



## Preparation of Hydrogels of Methacrylamide with Mono and Dicarboxylic Acids: Investigation of Their Swelling Behaviour

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### Abstract

Methacrylamide (MAAm) hydrogels were synthesized with mono- (crotonic acid, CrA) and dicarboxylic (maleic acid, MAA) acids via radical copolymerization, utilizing potassium persulfate (KPS) as the initiator and N, N'-methylenebisacrylamide (MBAAm) as the crosslinker. The swelling behavior of the resulting hydrogels was systematically investigated, with particular focus on the effects of monomer ratio, initiator and crosslinker concentrations, as well as polymerization temperature. These parameters were optimized to maximize the swelling ratio. For poly(MAAm/CrA) hydrogels, the formulation containing 85/15 MAAm/CrA (mol/mol), 2 mol% KPS, 1 mol% MBAAm, and synthesized at 55 °C exhibited the highest swelling capacity (480%) in distilled water. In contrast, for poly(MAAm/MAA) hydrogels, the composition of 75/25 MAAm/MAA (mol/mol) with 1 mol% KPS, 1 mol% MBAAm, and polymerized at 55 °C showed a maximum swelling of 1100%. Further investigations explored the influence of pH, temperature, and electrolyte concentration and type on the swelling properties of the hydrogels prepared under optimized conditions. Both hydrogels demonstrated peak swelling behavior at pH 7, with their swelling profiles varying in response to changes in temperature, electrolyte concentration, and electrolyte type. Swelling kinetics studies revealed that the MAAm/CrA hydrogel exhibited Fickian diffusion in distilled water at room temperature, while the MAAm/MAA hydrogel followed a non-Fickian diffusion mechanism. Scanning electron microscopy (SEM) analysis indicated that the hydrogels synthesized under optimal conditions possessed a porous and well-organized network structure.

**Keywords:** Poly(methacrylamide-co-crotonic acid), Poly(methacrylamide-co-maleic acid), Hydrogels, Swelling

### 1. INTRODUCTION

Hydrogels, discovered approximately sixty years ago, have captivated the scientific community and continue to inspire research due to their broad range of applications. These polymers possess the remarkable ability to absorb significant quantities of water or biological fluids within their three-dimensional, cross-linked networks [1,2], offering both advanced absorption capabilities and high storage capacity. Cross-linked polymers that can absorb solvents, with a solvent uptake of at least 20% of their mass, are classified as xerogels. When the solvent absorbed is water, these materials are referred to as hydrogels. Hydrogels feature a three-dimensional network with cross-links that allow them to swell in water without dissolving [3]. If the water content exceeds 100% of their mass, the hydrogel is classified as a superabsorbent polymer [4,5].

The substantial amount of liquid retained within hydrogels permits the diffusion of biological and chemical molecules, a property considered essential for applications such as biosensors and drug delivery systems [6]. Additionally, hydrogels find widespread use in various technological fields [7]. Hydrogels can be synthesized via a range of production methods [8] and exhibit the ability to respond to external physical, chemical, and biological stimuli, such as temperature [9,10], pH [11,12], light [13], and electric fields [10,14]. This responsiveness has led to their designation as "smart hydrogels." It has been demonstrated that the three-dimensional cross-linked structure of hydrogels, their cross-linking density, swelling ratio, environmental pH, and the synthesis medium significantly influence their properties [15-17]. The swelling behavior of environmentally sensitive hydrogels can be affected by specific stimuli, including the chemical structure of the monomers used in their synthesis, as well as factors such as temperature, ionic strength, pH, electric fields, and magnetic fields. Other specific stimuli may also impact the swelling characteristics of different types of environmentally sensitive hydrogels [9,18].

In this study, methacrylamide (MAAm) hydrogels were synthesized with monocarboxylic acid (crotonic acid, CrA) and dicarboxylic acid (maleic acid, MAA) via radical copolymerization, using potassium persulfate (KPS) as the initiator and methylenebisacrylamide

(MBAAm) as the crosslinker. The swelling behavior of the resulting hydrogels was systematically investigated. The effects of monomer ratio, initiator concentration, crosslinker concentration, and polymerization temperature on the swelling capacity were studied, and the polymerization conditions were optimized to achieve maximum swelling. Furthermore, the impact of pH, temperature, electrolyte concentration, and electrolyte type on the swelling behavior of the hydrogels synthesized under optimal conditions was examined. Swelling kinetics studies for poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels were carried out in pure water at room temperature. Based on these studies, the diffusion parameters of both hydrogels were determined.

## 2. MATERIALS AND METHODS

### 2.1 Materials

The monomers used in the synthesis of the hydrogels were methacrylamide (MAAm), crotonic acid (CrA), and maleic acid (MAA). N,N'-methylenebisacrylamide, utilized as the crosslinker, was obtained from Merck and used without further purification. Potassium persulfate (KPS), serving as the initiator, was of Aldrich brand and was also used as supplied, without any purification. Other chemicals, including NaCl, MgCl<sub>2</sub>, and AlCl<sub>3</sub>, were purchased from Merck and used directly without additional purification.

### 2.2 Preparation of Hydrogels

Maintaining a constant total monomer amount ( $n_T = 0.005$  mol), mixtures of MAAm/CrA and MAAm/MAA monomers were prepared at various molar ratios (100/0, 95/5, 85/15, 80/20, 75/25, 65/35, 60/40, 55/45, 50/50) and placed into separate 10.0 mL tubes. After adding 1 mol% KPS and 1.5 mol% MBAAm to these mixtures, the total volume was adjusted to 5.0 mL with distilled water. The mixtures were stirred until the initiator, crosslinker, and monomers were fully dissolved. The resulting solutions were then transferred into coded plastic pipettes with a 4 mm diameter and immersed in a water bath at 45°C for 24 hours. After 24 hours, the pipettes were cut open, and the hydrogels formed were removed and thoroughly washed with distilled water. The synthesized hydrogels were subsequently dried in an oven at 45°C for 48 hours.

### 2.3 Swelling Studies

Three samples each of the dried poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels were weighed and placed into six separate conical flasks, each containing 25 mL of distilled water. The mouths of the Erlenmeyer flasks were sealed with parafilm. After 24 hours, the swollen poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels were removed, placed on blotting paper to dry, and then weighed. The swelling percentages of all three hydrogel samples of the same type were calculated gravimetrically using the following equation:

$$\text{Percentage of swelling (\%S)} = [(m_t - m_0) / m_0] \times 100 \quad (1)$$

- $m_0$  is the initial mass of the dry hydrogel,
- $m_t$  is the mass of the swollen hydrogel after time  $t$ .

The effects of pH (3–10), temperature (10°C–40°C), electrolyte type (NaCl, MgCl<sub>2</sub>, AlCl<sub>3</sub>), and concentration (0.1–1.5 M) on swelling were investigated.

### 2.4 Swelling kinetics

The swelling values of poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels, prepared under optimal conditions, were determined gravimetrically at room temperature in a distilled water medium at various time intervals (5, 10, 15, 20, 25, 30, 35, 40, 45, 60, 75, 90, 120, 150, 180, 240, 300, 360, 420, 600, 1200 minutes). The time of immersion of the hydrogels in distilled water was designated as  $t=0$  minutes. The experiments were concluded when the swelling values of the hydrogels, monitored dynamically, stabilized without further change over time. The resulting swelling curves were analyzed to ascertain the type of solvent diffusion occurring within the prepared hydrogel structures. Initially, the  $M_t$  and  $t$  values in the early absorption phases, characterized by reduced absorption values ( $F \leq 0.6$ ), were identified. Then;

$$M_t = k \cdot t^n \quad (2)$$

$$F = M_t/M_\infty = k \cdot t^n \quad (3)$$

$M_t$ ; mass of solvent contained in the hydrogel at time  $t$ ,

$M_\infty$ ; mass of solvent contained in the hydrogel that has reached equilibrium,

$n$ ; an exponent indicating the type of diffusion of the solvent in the hydrogel,

$k$ ; constant that varies depending on the network structure of the gel,

$F$ ; is the ratio of the solvent absorbed by the gel at time  $t$  to the solvent in the equilibrium swelling and is defined as the swelling fraction.

Using the equations, the  $\ln(M_t) - \ln(t)$  graph was drawn for equation 2. The  $n$  diffusion exponent was found from the slopes of these graphs created for both gels, and the  $k$  network structure parameter was found from the cut-off values.

## 2.5 Characterization of hydrogels

### Scanning electron microscopy (SEM)

After the surfaces of the synthesized poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels, as well as the poly(MAAm) hydrogel samples, were coated with gold, micrographs were obtained using a LEO 440 microscope.

### Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the hydrogel samples was conducted using a PERKIN ELMER model thermal analysis instrument over a temperature range of 25 to 700 °C, under a helium atmosphere with a flow rate of 20 mL/min. The heating rate was set to 10 °C/min, starting from room temperature.

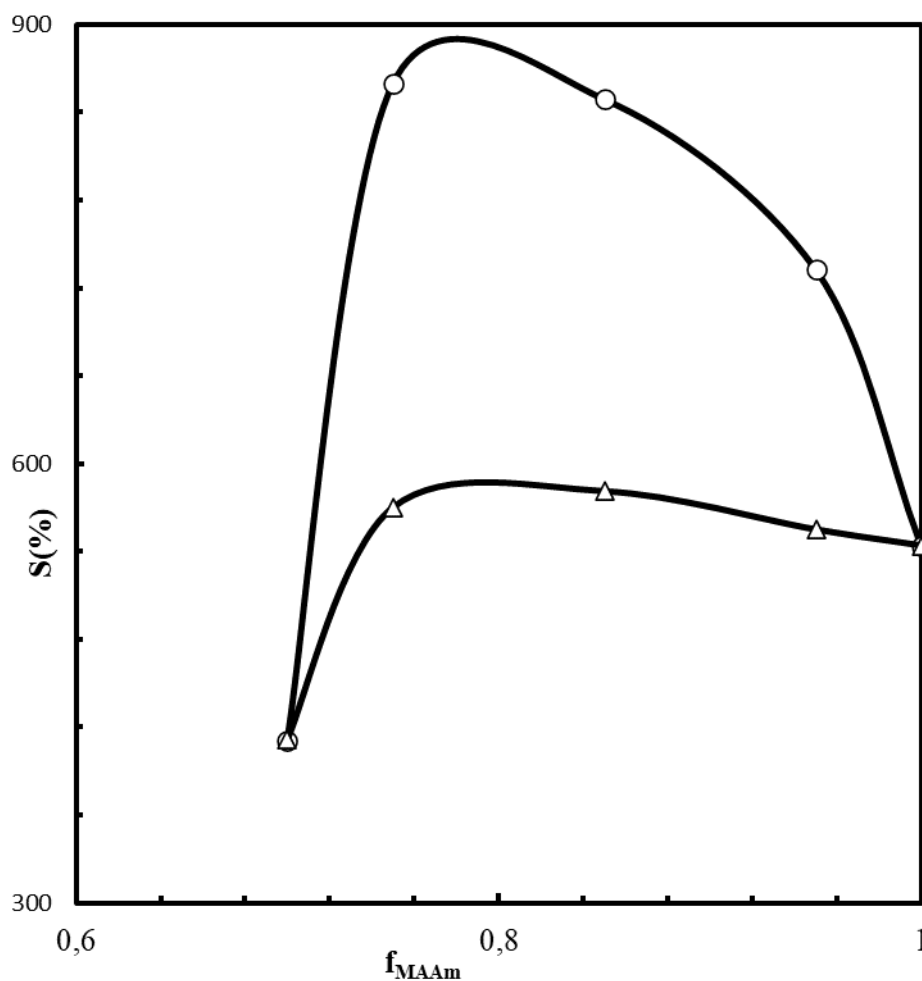
### Fourier transform infrared spectroscopy

ATR-FTIR spectra were obtained using a Perkin Elmer Spectrum 400 instrument for the structural characterization of the synthesized poly(MAAm/CrA), poly(MAAm/MAA) hydrogels, and poly(MAAm) hydrogel samples.

## 3. RESULTS AND DISCUSSION

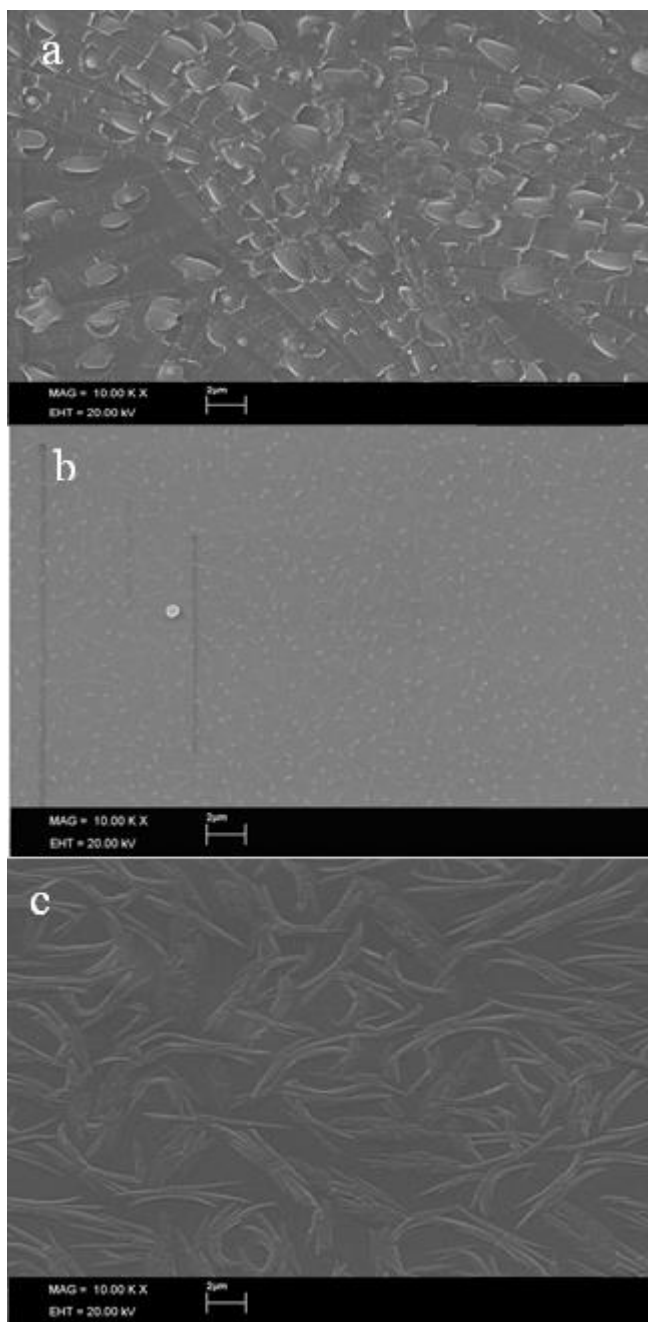
### 3.1 Effect of Monomer Ratio on Swelling

Figure 1 presents the swelling results of poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels synthesized at different monomer ratios and SEM images are shown in Fig. 2 and 3.

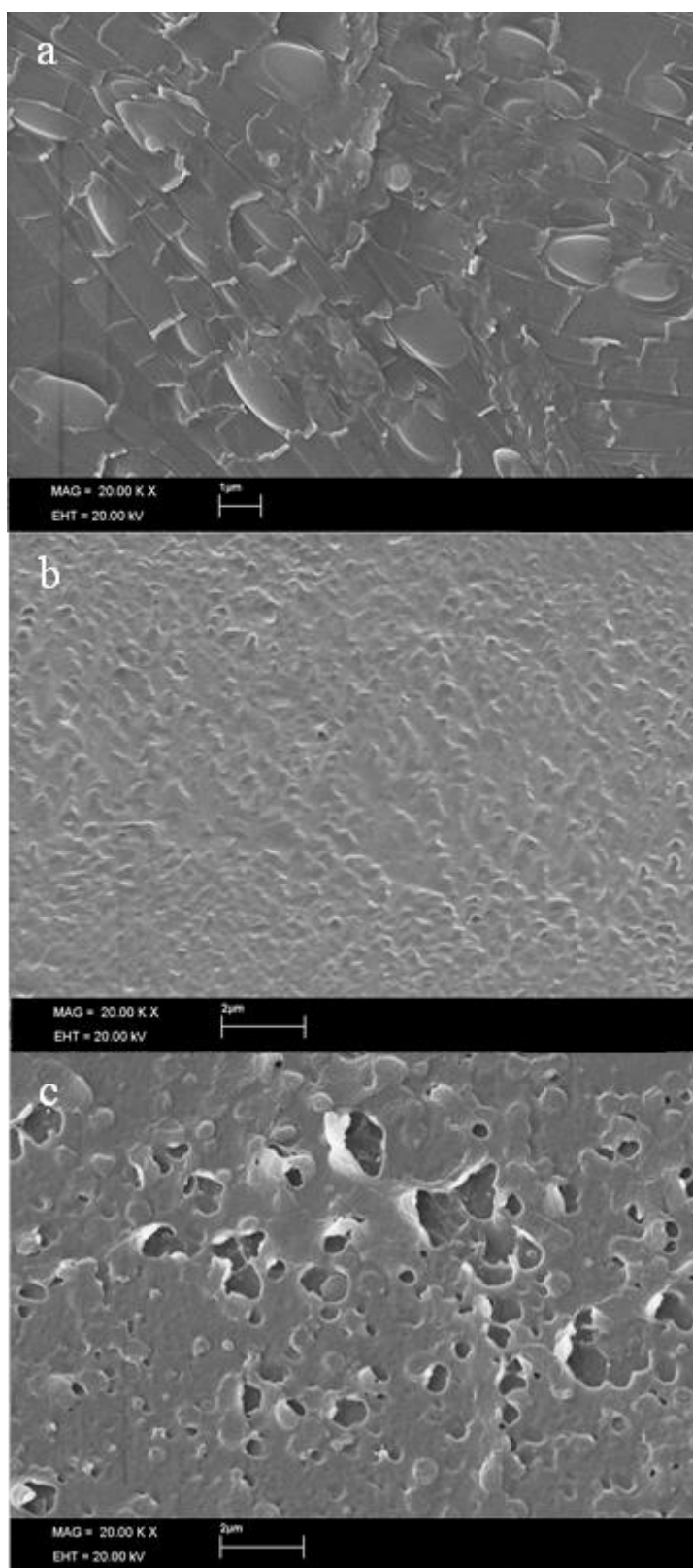


**Fig.1** Effect of monomer ratio on swelling [ $\Delta$ : MAAm/ CrA; o: MAAm/ MAA ( $n_t = 0.005$  mol;  $V_t = 5.0$  ml;  $T = 45$   $^{\circ}C$ ;  $t = 24$  hours, 1 mol% KPS, 1.5 mol% MBAAm)]

As shown in Fig. 1, an increase in the amounts of maleic acid and crotonic acid in the hydrogels leads to a corresponding increase in the swelling ratio. This phenomenon can be attributed to the hydrophilic carboxyl groups, which interact more readily with water and form hydrogen bonds, thereby facilitating greater swelling of the gel. The lower swelling value observed for the CrA gel compared to the MAA gel can be explained by the presence of a monocarboxyl group in crotonic acid, whereas maleic acid contains a dicarboxyl group [9]. The decline in swelling values of the hydrogels beyond the optimal ratio can be attributed to the strong hydrogen bonding between the carboxyl groups of CrA and MAA, which tightly hold the polymer chains together and hinder the diffusion of water molecules [4]. From Fig. 1, the optimal monomer ratio was determined to be 85/15 (mol/mol) for the poly(MAAm/CrA) hydrogel and 75/25 (mol/mol) for the poly(MAAm/MAA) hydrogel. One of the key factors influencing the swelling behavior of a hydrogel is its surface morphology. To investigate this, the structural surface morphologies of poly(MAAm/CrA), poly(MAAm/MAA) hydrogels, and PMAAm hydrogels with different monomer ratios were analyzed using scanning electron microscopy (SEM) (Fig. 2 and Fig. 3).



**Fig.2.** SEM images of poly(AAm/CrA) hydrogels prepared at different MAAm/CrA ratios. a) PMAAm, b) 95/5 MAAm/CrA, c) 85/15 MAAm/CrA



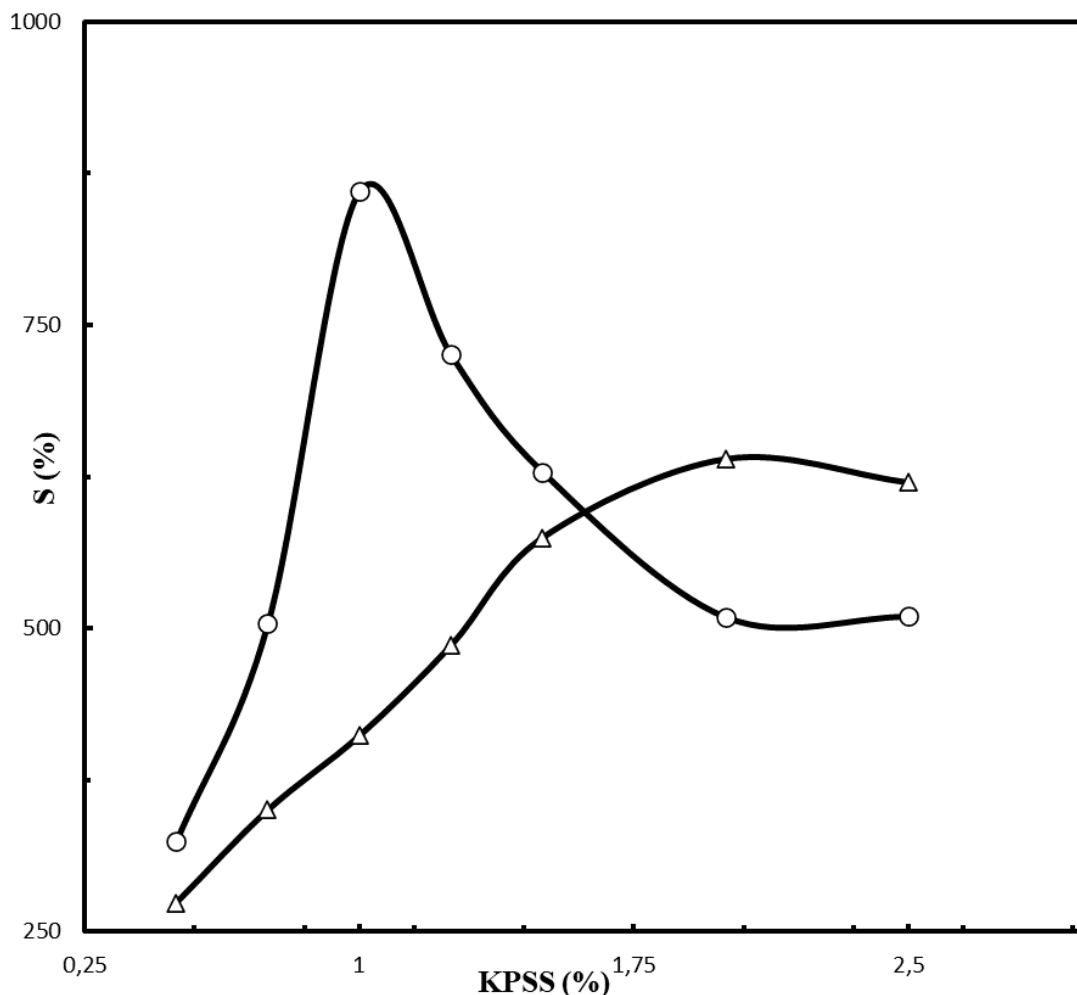
**Fig.3.** SEM images of poly(AAm/MAA) hydrogels prepared at different MAAm/MAA ratios. a) PMAAm, b) 95/5 MAAm/MAA, c) 75/25 MAAm/MAA

In the SEM images of the hydrogels prepared at different monomer ratios, it is evident that the hydrogel with the optimal monomer ratio exhibits a more porous and structured network compared to the hydrogels with other monomer ratios and the polymethacrylamide

hydrogel. The maximum swelling value of the hydrogels at the optimal monomer ratio can be attributed to the enhanced water retention and diffusion capabilities within the porous network structure [9, 12, 18].

### 3.2 Effect of initiator concentration on swelling

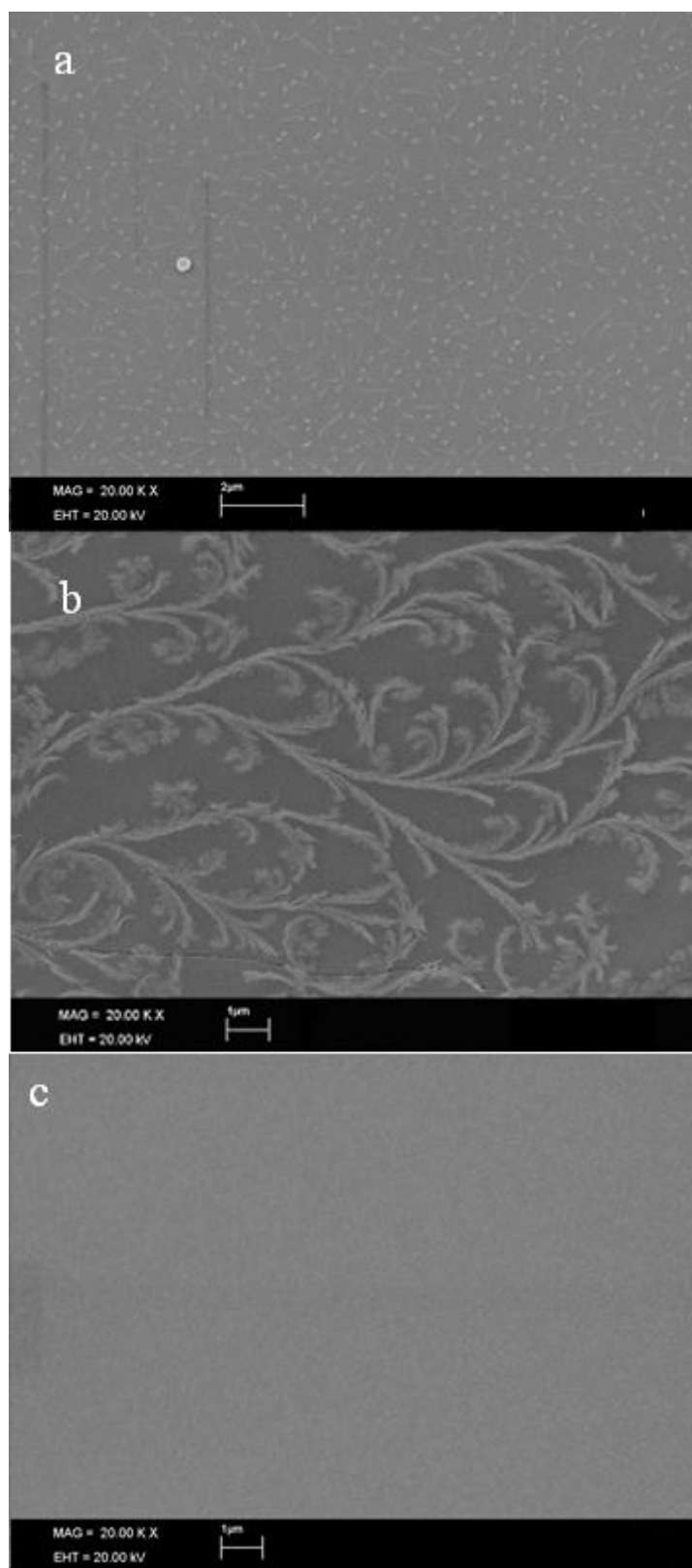
The swelling results of MAAm/CrA and MAAm/MAAM hydrogels synthesized at different initiator concentrations are shown in Fig.4.



**Fig.4.** Effect of initiator concentration on swelling [ $\Delta$ : poly(MAAm/ CrA); o: poly(MAAm/ MAA); nt= 0.005 mol; Wt = 5.0 ml; T = 45 0C; t = 24 h; MBAAm= 1.5%); MAAm/CrA =85/15( mol/mol), MAAm/MAA= 75/25( mol/mol)].

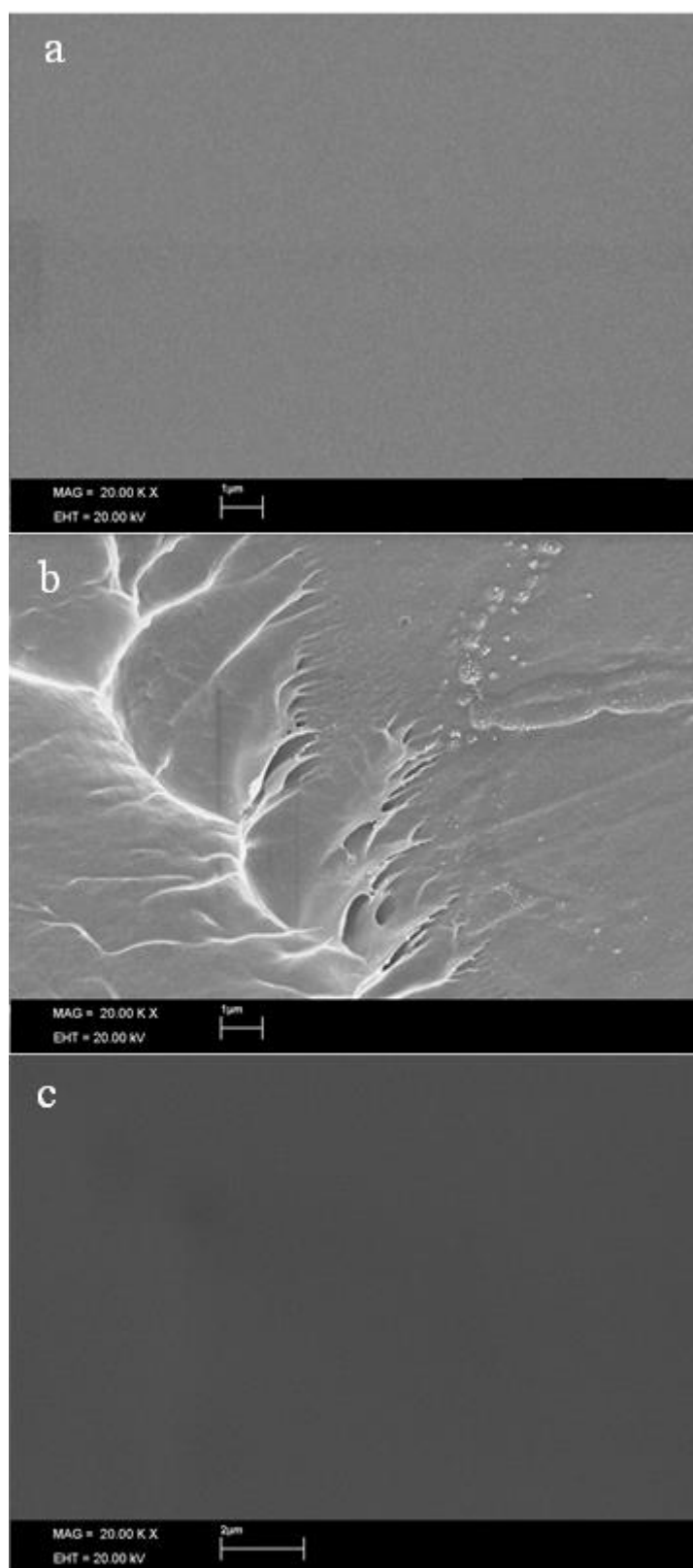
As shown in Fig. 4, when the amount of initiator is varied, the swelling values of poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels increase with the increasing initiator concentration, followed by a decrease after reaching a certain threshold. This behavior can be explained as follows: as the amount of KPS is increased, a greater number of free radicals are generated in the reaction medium. This increase in radicals facilitates the formation of optimal gel chains up to a certain concentration. However, if the initiator concentration continues to rise, the excessive radicals accelerate the gelation reaction, leading to the formation of short-chained hydrogels that terminate quickly. Since these short chains are unable to establish a sufficient network structure, the swelling value consequently decreases [23]. The optimal initiator concentrations were determined to be 2 mol% KPS for the poly(MAAm/CrA) hydrogel and 1 mol% KPS for the poly(MAAm/MAA) hydrogel. Additionally, SEM analyses of the poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels prepared at different KPS concentrations were conducted (Fig. 5 and 6).

As seen in Fig. 5 and 6, the hydrogel surfaces with the optimum KPS ratio are thought to have a network structure compared to the hydrogel surfaces with other KPS ratios. The maximum swelling value of the hydrogels with the optimum KPS ratio can be explained by the fact that water retention and water diffusion are higher in the network structure [19].



**Fig.5.** SEM images of poly(MAMa/CrA) hydrogels prepared at different KPS ratios. a) 1 mol% KPS, b) 2 mol% KPS, c) 2.5 mol% KPS

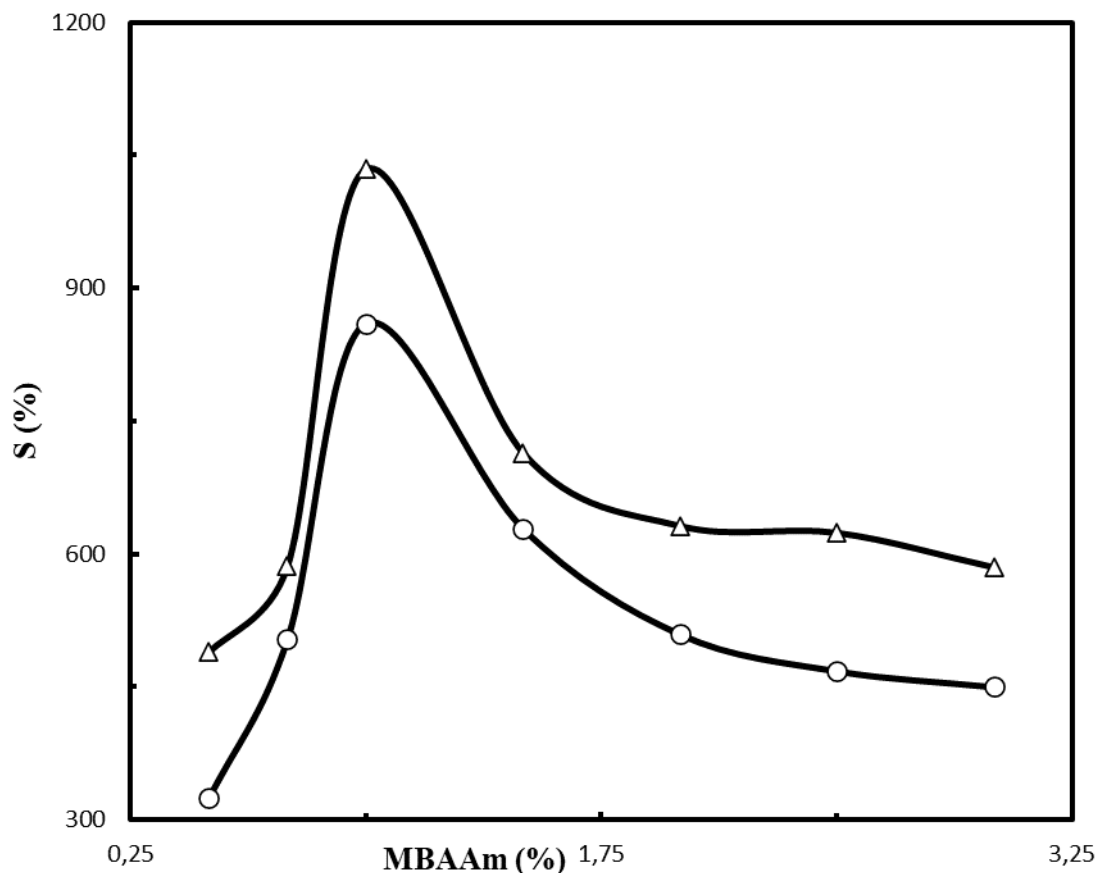




**Fig.6.** SEM images of poly(MAAm/MAA) hydrogels prepared at different KPS ratios. a) 0.5 mol% KPS, b) 1 mol% KPS, c) 2 mol% KPS

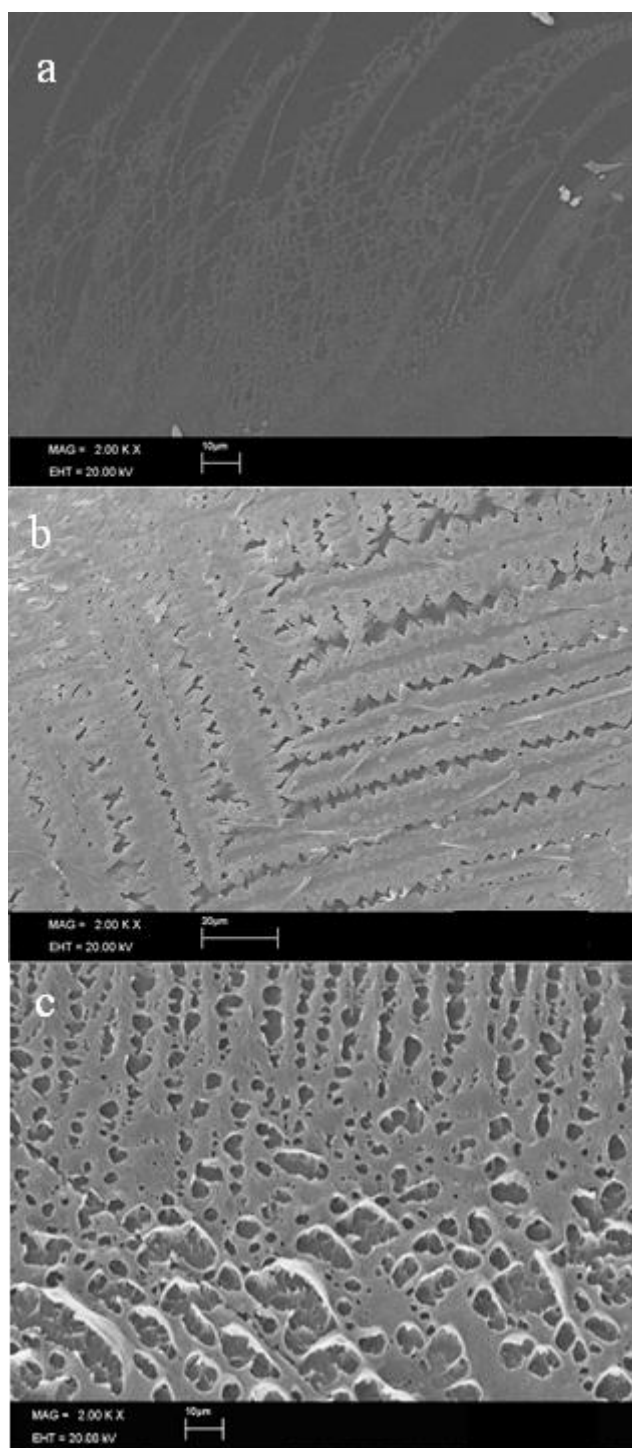
### 3.3 Effect of crosslinker concentration on swelling

The swelling values of MAAm/CrA and MAAm/MAAM hydrogels synthesized at different crosslinker concentrations are shown in Fig 7.

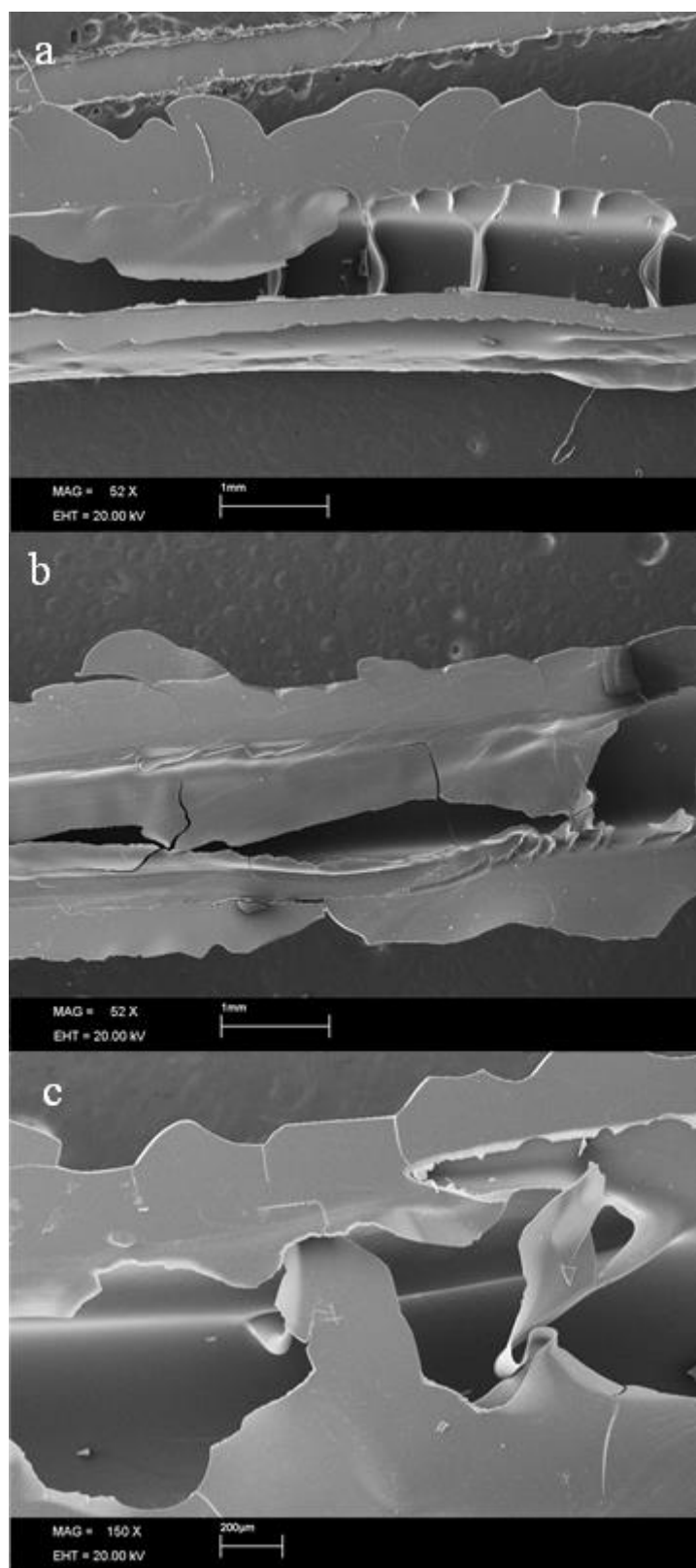


**Fig.7.** Effect of crosslinker concentration on swelling [ $\Delta$ : poly(MAAm/ CrA);  $\circ$ :poly( MAAm/ MAA);  $n_t= 0.005$  mol;  $V_T = 5.0$  mL;  $T = 45^\circ\text{C}$ ;  $t = 24$  hours; MAAm/CrA = 85/15 (mol/mol), 2 mol% KPS; MAAm/MAA= 75/25 (mol/mol), 1 mol% KPS]

As illustrated in Figure 7, when the amount of crosslinker is low, it is insufficient to bind a significant number of radicals during polymerization, leading to a reduction in the swelling values of both hydrogels [19, 20]. The swelling values of the hydrogels increase with the rising crosslinker concentration; however, beyond a certain threshold, the swelling values begin to decrease. This behavior can be explained as follows: an increased amount of crosslinker facilitates the formation of a crosslinked network structure, enhancing water retention and swelling capacity. Furthermore, as noted in the literature, crosslinked polymers are insoluble but can swell to a certain extent in solvents. The swelling rate is closely related to crosslink density; as the crosslink density increases, the degree of swelling of the polymer decreases. In cases of dense crosslinking, the polymer becomes less affected by solvents [4]. According to Figure 7, the optimal crosslinker concentration was determined to be 1 mol% MBAAm for both the poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels. Additionally, surface analyses of the hydrogels prepared at different MBAAm concentrations were conducted (Fig. 8 and 9).



**Fig.8.** SEM images of poly(MAAm/CrA) hydrogels prepared at different MBAAm ratios. a) 1 mol% MBAAm, b) 1.5 mol% MBAAm, c) 3 mol% MBAAm

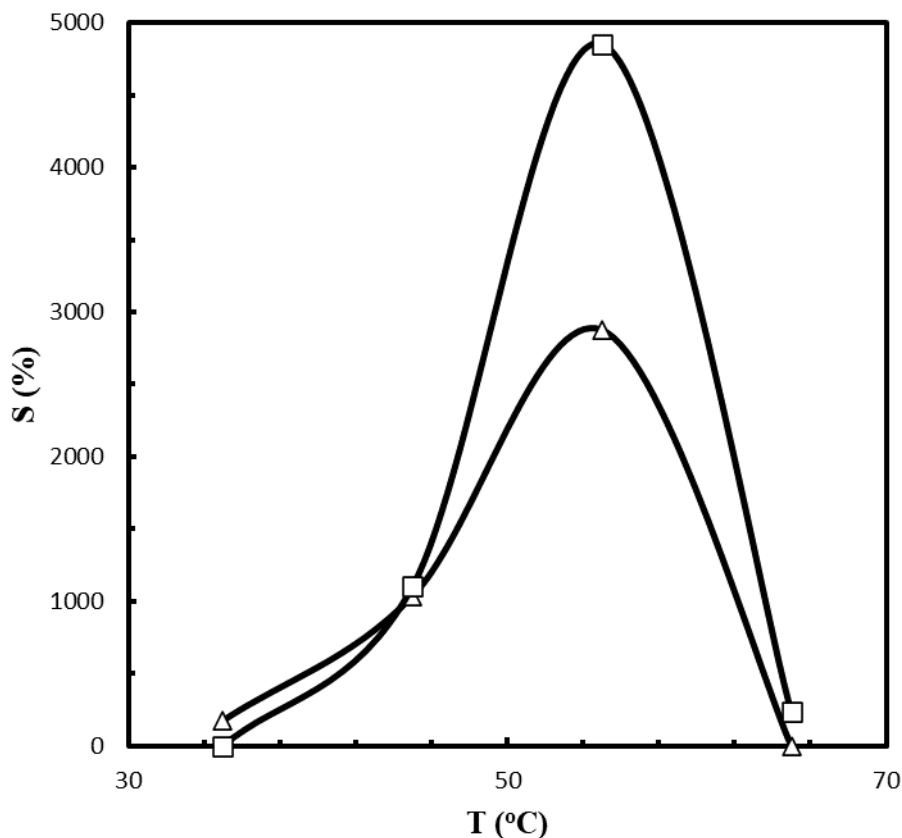


**Fig. 9.** SEM images of poly(MAAm/MAA) hydrogels prepared at different MBAAm ratios. a) 1 mol% MBAAm, b) 1.5 mol% MBAAm, c) 3 mol% MBAAm

As seen in Fig.8 and 9, it is thought that increasing the amount of crosslinker in hydrogels containing MBAAm above the optimum crosslinker ratio increases the crosslink density in the structure and causes the formation of a much tighter network structure, which in turn reduces water absorption [19].

### 3.4 Effect of reaction temperature on swelling

The swelling percentages of poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels synthesized at various reaction temperatures were plotted as a function of polymerization temperature. The resulting data are presented in Fig. 10.



**Fig.10.** Effect of Polymerization Temperature on Swelling [ $\Delta$ : poly(MAAm/ CrA);  $\circ$ : poly(MAAm/ MAA);  $n_t = 0.005$  mol;  $V_t = 5.0$  mL;  $t = 24$  hours; MAAm/CrA = 85/15 (mol/mol), 2 mol% KPS; MAAm/MAA= 75/25(mol/mol), 1 mol% KPS]

As depicted in Figure 10, the swelling values of both hydrogels increase up to approximately 55 °C, after which the swelling values of hydrogels synthesized at higher temperatures begin to decline. It is evident that the optimal reaction temperature for achieving maximum swelling in both hydrogels is 55 °C. At elevated temperatures, the collision rate of molecules in the reaction medium increases, leading to the degradation of some polymer chains due to high-energy initiator radicals, resulting in the formation of shorter chains (chain scission). Consequently, the swelling values decrease, as the short-chain gels formed struggle to establish an effective network structure [20, 21].

### 3.5 Behavior of poly(MAAm/CrA) and poly(MAAm/MAA) Hydrogels Prepared under Optimum Conditions

Swelling behaviors of hydrogels prepared under optimum conditions at different pHs are given in Fig. 11 and 12.

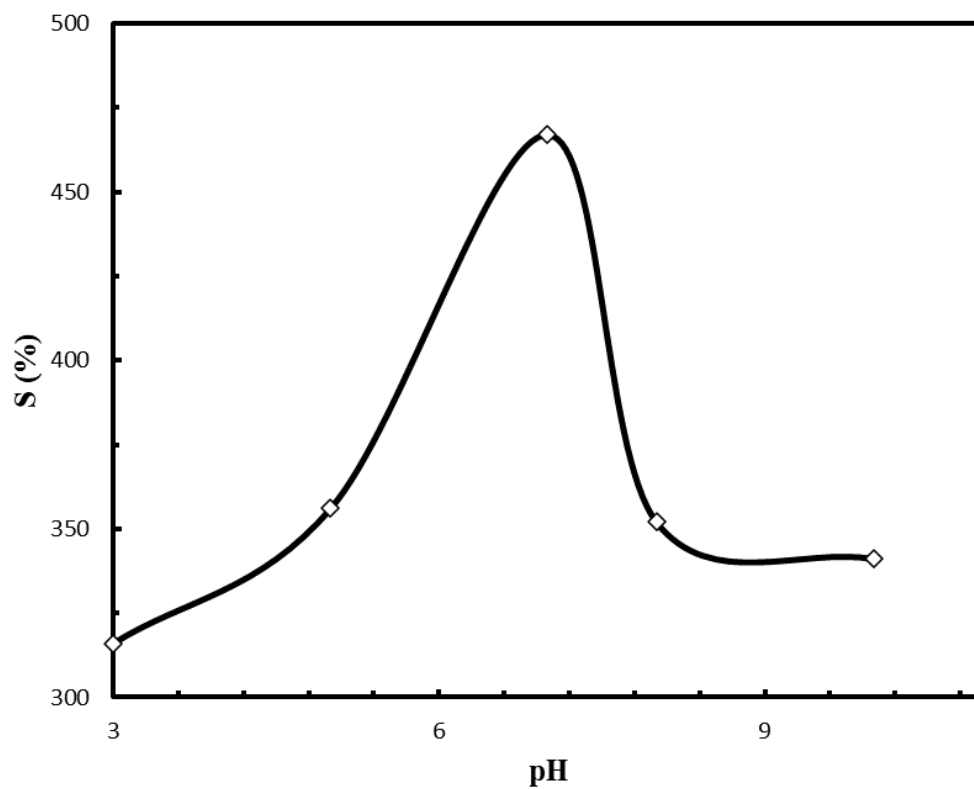


Fig.11. pH effect on the swelling behavior of the poly(MAAm/CrA) hydrogel.

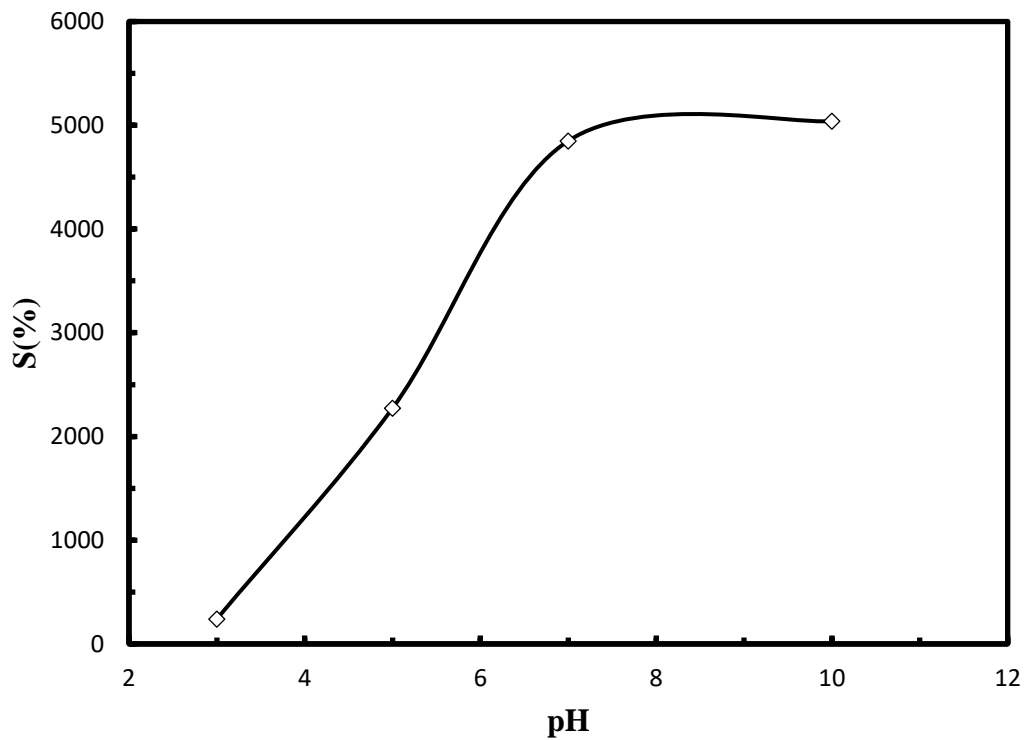
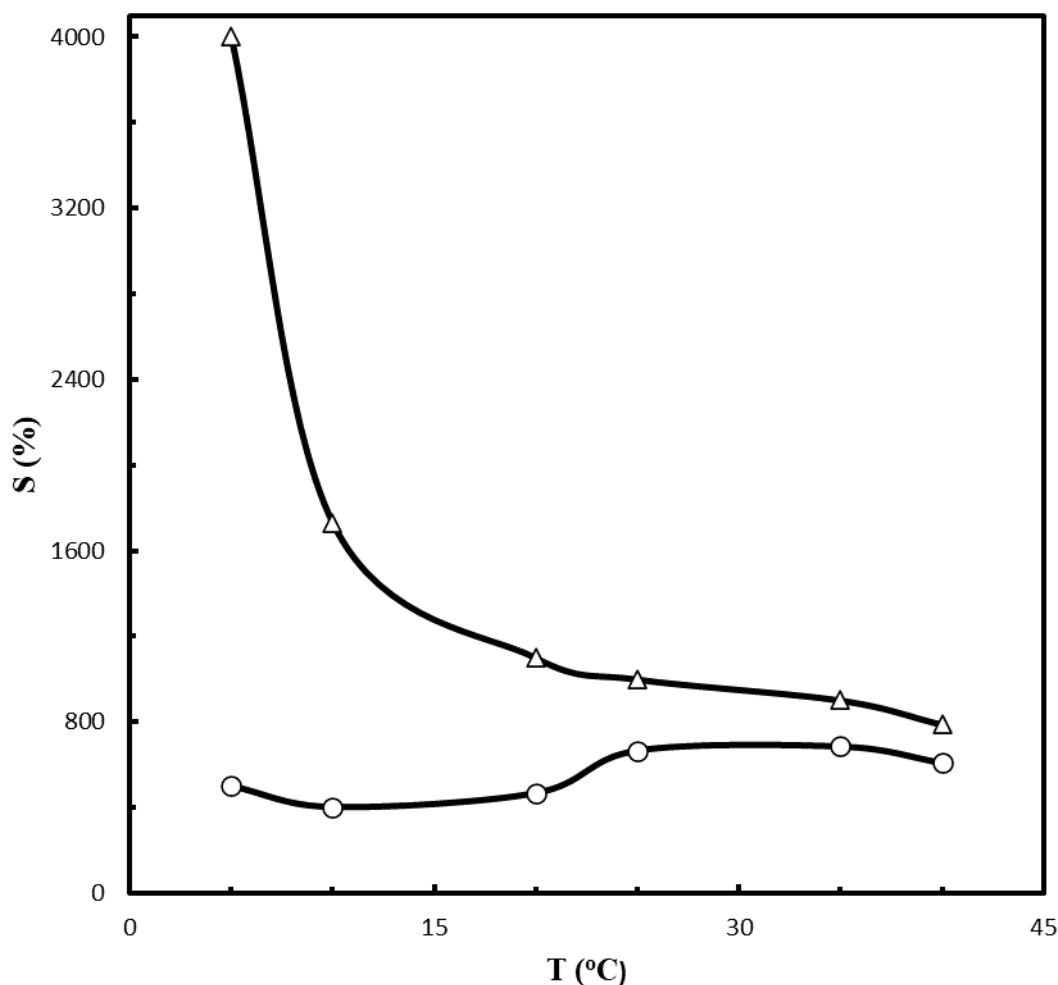


Fig.12. pH effect on the swelling behavior of the poly(MAAm/MAA) hydrogel.

As illustrated in Fig. 11, the swelling value of the poly(MAAm/CrA) hydrogel increases with rising pH, reaching a maximum at pH = 7, after which it decreases with further increases in pH. CrA is a monoprotic weak acid with a pKa value of 4.65. At low pH values, the carboxyl group of CrA remains inadequately ionized, resulting in relatively low electrostatic repulsion within the hydrogel and consequently a low swelling value [5].

In Fig. 12, MAA in the poly(MAAm/MAA) hydrogel is a diprotic acid with two ionization constants ( $pK_{a1} = 3.85$ ,  $pK_{a2} = 5.45$ ). At pH values near these ionization constants, one would expect to observe two sharp increases in the equilibrium swelling values; however, a single S-shaped curve was obtained. This phenomenon can be attributed to the overlap of the swelling curves at pH values corresponding to the first and second ionization constants, as the ionization constants of MAA are quite close to each other [22]. Furthermore, it is observed that the swelling values in both hydrogels are maximized at pH = 7. This can be explained by the fact that the carboxylic groups in both hydrogels are fully ionized at pH = 7, imparting a negative net charge to the network structure. When negative charges predominate in the network, the resulting electrostatic repulsion among like charges facilitates the diffusion of additional water into the openings created as the mesh bonds stretch, leading to significant swelling of the structure.

The variation in swelling with ambient temperature for both hydrogels prepared under optimal conditions is depicted in Fig. 13.

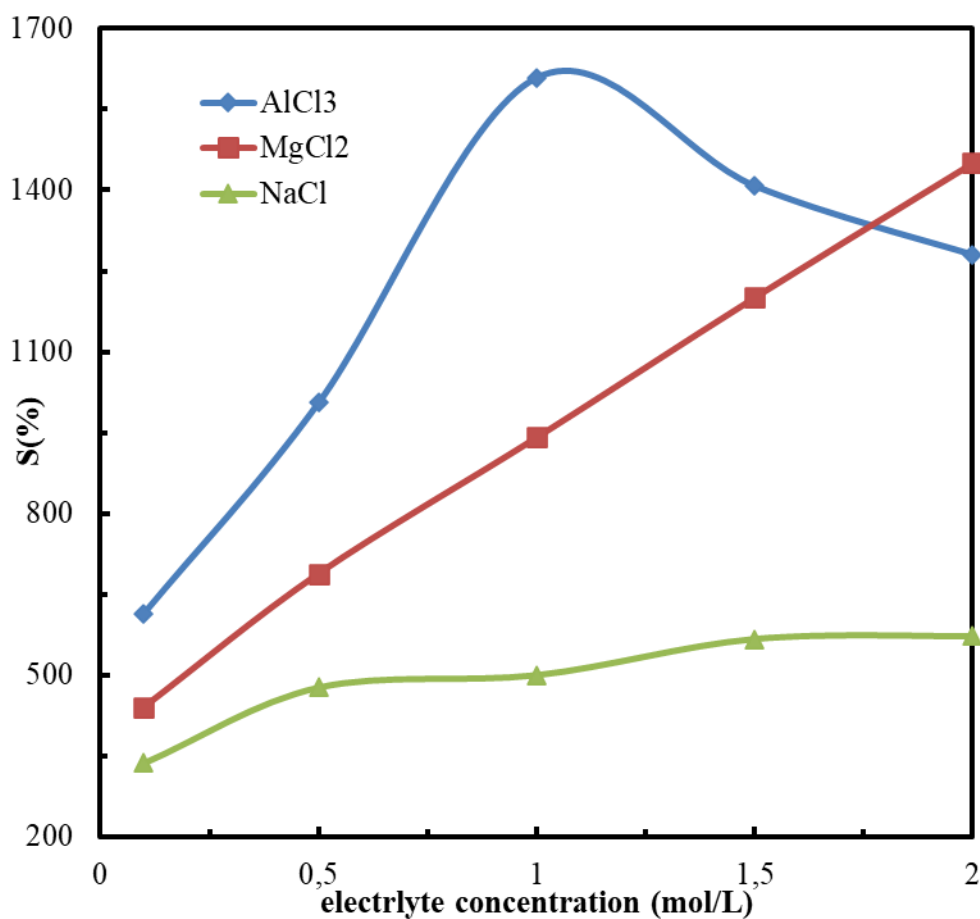


**Fig.13.** Effect of ambient temperature on swelling behavior of the hydrogels [ $\Delta$ : poly(MAAm/ CrA); o: poly(MAAm/ MAA)]

As depicted in Fig. 13, the swelling value of poly(MAAm/CrA) hydrogels exhibits a partial increase with rising ambient temperature, peaking at approximately 35 °C before decreasing. This observation suggests that a reversible phase transition occurs in the poly(MAAm/CrA) hydrogel at this temperature, leading to alterations in the hydrophilic/hydrophobic balance of the hydrogel chains. It can be inferred that hydrophilic interactions dominate within the temperature range of 5-35 °C, resulting in a gradual increase in swelling values. Conversely, above 35 °C, hydrophobic interactions become predominant, weakening the hydrogen bonds between the

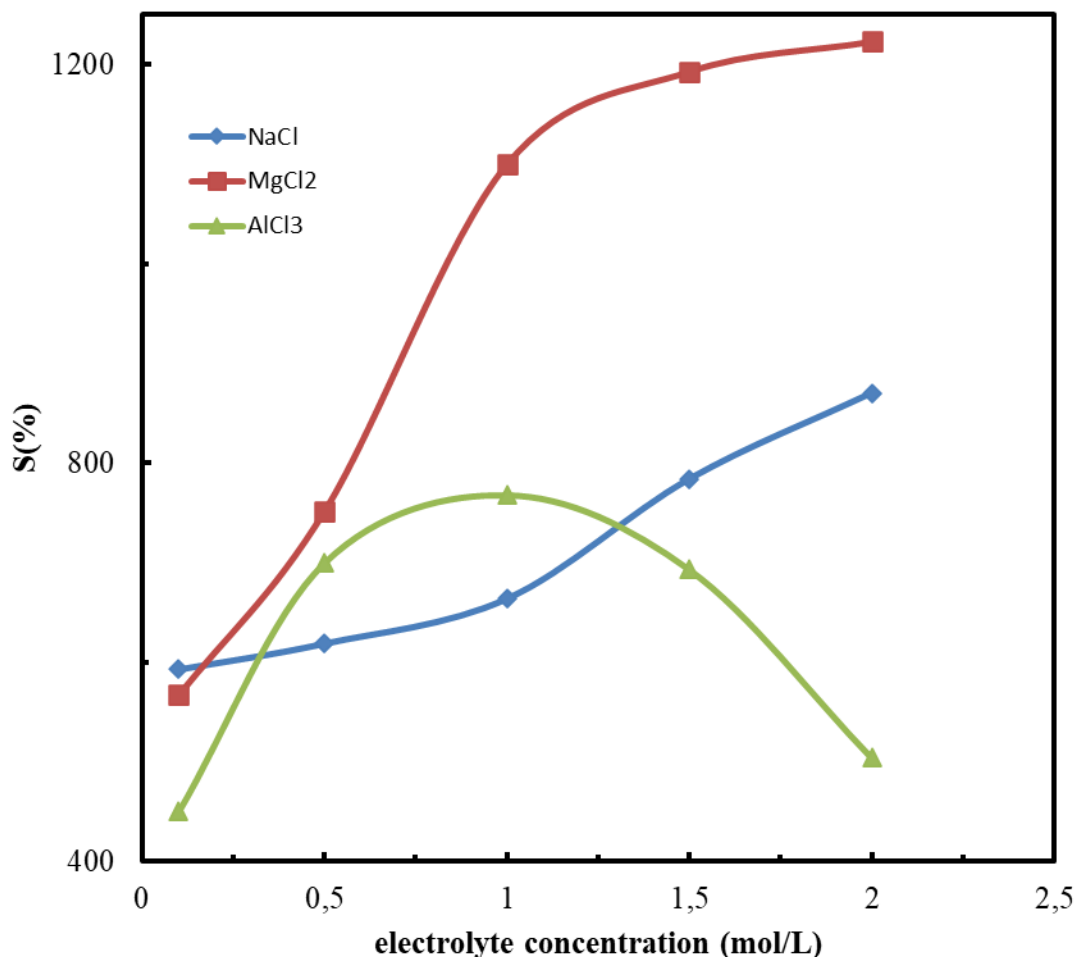
hydrophilic groups and water molecules, thereby causing a decrease in swelling values. In the case of poly(MAAm/MAA) hydrogels, the swelling value consistently decreases with increasing ambient temperature. At lower temperatures, the hydrophilic groups within the hydrogel form robust hydrogen bonds with water molecules, which enhances the amount of water diffusing into the hydrogel and subsequently increases the swelling value. However, as the temperature rises, the activation of hydrophobic groups within the hydrogel weakens these strong hydrogen bonds, facilitating the diffusion of water out of the hydrogel structure and leading to a reduction in swelling values [22].

The effects of electrolyte type and concentration on the swelling behavior of poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels synthesized under optimal conditions are illustrated in Figs. 14 and 15, respectively.



**Fig.14.** Swelling behaviour of the poly(MAAm/CrA) hydrogels depending on electrolyte type and concentration



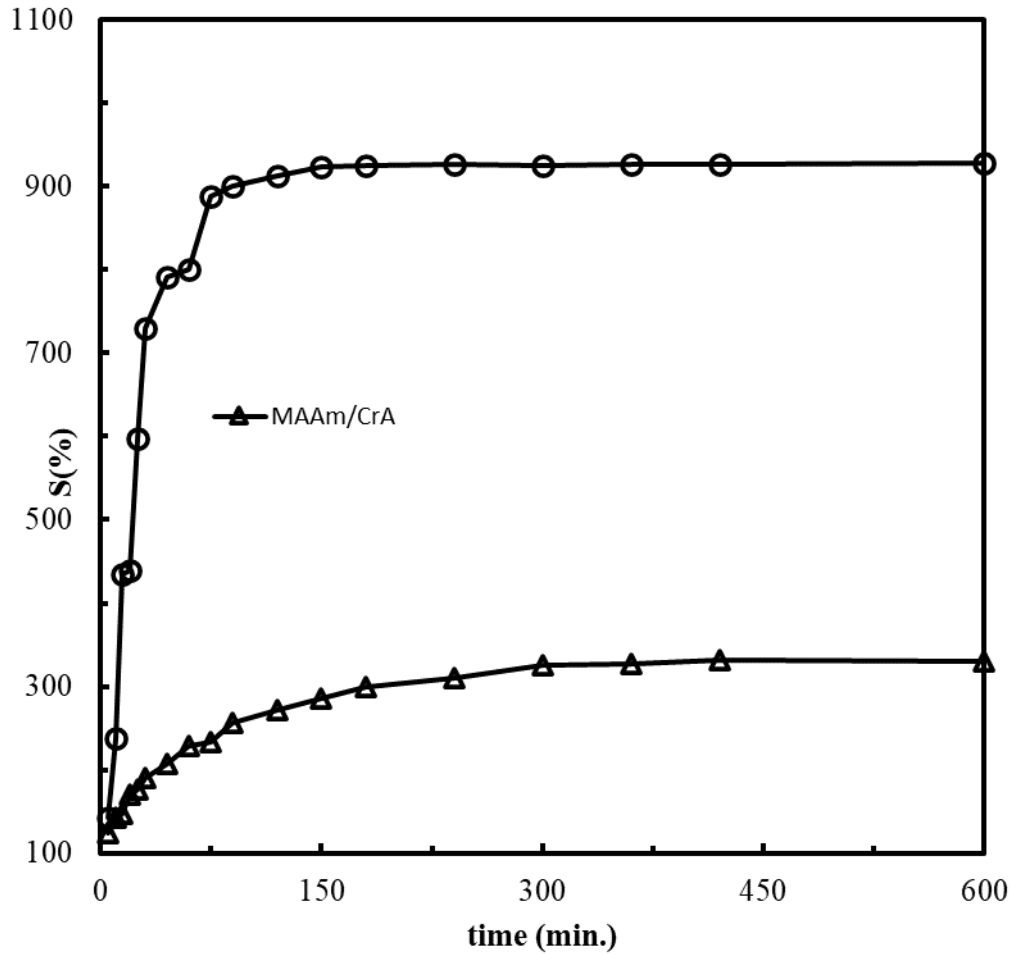


**Fig.15.** Swelling behaviour of the poly(MAAm/MAA) hydrogels depending on electrolyte type and concentration

As illustrated in Figs. 14 and 15, the swelling values of both hydrogels increase with rising ion concentrations in NaCl and MgCl<sub>2</sub> solutions. In the case of AlCl<sub>3</sub> solutions, swelling values increase up to a concentration of 1 M, after which a decline is observed. Initially, the cations that diffuse into the hydrogel contribute to swelling due to osmotic pressure balance. The cation types differ in their charge: Na<sup>+</sup> is monovalent, Mg<sup>2+</sup> is bivalent, and Al<sup>3+</sup> is trivalent. While it is anticipated that cations neutralizing varying numbers of carboxyl groups according to their valences would diminish swelling values by reducing electrostatic repulsion among the polymer chains, this effect is notably observed only for the Al<sup>3+</sup> cation. This phenomenon may arise because these cations can hinder hydrogen bond formation by obstructing the functional groups within the hydrogel matrix. Consequently, the increasing concentration of trivalent Al<sup>3+</sup> ions likely decrease swelling values beyond a certain threshold in both hydrogels. Furthermore, the +3 charged aluminum ion may exert a cross-linking effect between hydrogel chains, reducing swelling due to its tridentate structure. In contrast, other cation types, owing to their lower valence, are unlikely to generate a significant barrier effect by sufficiently enhancing interactions between the polymer chains [9, 23].

### 3.6 Swelling kinetics of the hydrogels

The swelling-time graphs of the hydrogels prepared under optimized conditions are shown in Fig.16.



**Fig.16.** Swelling-time graphs of hydrogels, [ $\Delta$ : poly(MAAm/ CrA);  $\circ$ : poly(MAAm/ MAA)]

As seen in Fig.16, the mass percent swelling values of both hydrogels initially increase rapidly with time and then increase slowly. In later times, the swelling values reach an unchanging value. This value is used as  $(M^\infty)$  assuming that the swelling of the hydrogel reaches equilibrium at the unchanging percent swelling value. In addition, as seen in Fig. 16, the poly(AAm/MAA) hydrogel swells faster than the poly(AAm/CrA) hydrogel, which can be explained by the fact that the bifunctional carboxylic acid groups in MAA will form more hydrogen bonds with the water molecules in the environment per unit time and that the swelling value of the hydrogel will be higher than the CrA hydrogel due to the diffusion of more water into the hydrogel [24, 25].

The  $\ln(M_t)-\ln(t)$  graph was created to find the type of solvent diffusion into both hydrogel structures (Fig.17). The determined diffusion constants are given in Table 1.

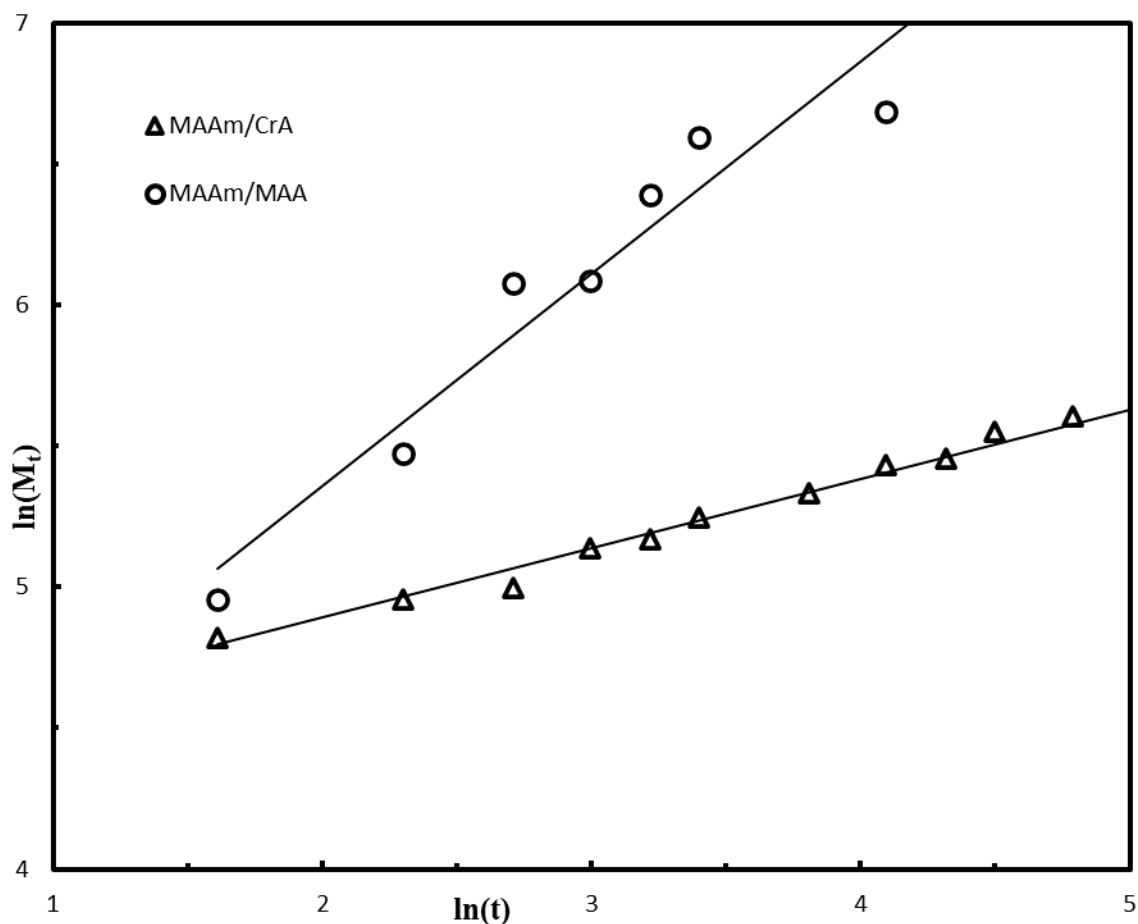


Fig.17.  $\ln(Mt)$ - $\ln(t)$  plot of hydrogels.

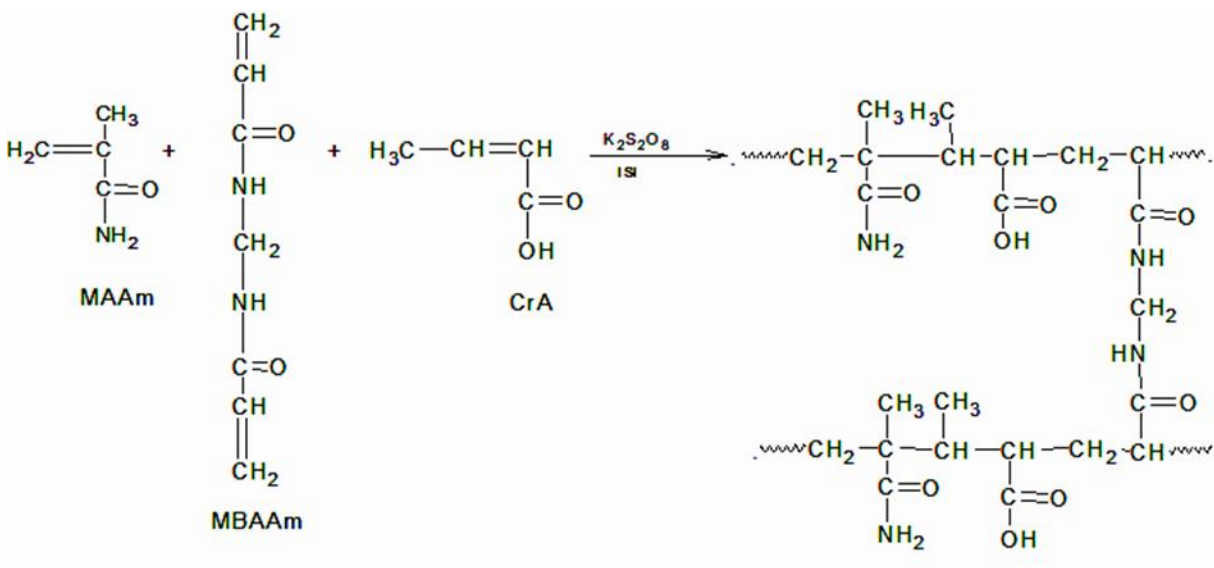
Table 1 Diffusion parameters of poly(MAAm/CrA) and poly(MAAm/MAA) hydrogels

Type of hydrogel	n	k	R <sup>2</sup>	Equation
poly(MAAm/CrA)	0,245	4,398	0,990	$y=0,245x+4,398$
poly(MAAm/MAA)	0,752	3,851	0,928	$y=0,752x+3,851$

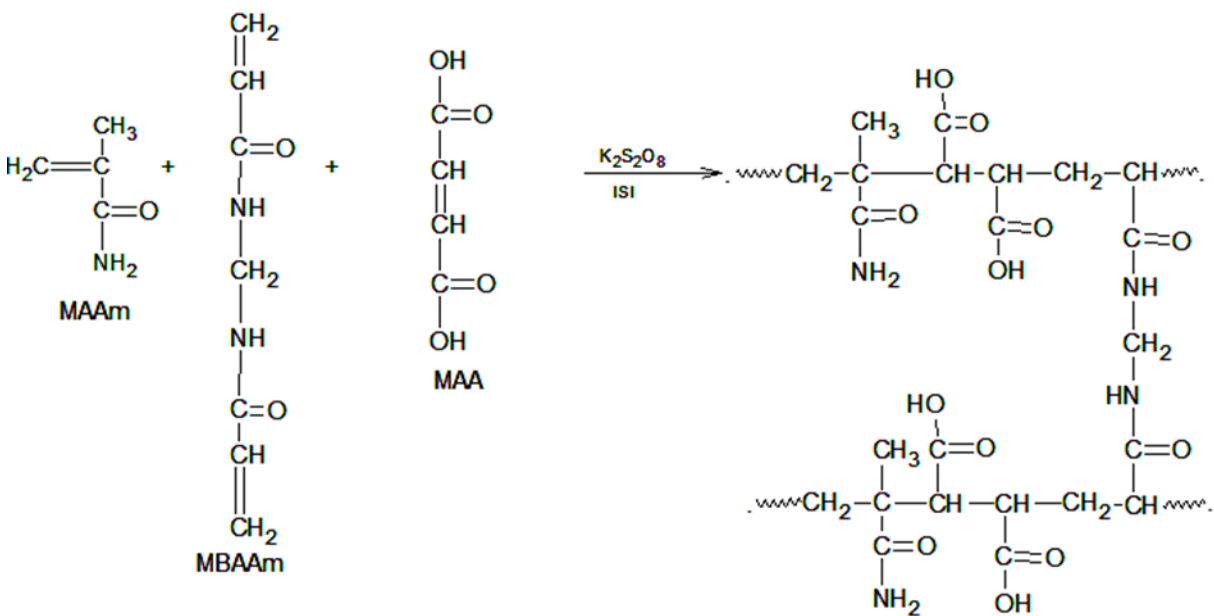
As seen in Table 1, the diffusion exponent value of  $n$  in the poly(MAAm/CrA) hydrogel is less than 0.5, indicating that there is Fick type diffusion in the gel, and this indicates that the relaxation rate in the poly(MAAm/CrA) hydrogel is faster than the diffusion rate. Similarly, the diffusion exponent value for the poly(MAAm/MAA) hydrogel is in the range of  $0.5 < n < 1.0$ , indicating that the type of diffusion falls into the class of non-Fick type or anomalous diffusion [26,11], and diffusion and settling are simultaneously effective in water diffusion into poly(MAAm/MAA) hydrogels.

#### 4. CHARACTERIZATION OF HYDROGELS

The chemical structures of the synthesized poly(AAm/CrA) and poly(MAAm(MAA) hydrogels are given in Schemes 1 and 2, respectively.



**Scheme 1.** Chemical structure of MAAm/CrA hydrogel



**Scheme 2.** Chemical structure of MAAm/MAA hydrogel

#### 4.1 FTIR analysis

Structural characterization of the hydrogels prepared under optimum conditions was performed by FTIR analysis, and the results are given in Fig.18. When the FTIR spectra of the hydrogels prepared with methacrylamide using crotonic acid and malic acid are examined, seen the presence of new bands, especially the -C-OH stretching band observed at 865 cm<sup>-1</sup>, in the poly(AAm/CrA) and poly(AAm/MAA) hydrogels that are not seen that of the methacrylamide spectrum, it confirms the synthesis of the poly(AAm/CrA) and poly(AAm/MAA) hydrogels.

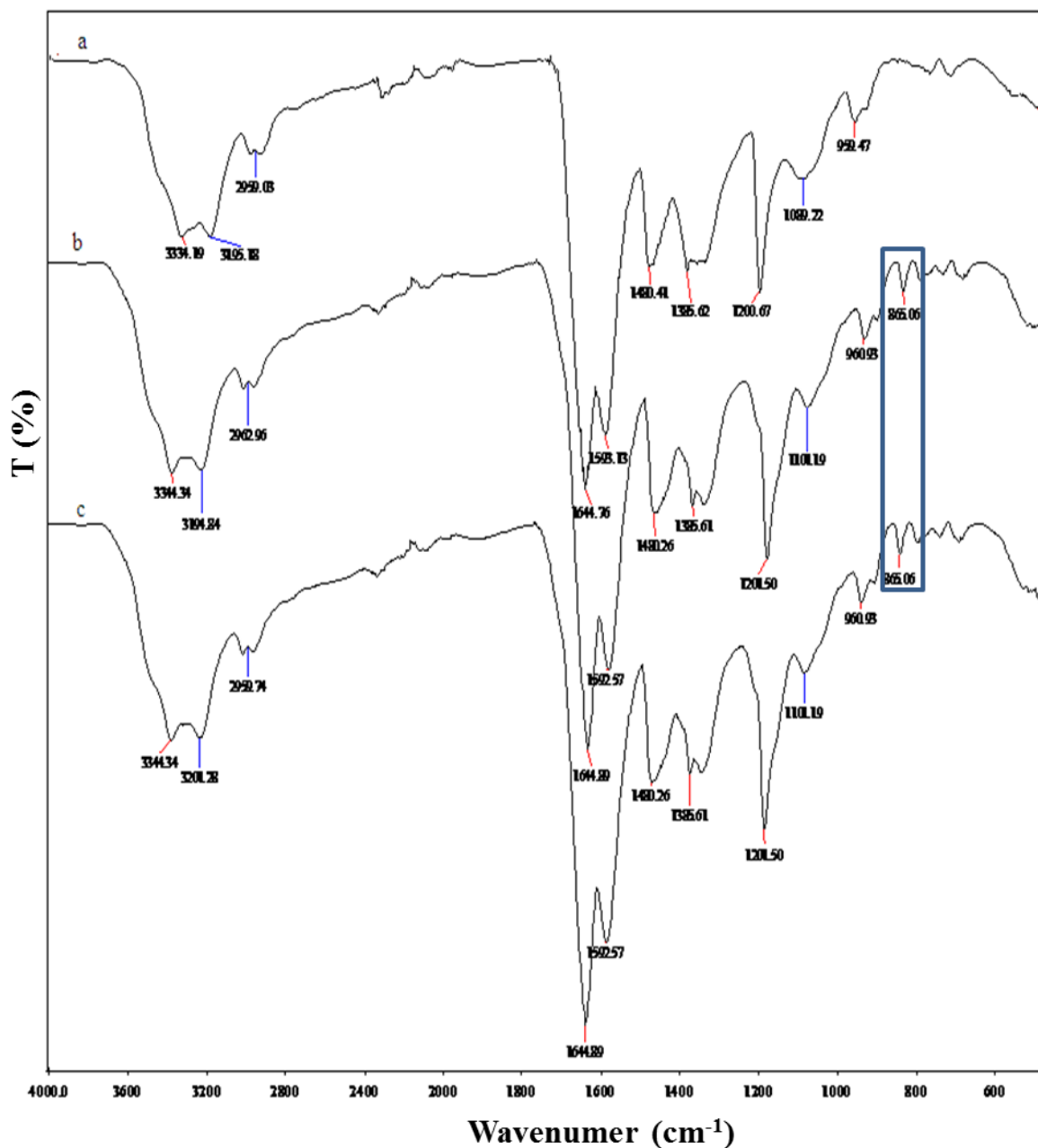
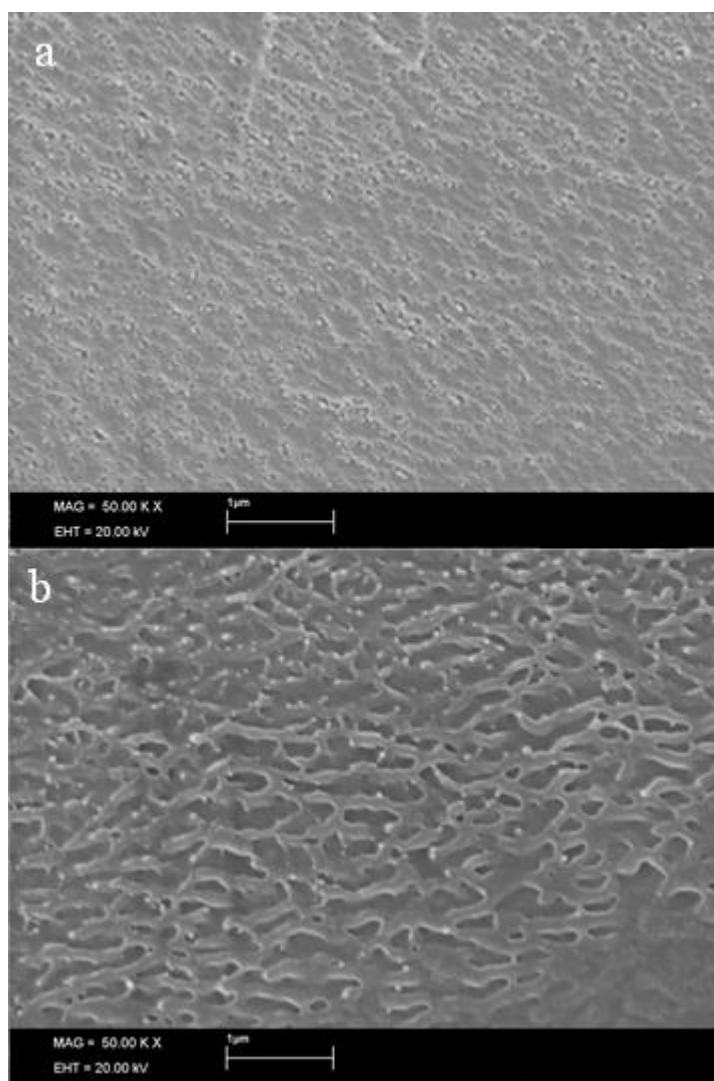


Fig.18. FTIR spectra of prepared hydrogels a) poly(MAAm); b) poly(MAAm/CrA); c) poly(MAAm/MAA)

#### 4.2 Scanning Electron Microscope (SEM)

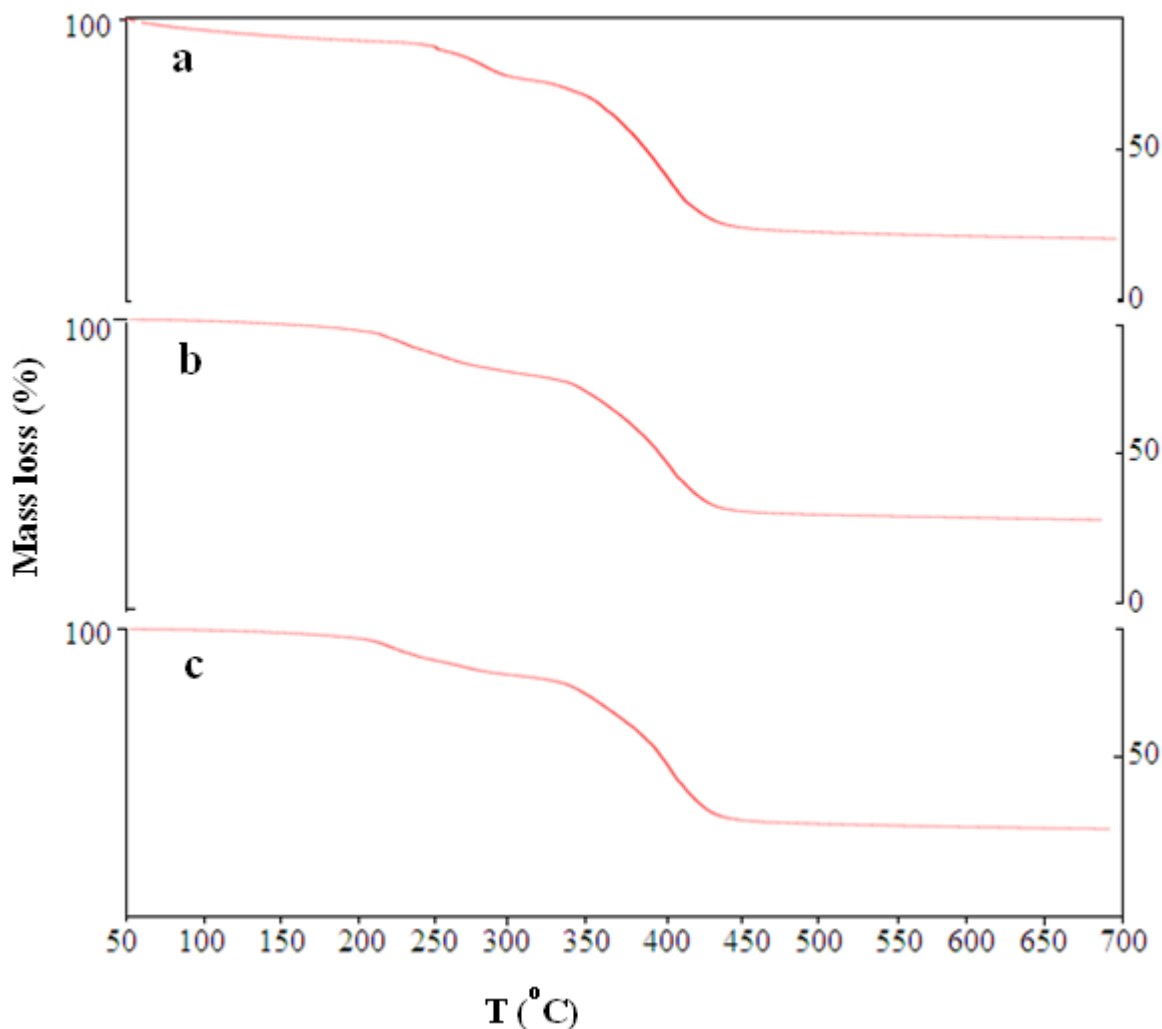
From the SEM images (Fig.19) of the hydrogels prepared under optimum conditions, it can be said that poly(MAAm/MAA) hydrogels form a more regular network structure, homogeneous pore size and cross-linking model with appropriate geometry compared to poly(MAAm/CrA) hydrogels. This can be considered as a superior feature of MAA hydrogels over CrA hydrogels in terms of water diffusion into the hydrogel structure and water retention in the network structure.



**Fig.19.** SEM images of the hydrogels prepared under optimum conditions (a) poly(MAAm/CrA), (b) poly(MAAm/MAA)

#### 4.3 Thermal Characterization (TGA)

The thermogram curves of the poly(MAAm/CrA), poly(MAAm/MAAM) and poly(MAAm) hydrogels synthesized under optimum conditions are given comparatively in Fig.20. As seen in Fig.20; poly(MAAm) hydrogel degrades in three steps, while the other two copolymer hydrogels degrade in two steps.



**Fig.20.** Thermogram curves of hydrogels prepared under optimum conditions a) poly(MAAm), b) poly(MAAm/CrA), c) poly(MAAm/MAA)

While poly(MAAm) hydrogel starts to degrade around 100 oC, MAAm/CrA and MAAm/MAA hydrogels start to degrade in the range of 200-240 oC (Table 2). The degradation of poly(AAm/CrA), poly(AAm/MAA) hydrogels at higher temperatures can be attributed to CrA and MAA entering the structure of poly(AAm). As CrA and MAA enter the structure of poly(MAAm), the thermal stability of the hydrogel increases due to the formation of intramolecular or intermolecular hydrogen bonds by the carboxyl groups [5].

Hydrogel Type	TDI (°C)	TDS (°C)	TDF (°C)	Mass loss (%)	Remaining waste (%)
poly(MAAm)	100	280	320	90	10
poly(MAAm/CrA)	220	325	-	87	13
poly(MAAm/MAA)	240	340	-	88	12

## 5. CONCLUSION

Hydrogels of methacrylamide (MAAm) were synthesized using monocarboxylic (crotonic acid, CrA) and dicarboxylic (maleic acid, MAA) acids through radical copolymerization. This process employed potassium persulfate (KPS) as the initiator and methylenebisacrylamide (MBAAm) as the crosslinker. In the MAAm/CrA hydrogel, a maximum swelling ratio of 480% was observed for samples prepared with an 85/15 mol/mol ratio of MAAm to CrA, incorporating 2 mol% KPS, 1 mol% MBAAm, and polymerized at 55 °C. Conversely, the MAAm/MAA hydrogels exhibited a maximum swelling ratio of 1100% under conditions of a 75/25 mol/mol ratio of MAAm to MAA, with 1 mol% KPS, 1 mol% MBAAm, also at 55 °C. The swelling ratio and surface morphology of the hydrogels were found to vary significantly based on the monomer ratios, initiator concentration, and crosslinker levels. Swelling kinetics studies conducted in distilled water at room temperature revealed that the MAAm/CrA hydrogel exhibited Fickian diffusion behavior, while the MAAm/MAA hydrogel demonstrated Non-Fickian diffusion characteristics.

## AUTHOR'S CONTRIBUTIONS

The authors contributed equally.

## CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## RESEARCH AND PUBLICATION ETHICS

The author declares that this study complies with Research and Publication Ethics.

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