperature

Temperature dependent swelling of hydrogels was studied at 100C to 60^{0}C (Table -2).Swelling increases with increase in temperature. This increase is due to high temperature which provide energy to Hydrogel network and created more spaces in it's structure which in turn increased it's water absorption /retention ability. At high temperature, some Hydrogel sample was broken and difficult to strain. This behaviour might be due to it's low gel content.

The effect of temperature on swelling of hydrogels may be (a) swelling decreased with temperature (b)a combined effect of swelling decreasing with temperature down to a minimum value and there after increasing at higher temperature(c)swelling increases with temperature(or)(d)an unusual addition case is a hydrogel which undergoes an increase in swelling with temperature up to a maximum and thereafter a decrease in swelling. The hydrogels are swollen at low temperatures while they are collapsed at high temperatures.

Table-2 : **Maximum swelling of poly (NCA-co-AM/MPTMACl) Hydrogels at various temperatures**

S.NO	Weight of MPTMACl(g)	10^0C	20^0C	30^0C	40^0C	50^0C	60^0C
1	0.1	2975.8	1847.4	**3913.0**	3859.4	3203	2317.8
2	0.3	4844.0	5911.1	**9626.9**	7570	7903.4	8947.7
3	0.5	5362.5	6057.6	**8455.9**	7491.7	6340	6836.5
4	0.7	5909.4	6420.3	**7293.3**	6978.1	5484.3	5351.8

Effect of ionic strength (NaCl and KCl)

Different concentration of NaCl have been used to see the effect of electrolyte concentration on swelling of hydrogel. The swelling decreased as the concentration of NaCl increased in the solution. It was due to the fact that an increase of the ionic strength of the solution leads to a decrease in the swelling ratio of the hydrogels. In water, the hydrogels have maximum osmotic pressure, hence the maximum swelling. But when the hydrogel was placed in NaCl solution, the osmotic pressure of ionic hydrogel is lower due to Na+ and Cl^- ions. This phenomenon was observed in the swelling of ionic hydrogels and attributed to a charge screening effect of the additional cations causing a non-perfect anion-anion electrostatic repulsion. This led to a decrease in osmotic pressure difference between the composite network and the external solution.

In the salt solution of monovalent electrolytes, the swellability decreases in comparison to that in pure deionised water. The extent of swelling was more in the presence on NaCl than in KCl. Disruption and desolvation of the (-C=O, SO_3^-, H_2O) hydrogen bonds allow attractive interchain hydrophobic interaction and hydrogen bonding to dominate. Thus the gel deswells and contracts. The presence of Na^+ and K^+ ions deswell the polymeric gel, being incapable of breaking strong attractive forces between the permanent charges of the polymeric backbone. More over , the smaller hydration sphere of bigger cation is able to penetrate the gel crosslinks where as the smaller ions(Na^+, K^+)with larger hydration sphere were unable to penetrate the gel network, thus deswells the gel.

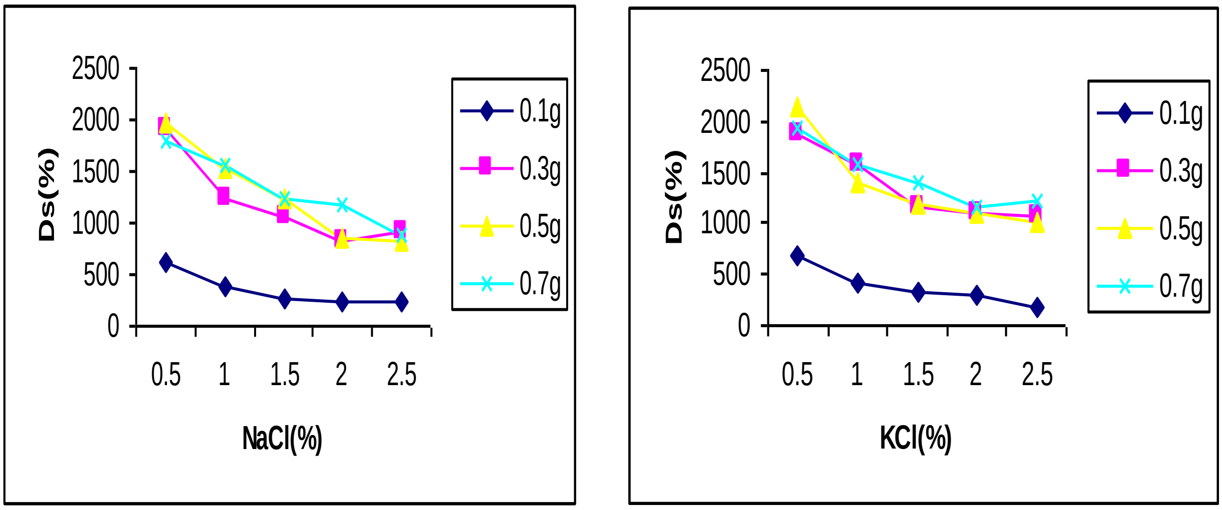


Figure-5: Effect of electrolytes on swelling of Poly (N-cyclohexyl acrylamide -co-acrylamide / [3- (Methacryloylamino) propyl] tri methyl ammonium chloride) Hydrogels

Diffusion studies

The following equation is used to determine the nature of diffusion of water into nanocomposite hydrogels:

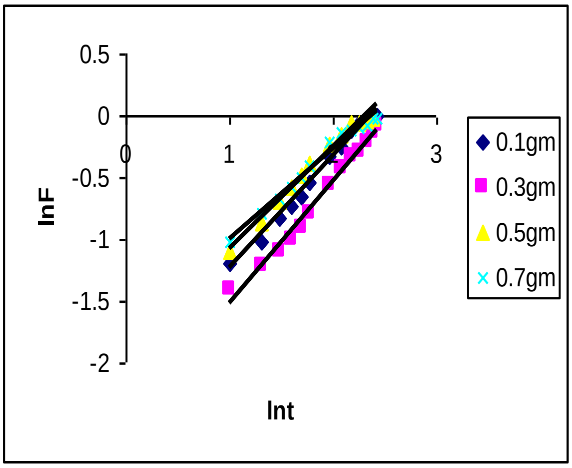
$$F=M_t/M_\infty=kt^n \quad \text{----------------- (2)}$$

Where F is the fractional uptake at time t, Mt and M_∞ denotes the amount of solvent or dyes diffused into the gel at time t and infinite time(at equilibrium),respectively is a constant related to the network, and the exponent n is a number to determine the type of diffusion. For Fickian kinetics in which the rate of penetrant diffusion is rate limiting, n equals 0.5. If during the swelling, a non-Fickian process occurs, n will have a value between 0.5 and 1.0. To obtain n, lnF was plotted versus lnt (values of t should be expressed in seconds) and the slope is the value of n and k is the intercept of the lines. The diffusion of water through polymer network is associated with the physical-chemical properties of the hydrogels. Plot of lnF Vs lnt curves of Poly(NCA-co-AM/ MPTMACl) Hydrogels in water are given in Figure-6, and the n-values are shown in Table-3 It can be observed that these results support non-Fickian character (anomolous). In Non-Fickian the diffusion and relaxation rate comparable. [15, 16].

The value of 'n' higher than 0.5 indicating diffusion of water to the interior of all the hydrogels, follows an anomalous mechanism. The anomalous behavior of the hydrogel is due to the regularity of of the chain and strong interaction via the formation of hydrogen bonding, leading to a compact structure which would prove the anomalous aspects of diffusion even for a molecule as small as water [17].

Table-3:. Maximum swelling and diffusion parameters of poly (NCA-co-AM/MPTMACl) Hydrogels in distilled water

S.No.	Weight of MPTMACl (g)	Maximum Ds (%)	n	k
1	0.1	3913	0.91	**-2.14**
2	0.3	9626.9	0.98	**-2.49**
3	0.5	8455.9	0.82	**-1.89**
4	**0.7**	**7293.3**	**0.73**	**-1.72**



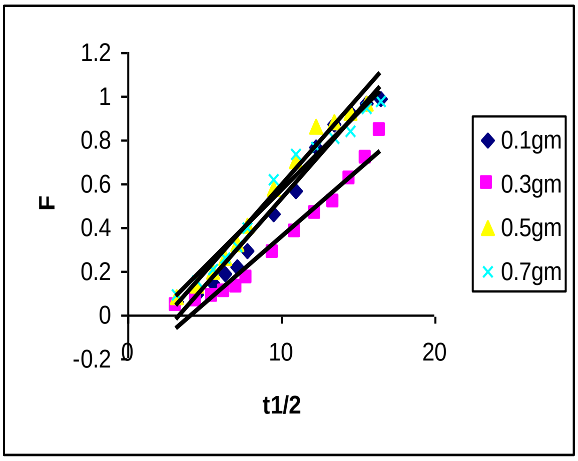
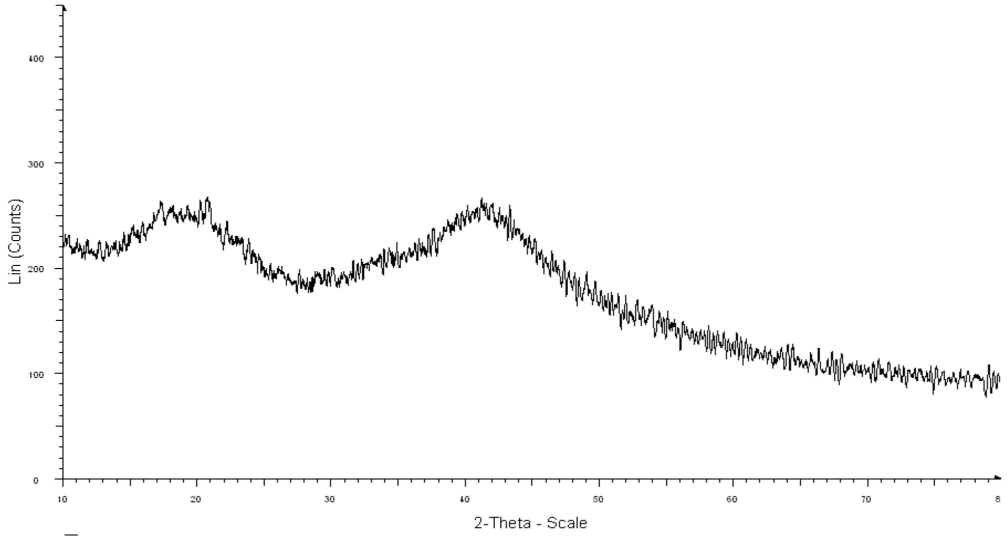


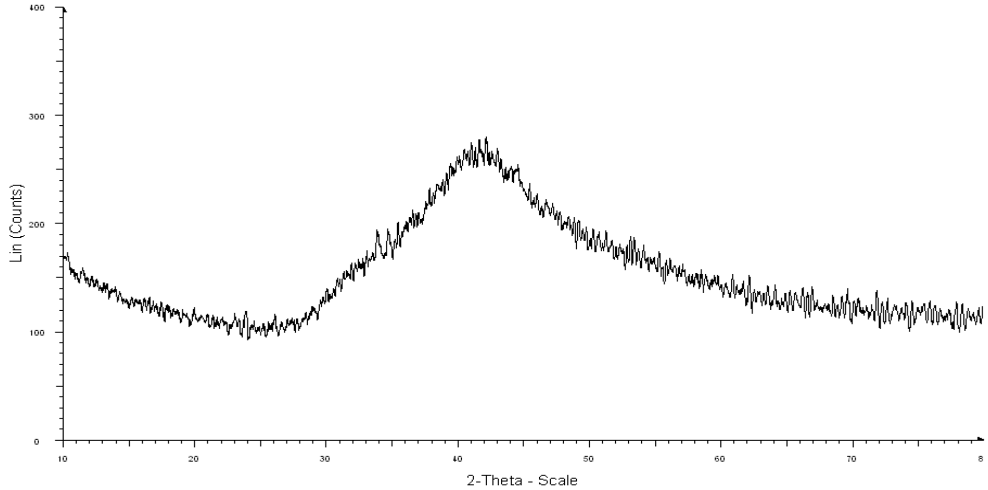
Figure-6: Plots of lnF Vs – lnt and F Vs $t_{1/2}$ curves of Poly(NCA-co-AM/MPTMACl) Hydrogels in distilled water.

XRD Studies:

The XRD patterns of Poly (NCA-co-AM/ MPTMACl) are given in Figure -7 containing different content of MPTMACl. There are two different peaks, are observed at 2θ : 21 & 41 with different intensity. These peaks showed a peak broadening and it conforms that the Hydrogels are more amorphous and less crystalline in nature. When the content of MPTMACl is 0.3g, the peak intensity also varies with more peak broadening. Therefore 0.3g of MPTMACl containing Hydrogel is more amorphous than 0.1g of MPTMACl containing Hydrogel. Also it conform that more the amorphous more will be the swelling [2-4].



(a)



(b)

Figure-7: XRD patterns of Poly (NCA-co-AM/MPTMACl) (a) 0.1g (b) 0.3g of MPTMA Cl

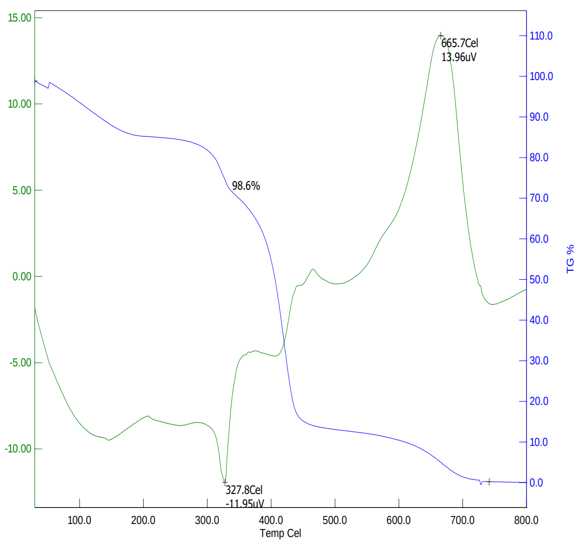
Thermogravimetric Analysis

The TGA plots of Poly (NCA-co-AM/MPTMACl) Hydrogels are given in Figure-8 and the stages of decomposition temperature and weight loss at various levels are given in Table-4. The initial weight loss of the Hydrogel containing 0.1g and 0.3g of MPTMACl are 17 and 9 respectively. The initial weight loss is due to the evaporation of free water and inter layered water present in the sample.The first stage and the second stage is attributed to the thermal decomposition of the amide group of MPTMACl and the decomposition of crosslinker respectively. The final stage [FDT] is due to the breakdown of the polymer backbone.The residual weight percentage is 17 and 15%. From the data, we can conclude that 0.3g of MPTMACl Hydrogels is slightly more stable than 0.1g of MPTMACl Hydrogel .

Table -4: Thermal behavior of Poly (NCA-co-AM/MPTMACl) Hydrogels

Hydrogels	(IDT) (Initial weight loss %)	Decomposition Temperature (^{0}C) (% weight loss)			Residual weight %	(FDT)
		Stage 1	Stage 2	Stage 3		
0.1 g of MPTMACl	175 (17)	275 (12)	370 (10)	440 (44)	17	630
0.3 g of MPTMACl	150 (9)	190 (13)	310 (24)	430 (39)	15	700

IDT: Initial decomposition Temperature ; FDT: Final decomposition Temperature

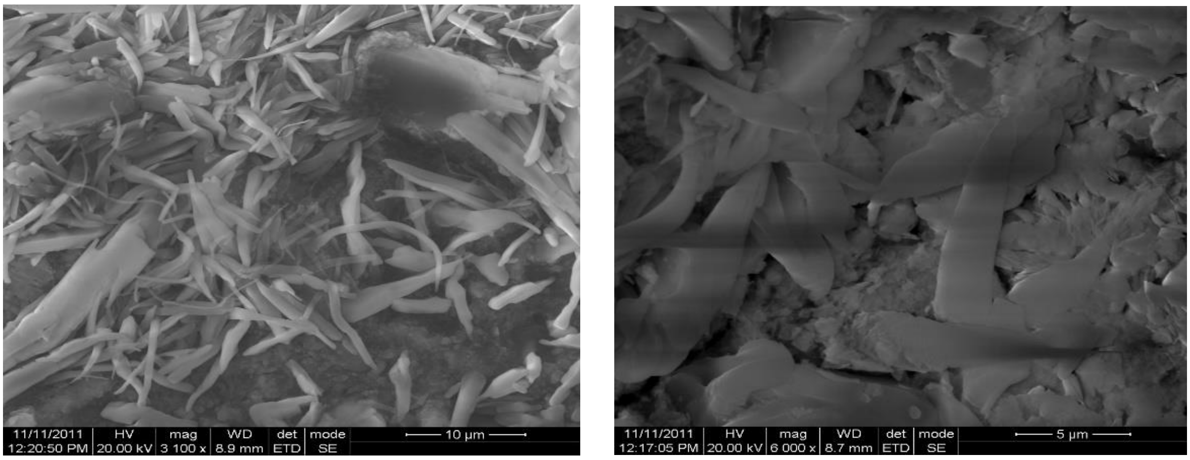


(a) (b)

Figure -8 : TGA plots of Poly (NCA-co-AM/MPTMACl)Hydrogels (a)0.1 g (b) 0.3 g of MPTMACl

SEM analysis

The SEM analysis of poly (NCA-co-AM/MPTMACl) Hydrogels are shown in Figure-9. It showed stick shaped morphology along with sponge loke structure. 0.3 g of MPTMA Cl has more sponge like structure uniformly spread throughout the matrix and hence more swelling.



(a) **((b)**

Figure -9: SEM images of Poly (NTA-co-AM /MPTMACl)Hydrogels (a)0.1 g(b) 0.3 g of MPTMACl

Conclusions

The 3-(Methacryloylaminopropyl) trimethylammonium chloride based hydrogels were synthesized by free radical copolymerization in methanol/water medium at 60^0C. The presence of monomeric units in the hydrogel was confirmed by IR spectroscopy. The surface morphology of hydrogel was studied by SEM analysis indicating sponge like structure. TGA analysis of hydrogel showed double stage decomposition. The swelling behavior of hydrogels increased with increasing amount of MPTMACl content. At higher content of MPTMACl, the swelling rate decreased.

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