

Swelling Kinetics Modeling of Cationic Methacrylamide-Based Hydrogels

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Abstract: Cationic hydrophilic hydrogels containing methacrylamide (as the basic monomer) were synthesized by the free radical polymerization. Methacrylamido propyl trimethyl ammonium chloride (MAPTAC) and N, N'-methylene-bis-acrylamide (Bis) were used as the cationic agent and the crosslinker, respectively. The effects of various concentrations of all monomers and the crosslinker density on the swelling behaviour were investigated. The diffusion coefficient was determined. The kinetic constant of diffusion and the swelling exponent were calculated. The irregular behaviour related to the non-Fickian anomalous which explains swelling mechanism was more observed when the crosslinker amounts increased. The diffusion coefficient of the solvent into the network decreased with increasing the crosslinker amounts and all monomers concentration. The experimental data were in good agreement with the modelled data (the error percentage was around 5%).

Key words: Cationic hydrogels • Kinetic • Modeling • Swelling mechanism • Methacrylamide

INTRODUCTION

Hydrogels are three-dimensional networks which are formed by copolymerization of monomers with crosslinking agents [1]. These gels are able to absorb considerable amounts of water due to their hydrophilic characteristics [2, 3]. Networks with desired properties can be synthesized by utilizing various co-monomers or changing in the network structure [4-6]. These networks are sensitive to the environmental instigators such as pH [2, 7], temperature [4, 8] and ionic strength [7] of the solution. According to these characteristics, hydrogels have plenty of applications in agriculture [9], medicine injection and release [6], micro-fluid systems [10], contact lenses [2], industrial wastewater treatments [7, 11].

Methacrylamide-based hydrogels are attended more than the other hydrogels because of their high water absorbency (due to existing hydrophilic amide groups), high mechanical stability of the swollen hydrogels and their green characteristics. Cationic and anionic co-monomers in hydrogel structures improve both mechanical stability and the amount of swelling. In addition, the gels are sensitive to environmental conditions such as pH and ionic strength of the solution [3].

In this study, Methacrylamide-based hydrogels were synthesized by using MAPTAC as the cationic ionizable co-monomer. The effects of some parameters such as amount of monomers and density of the crosslinker inside the network on the swelling behaviour of these gels were investigated. Then network parameters such as kinetic coefficient, solution diffusivity coefficient inside the network and diffusion mechanism were determined by using common kinetic models.

Experimental

Materials: Methacrylamide (MAAm), N,N,N',N'-tetramethyl ethylene diamine (TEMED) and N,N'-methylene bis-acrylamide (Bis) were purchased from Merck Company. Ammonium persulphate (APS) was obtained from Fisher Company. Methacrylamido propyl trimethyl ammonium chloride (MAPTAC), (50 wt.% solution in water) was supplied by Aldrich Company. Double distilled and deionized water were used for the synthesis of hydrogels and swelling experiments.

Hydrogel Synthesis: Cationic hydrogels were synthesized by radical copolymerization of methacrylamide as the basic monomer. MAPTAC, Bis, APS and TEMED were used as the cationic ionizable agent, crosslinker, initiator

and activator, respectively. Polymerization process is started by the reaction between APS and TEMED which forms an activated molecule. The TEMED activated molecule has an unpaired electron valance and reacts with MAAm, MAPTAC and Bis. The polymerization (copolymerization) process is started and this process will continue until the network is fully formed.

The nominal hydrogel composition is determined by the relative amounts of monomers and water present in the pre-gel reaction solution. The following variables define the gel composition.

$$\%T = \frac{\text{Mass of all monomers(g)}}{\text{Volume of water (mL)}} \times 100$$

$$\%C = \frac{\text{Mole of bis in feed solution}}{\text{All monomers (mole) in feed solution}} \times 100$$

$$\%MAPTAC = \frac{\text{Mole of MAPTAC in feed solution}}{\text{All monomers (molre) in feed solution}} \times 100$$

A Teflon coated reactor containing aqueous monomers solution was placed in thermo-stated water bath to reach 50°C and stirred with a mechanical stirrer until the monomers were completely dissolved (about 30 minutes). The APS solution and TEMED (60 mg for both of them) were added to the monomers solution. The hydrogel was obtained from the reactor after 24 hours [5]. It was cut into small pieces, rinsed with distilled water in several times to remove possible unreacted monomers and impurities. They were dried at 40 °C in a vacuum oven and were ground with a mechanical mill. The ground hydrogel particles were meshed ranging from 0.05 to 0.2 mm and stored in desiccator for further experiments.

Two different sets of hydrogels were synthesized for the experiments. In Set 1, the amount of all monomers (%T) varies with constant amounts of the crosslinker (%C) and ionic monomer (%MAPTAC). In Set 2, %T and %MAPTAC are kept constant and %C varies. The feedstock solution of hydrogels properties are listed in

Table 1. The temperature and the amount of the initiator were kept in 50 °C and 5%, respectively.

Swelling Kinetics: Dried hydrogels were weighed and then immersed in distilled water to swell. The samples were taken out the water, water was precisely removed from their surfaces and the samples were weighed. The experiments were carried out at 27 ± 0.5 °C. The swelling ratio was calculated using the following equation:

$$SR = \frac{W_t - W_0}{W_0} \quad (1)$$

where, SR , W_t and W_0 are the swelling weight ratio, weight of swollen hydrogel at time t and the dried hydrogel (before swelling), respectively. When there is no change in the weight of the hydrogel, hydrogel is in chemical equilibrium with its surrounding solution. The equilibrium swelling weight ratio (ESR) and the equilibrium water content (EW) are calculated using equations (2) and (3), respectively.

$$ESR = \frac{W_{max} - W_0}{W_0} \quad (2)$$

$$EW = \frac{W_{max} - W_0}{W_{max}} \quad (3)$$

W_{max} is the maximum hydrogel weight which occurs at equilibrium state.

Determination of Swelling Mechanism: The water penetrates the hydrophilic network of the hydrogel when it contacts water. In this process, water molecules migrate into the network through the free spaces between the polymer chains or spaces where form during the diffusion process. The relaxation rate (the mobility of the polymer chains which results in the diffusion of water into the network) depends on the network structure and the characteristics of the diffuser solvent [12]. A change in the hydrogel structure changes swelling behaviour. The analysis of the diffusion mechanism in all hydrophilic networks is described by the following equation [13]:

Table 1: Composition of the monomers and crosslinker in the solution for all synthesized hydrogels

	Sample no.	%T	%C	% MAPTAC
Set 1	HG-1	10	0.1	5
	HG-2	20	0.1	5
	HG-3	30	0.1	5
	HG-4	40	0.1	5
Set 2	HG-5	10	0.1	5
	HG-6	10	0.2	5
	HG-7	10	0.3	5
	HG-8	10	0.5	5

$$SR = K_p t^{n_p} \quad (4)$$

where, K_p and n_p are the kinetic constant of water diffusion into the network and the swelling exponent (which depends on the diffusion mechanism), respectively. The molecular diffusion rate is less than the relaxation rate and the diffusion behaviour follows the Fickian diffusion when $n_p = 0.5$. The molecular diffusion rate is more than the relaxation rate when $n_p = 1$. Both items of molecular diffusion and relaxation rate affect on diffusion when $n_p = 0.5-1$. The diffusion rate increases in comparison with the relaxation rate when n_p increases from 0.5 to 1 [14]. A straight line will be obtained by plotting $\ln (SR)$ versus $\ln (t)$ for the initial 60% of swelling. The slope of this line displays n_p and its intersect shows $\ln (K_p)$.

Swelling Rate and Diffusion Coefficient Determination:

There are various methods for determination of swelling rate and solvent diffusion coefficient for the gel network. According to one of these methods which is called Short Time Approximation [11], degree of swelling (Q) can be calculated:

$$Q = \frac{M(t)}{M_{\max}} = 4 \left[\frac{D t}{\pi r^2} \right]^{1/2} - \pi \left[\frac{D t}{\pi r^2} \right] - \frac{\pi}{3} \left[\frac{D t}{\pi r^2} \right]^{3/2} + \quad (5)$$

where, D , t and r are diffusion coefficient, time and average particles radius. A linear curve is obtained by plotting Q versus $t^{1/2}$. The slope of this curve demonstrates the solvent diffusion factor for the gel network.

$$\text{slope} = 4 \left(\frac{D}{\pi r^2} \right)^{1/2} \Rightarrow D = \pi \left(\frac{\text{slope} \times r}{4} \right)^2 \quad (6)$$

This method is used to determine the solvent diffusion coefficient within the gel network although the mentioned method is applicable for the initial 60% of swelling [15]. The mentioned method is not suitable for studying complete swelling behaviour and another method should be applied in order to fulfil this demand.

Swelling of hydrogels is expressed by the following equation [15]:

$$\frac{dQ}{dt} = K_{RS} (Q_{\max} - Q) \quad (7)$$

where, Q_{\max} and K_{RS} are the ratio of maximum weight of gel at equilibrium condition to that of the dry gel and swelling rate constant which depends on the maximum amount of

water uptake and solvent diffusion coefficient [15]. The above equation is solved by assuming $Q(0) = 1$ (at $t = 0$) as an initial condition.

$$-\ln \left(\frac{Q - Q_{\max}}{1 - Q_{\max}} \right) = K_{RS} t \quad (8)$$

RESULTS AND DISCUSSION

The swelling rate of the cationic hydrogels from the set 1 is shown in Figure 1. Table 2 illustrates the maximum swelling ratio and equilibrium water content for these hydrogels. All synthesized hydrogels are able to absorb a lot of water.

The swelling properties of the hydrogels depend on the swelling parameters (such as temperature and the solution) and the synthesis conditions [2, 15-17]. The swelling behaviour and hydrogels structure vary with all monomers concentration of the feed. As shown in Figure 1, the swelling ratio of the synthesized hydrophilic hydrogels decreases with increasing all monomers concentration in the feedstock. This output is supported by literature [16, 17].

Figure 2 shows the rate of the hydrogels swelling for set 2. All synthesized cationic hydrogels are able to absorb considerable amounts of water. Table 2 shows the equilibrium water content and the maximum swelling ratio for these hydrogels. The hydrogels swelling decreases with increasing amount of crosslinker in the network. Since the number of crosslinks inside the network per volume unit increases and free spaces for water molecules decrease (the network gets more elastic and less rigid characteristics) and the number of hydrophilic amide groups between two crosslinks decreases (the hydrophilicity of the network decreases) so, water uptake decreases [12, 18].

Figures 3 and 4 show $\ln (SR)$ versus $\ln (t)$ for the sets of 1 and 2, respectively. The values of n_p obtained from these figures are shown in Table 2.

Since the values of n_p are between 0.5 and 1 for all synthesized hydrogels, the diffusion behaviour is non-Fickian one. Based on Peppas *et al.* theoretical and experimental effort, the experiments were carried out at temperatures less than T_g for the networks [13]. Therefore, the network changed from glassy to rubbery state during the swelling (a low relaxation rate). The value of the swelling exponent increases (a more rigid structure) when amount of crosslinker increases. Therefore, the diffusion behaviour follows anomalous diffusion as the network chains mobility (relaxation rate) reduces [18].

Table 2: Equilibrium swelling ratio (ESR), Equilibrium water content (EWC), swelling exponent (n_p), diffusion coefficient (D) and swelling constant rate (K_{is}) calculated for the synthesized hydrogels

	Sample no.	%T	%C	% MAPTAC
Set 1	HG-1	10	0.1	5
	HG-2	20	0.1	5
	HG-3	30	0.1	5
	HG-4	40	0.1	5
Set 2	HG-5	10	0.1	5
	HG-6	10	0.2	5
	HG-7	10	0.3	5
	HG-8	10	0.5	5

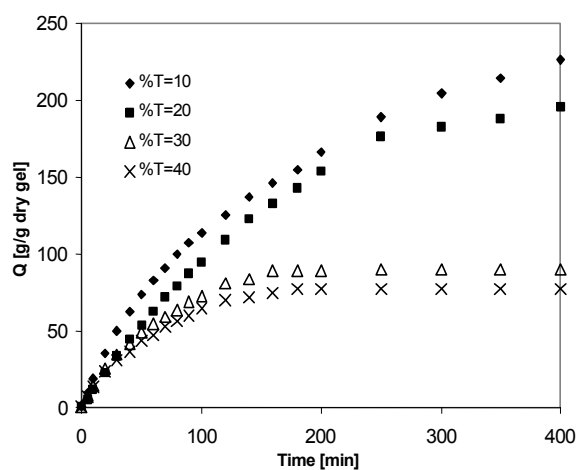


Fig. 1: Swelling rate of hydrogels for set 1 (%C = 0.1)

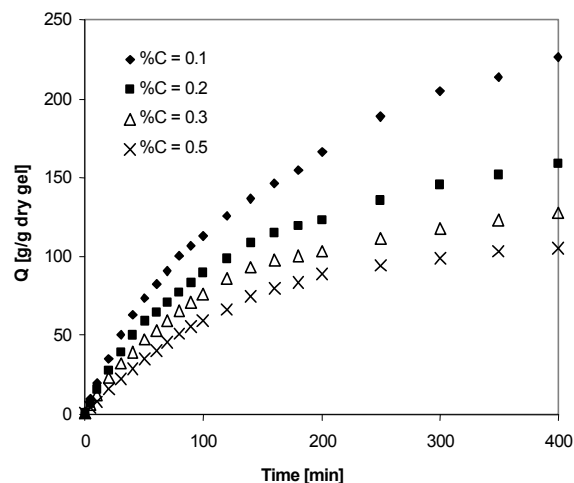


Fig. 2: Swelling rate of hydrogels for set 2 (%T=10)

Figures 5 and 6 show swelling ratio (Q) versus the square root of time ($t^{1/2}$) for the sets of 1 and 2, respectively. The diffusion coefficient of the solvent into the network was calculated using the slopes of the straight lines of Figures 5 and 6 and equation (6). All of the calculated coefficients have been listed in Table 2,

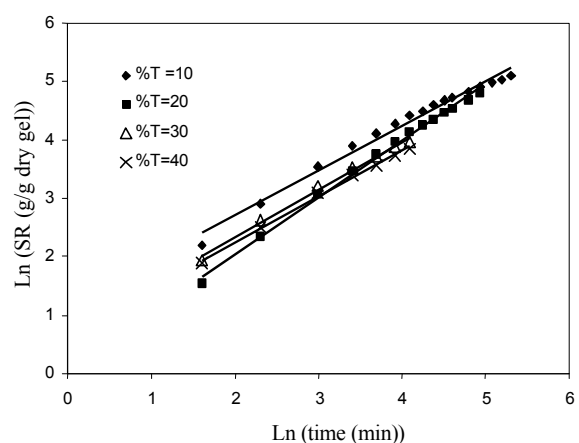


Fig. 3: Swelling mechanism analysis of hydrogels for set 1. SR (swelling ratio) (g/g dry gel) versus time (min).

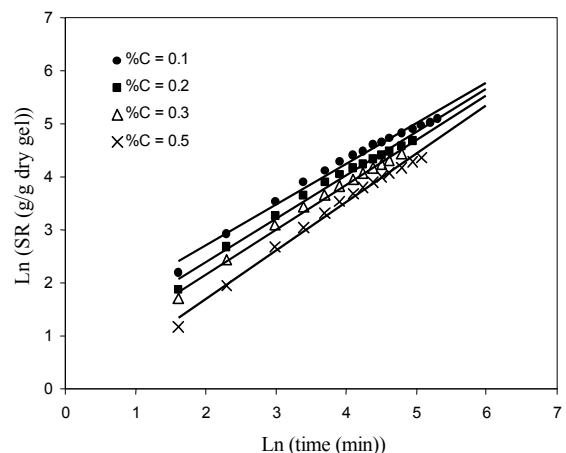


Fig. 4: Swelling mechanism analysis of hydrogels for set 2. SR (swelling ratio) (g/g dry gel) versus time (min).

as well. The diffusion coefficient decreases with increasing the crosslinker concentration. Table 2 shows that the swelling exponent increases with decreasing the diffusion coefficient. The swelling exponent enhancement

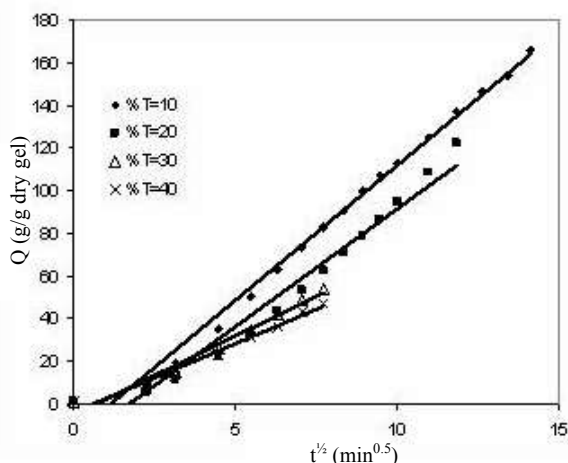


Fig. 5: Diffusion coefficient analysis of hydrogels for set 1. Q (swelling ratio) (g/g dry gel) versus $t^{0.5}$ ($\text{min}^{0.5}$).

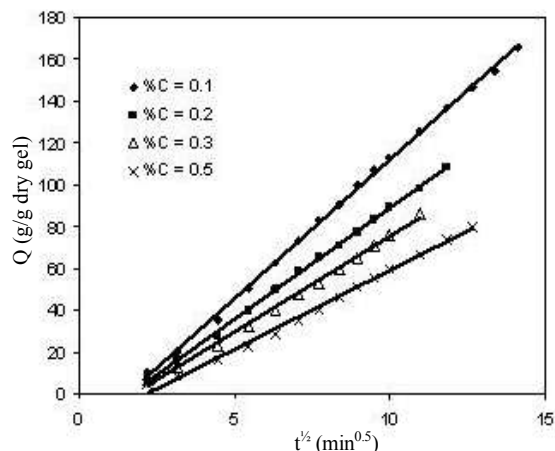


Fig. 6: Diffusion coefficient analysis of hydrogels for set 1. Q (swelling ratio) (g/g dry gel) versus $t^{0.5}$ ($\text{min}^{0.5}$).

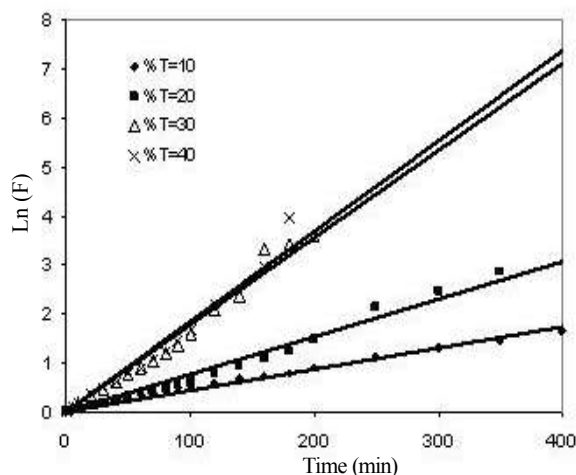


Fig. 7: Swelling rate analysis of hydrogels for set 1. Fractional approach to the equilibrium state (F) versus time (min).

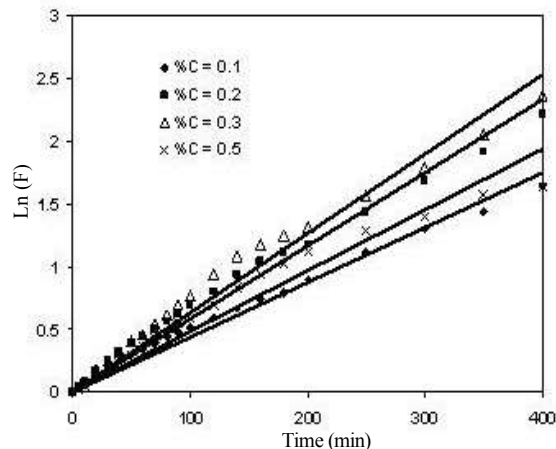


Fig. 8: Swelling rate analysis of hydrogels for set 2. Fractional approach to the equilibrium state (F) versus time (min).

decreases the relaxation rate. Since the synthesized cationic hydrogels follow non-Fickian behaviour so, their diffusion mechanisms are dominated by the relaxation rate (the relaxation rate enhancement reduces the diffusion coefficient) [14].

The same behaviour is observed for the set 2. The solvent diffusion coefficient in the network decreases with increasing all monomers initial concentration. All monomers concentration enhancement creates a denser network.

Figures 7 and 8 show $\ln(F)$ (F is fractional approach to the equilibrium state) versus time. The experimental data were analyzed by a linear regression and intercept was adjusted in zero according to equation (8). There is a good agreement between the experimental data and

the kinetic model. The slopes of the lines which introduce K_{RS} (solvent absorbency in the network) and correlation index (R^2) have been listed in Table 2, as well.

CONCLUSION

Cationic methacrylamide-based hydrogels were synthesized by aqueous free radical polymerization. Swelling and equilibrium behaviour of these gels in distilled water were studied. The effects of synthesis parameters such as the amount of the crosslinkers and all monomers concentration on the hydrogels behaviour were investigated. Common kinetic models were applied to consider the swelling mechanism and the diffusion coefficient.

The final swelling ratio decreased with decreasing the amount of crosslinker although the network elasticity increased and the hydrophilicity decreased. The final swelling ratio decreased with increasing all monomers concentration. In addition, the equilibrium water content of the hydrogels was more than 80%. Further, diffusion behaviour of the synthesized hydrogels was non-Fickian one. The diffusion coefficient increased with increasing the amount of crosslinker or/and all monomers concentration.

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