

SYNTHESIS AND CHARACTERIZATION STUDIES OF A SERIES OF *N*-VINYL IMIDAZOLE-BASED HYDROGEL

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ABSTRACT

In this study, poly[*N*-vinyl imidazole-co-(2-dimethylaminoethyl methacrylate)] hydrogels with various mole percentages of monomers were prepared by free radical solution polymerization in aqueous media. *N,N'*-methylenebisacrylamide and 2,2'-azobisisobutyronitrile were used as cross-linker and initiator, respectively. A Fourier transform infrared spectrophotometer, scanning electron microscope and thermogravimetric analyzer were used for the characterization of the hydrogels. The swelling behavior of the hydrogels in aqueous solution was investigated at pH 6.0 and 25°C. The results showed that swelling characteristics were affected by the 2-dimethylaminoethyl methacrylate content of the copolymeric hydrogel. The swelling degree of hydrogels increased from 4.2 g g⁻¹ to 25.4 g g⁻¹ by increasing the 2-dimethylaminoethyl methacrylate concentration from 0 to 15% with respect to the total moles of the monomers.

Keywords: *N*-vinyl imidazole, 2-Dimethylaminoethyl methacrylate, Copolymer, Hydrogel, Swelling

1. INTRODUCTION

Hydrogels are hydrophilic polymers that have three dimensional cross-linked networks. They do not dissolve in water, but they can swell up a great deal by absorbing water in aqueous solutions. Hydrogels are sensitive to heat, pH, ionic strength, electric and magnetic fields, and may exhibit dramatic and reversible volume changes under these effects. Due to their excellent characteristics, hydrogels have attracted researchers' attention and exhibit potential applications in many fields from agriculture to medicine [1-9]. One of the most important factors determining the properties and applications of a hydrogel is its water absorption characteristics. The swelling behavior of hydrogels is related to various parameters such as the equilibrium degree of swelling, the diffusion parameters and the cross-linker content [10-13].

Although poly(*N*-vinyl imidazole) (p-VIm) hydrogels are neutral, the imidazole groups on the polymeric backbone have weak base character. Hence, p-VIm hydrogels exhibit reversible volume changes depending on the pH values of the aqueous solution because they can be easily protonated in acidic solutions [14]. *N*-vinyl imidazole (VIm) based hydrogels have attracted considerable attention. These kinds of hydrogels are frequently used as a protein carrier [15], a membrane for the anion exchange processes [16] and an adsorbent to remove some heavy metals from aqueous solutions [17-19].

To prepare new polymeric materials with special properties and expand the range of p-VIm use, some works have been carried out on the synthesis of various VIm-based hydrogels. Although several groups of VIm-based hydrogels have been synthesized and characterized, the interaction between 2-dimethylaminoethyl methacrylate (DMA) and VIm has not been studied up to now. Pekel and Guven [19] synthesized poly(*N*-vinylimidazole-co-maleic acid) hydrogel by γ -irradiation of a ternary systems composed of *N*-vinylimidazole/maleic acid/water. They also determined their adsorption capacity for Cu²⁺, Co²⁺, Cd²⁺ and Pb²⁺ ions. In another study, synthesis of various compositions and the swelling behavior of poly(acrylamide-co-*N*-vinylimidazole) hydrogels were investigated. The highest equilibrium swelling was obtained under basic conditions at high temperature [1]. Uzun and Karadag [20] prepared the ternary semi interpenetrating hydrogels with acrylamide, *N*-vinylimidazole and

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poly(ethyleneglycol), and swelling experiments were performed in water at 25°C. Their investigations revealed that the swelling degree was highly dependent on the chemical composition of the hydrogels and reached up to 4167%. Feng et al. [21] grafted p-VIm-based branches onto polymeric chitosan chains for the selective adsorption of Hg^{2+} ions from the aqueous solution. This prepared hydrogel was found to exhibit good reusability in the adsorption process.

An effective adsorbent character is shown by p-VIm due to its high levels of swelling degree, particularly at low pH values. Since the efficiency of p-VIm decreases with increasing pH [22], it is important to produce VIm-based copolymers that can show significant swelling properties especially when the pH is neutral. The main goal of this study is to obtain this kind of copolymeric hydrogel, and, in this sense, DMA with a pKa value of approximately 8.1 is a proper monomer. VIm-based copolymeric hydrogels containing different percentages of DMA were prepared by free radical solution polymerization in aqueous solution in the presence of *N,N'*-methylenebisacrylamide (BAAM) and 2,2'-azobisisobutyronitrile (AIBN) as a cross-linking agent and initiator, respectively. The swelling properties of the hydrogels were investigated at a pH of 6.0 to demonstrate their swelling characteristics at nearly neutral media for aqueous solutions. Swelling curves were obtained for the copolymeric hydrogels, and the kinetic parameters were calculated from these curves.

2. EXPERIMENTAL

2.1. Materials

N-vinyl imidazole, *N,N'*-methylenebisacrylamide, 2,2'-azobisisobutyronitrile, 2-dimethylaminoethyl methacrylate and potassium bromide were purchased from Sigma-Aldrich (USA).

2.2. Preparation of Hydrogels

The p-VIm hydrogel was prepared according to existing literature [22]. To synthesize the copolymer containing 1% mole percentage of DMA (denoted by p-VIm-co-DMA_1), 20 mg of AIBN was dissolved in 20 ml of VIm, 0.51 g of BAAM and 0.45 ml DMA were added to this solution with 50 ml of distilled water. This mixture was immersed in a water bath at 80°C to be polymerized for 2 hours. The resulting hydrogel was left in deionized water for 24 hours and then dried in a vacuum oven at 60°C. Copolymeric hydrogels containing mole percentages of 2.5, 5, 10, and 15% DMA (p-VIm-co-DMA_2.5, p-VIm-co-DMA_5, p-VIm-co-DMA_10 and p-VIm-co-DMA_15, respectively) were prepared using the same procedure used for the p-VIm hydrogel. The possible chemical structure of the copolymeric hydrogels is given in Figure 1. The abbreviations used in this study and their explanations are listed in Table 1.

Table 1. The list of abbreviations

Abbreviation	Explanation
AIBN	2,2'-azobisisobutyronitrile
DMA	2-dimethylaminoethyl methacrylate
p-VIm-co-DMA_1	Copolymer containing mole percentage of 1% DMA
p-VIm-co-DMA_2.5	Copolymer containing mole percentage of 2.5% DMA
p-VIm-co-DMA_5	Copolymer containing mole percentage of 5% DMA
p-VIm-co-DMA_10	Copolymer containing mole percentage of 10% DMA
p-VIm-co-DMA_15	Copolymer containing mole percentage of 15% DMA
FTIR	Fourier transform infrared
VIm	<i>N</i> -vinyl imidazole
BAAM	<i>N,N'</i> -methylenebisacrylamide
p-VIm	Poly(<i>N</i> -vinyl imidazole)
SEM	Scanning electron microscope
TG	Thermogravimetric
S (g g ⁻¹)	The swelling degree
S_{∞}	The swelling degree at an equilibrium state
S_t	The swelling degree at time t
k_s	The swelling rate constant
W_d (g)	The weight of dry sample
W_s (g)	The weight of swollen sample

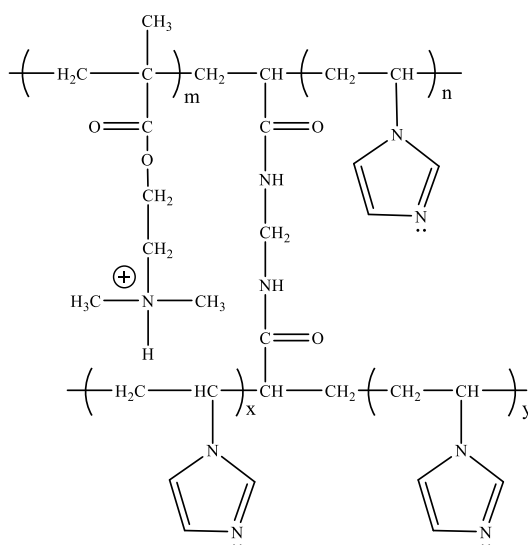


Figure 1. Schematic representation of the possible structure of copolymers in aqueous media at pH 6.0

2.3. Characterization of Hydrogels

The Fourier transform infrared (FTIR) spectrophotometric analysis of the hydrogels was performed with a Perkin Elmer Spectrum 100 in the 4000 to 400 cm^{-1} range by preparing potassium bromide discs. A scanning electron microscope (SEM, Carl Zeiss Ultra Plus) was used to investigate the surface morphologies of the hydrogels after freeze drying (for 24 hours, at -50°C and at 0.1 mbar pressure, using a Christ/Alpha 1-4 freeze dryer) and gold coating processes. Thermogravimetric (TG) analyses of the hydrogels were done in a Nitrogen atmosphere (having a flow rate of 30 ml/min) with a TG analyzer (TGA, Setaram Labsys) from 25 to 800°C at a heating rate of $10^{\circ}\text{C min}^{-1}$.

2.4. Determination of Swelling Degree

The swelling process of hydrogels was examined gravimetrically at 25°C . A certain amount of dried hydrogel was immersed into deionized water (at pH 6.0) and the swollen gel was then removed from the swelling media at regular time intervals. After wiping away the excess water with a filter paper, the hydrogel was weighed and put back in the same media again. The swelling degree (S) of the hydrogel was calculated using Eq. 1:

$$S = \frac{W_s - W_d}{W_d} \quad (1)$$

where S (g g^{-1}) is the amount of absorbed water per gram of hydrogel, and W_s (g) and W_d (g) are the weights of the swollen and dry samples, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Hydrogels

FTIR spectra of p-VIm and p-VIm-co-DMA₁₅ hydrogels are shown in Figure 2. Characteristic bands for p-VIm are observed at 3100 cm^{-1} (C–H ring stretching), 2940 cm^{-1} (C–H and CH_2 stretching on the main chain), 1650 cm^{-1} (C=C ring stretching), 1500 cm^{-1} (C–C and C=N ring stretching), 1280 , 1230 , 1085 and 915 cm^{-1} (C–H ring bending and C–N ring stretching) [23]. In

addition, the presence of C=O stretching vibration band at 1720 cm^{-1} and asymmetric stretching vibration band of C–O–C at 1145 cm^{-1} indicates that the copolymer was successfully synthesized.

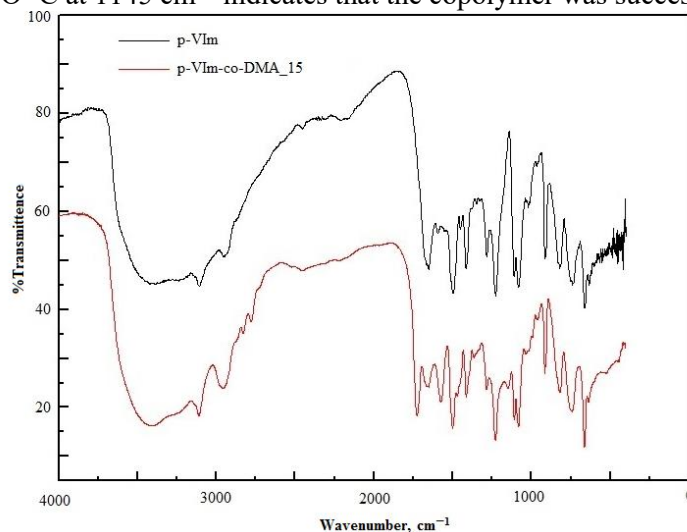


Figure 2. FTIR spectra of p-VIm and p-VIm-co-DMA_15

SEM images of the hydrogels (Figure 3 a-f) show that hydrogels have a very porous, spongy and leaf-like morphology, which possibly causes increased surface area. It can be concluded that this kind of morphological structure would potentially bring easier and faster diffusion of water molecules into the polymeric network [24].

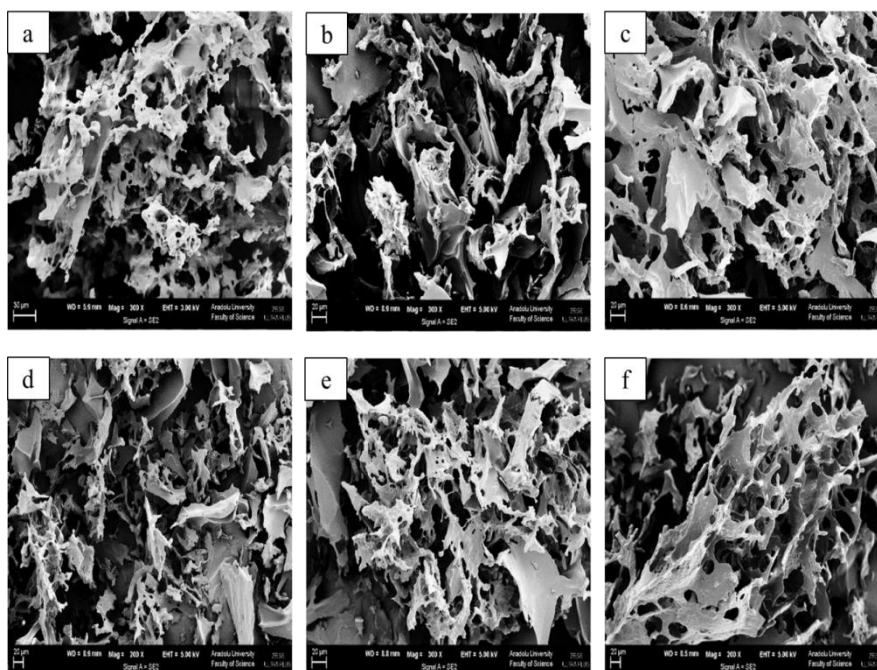


Figure 3. SEM images of (a) p-VIm, (b) p-VIm-co-DMA_1, (c) p-VIm-co-DMA_2.5, (d) p-VIm-co-DMA_5, (e) p-VIm-co-DMA_10, (f) p-VIm-co-DMA_15

The TG curves of the hydrogels are shown in Figure 4 and the results are given in Table 2. As seen in Figure 4, there was one thermal decomposition step for p-VIm, while two steps were observed for copolymeric hydrogels. This two-step thermal decomposition process for copolymeric hydrogels may

be a result of the decomposition of the two different kinds of moieties: DMA and VIm. The first weight loss steps of hydrogels (from 50 to 160°C) can be attributed to the water loss and to volatile compounds adsorbed at their surfaces. For p-VIm, a weight loss is observed due to the decomposition of the polymeric networks in the temperature range from 310 to 480°C [22]. In contrast, the first decomposition step of the copolymeric hydrogels shifted to lower temperatures (from 150 to 330°C). It was observed that as the DMA content in the polymeric matrix increases, the weight loss increases. The second decomposition step of the copolymeric hydrogels, which resulted in higher weight losses than those of first steps, were observed in the range from 300 to 530°C and can be ascribed to the decomposition of the VIm moieties of the polymeric backbone. The thermal stability of p-VIm is also found to be decreased considerably as a result of copolymerization.

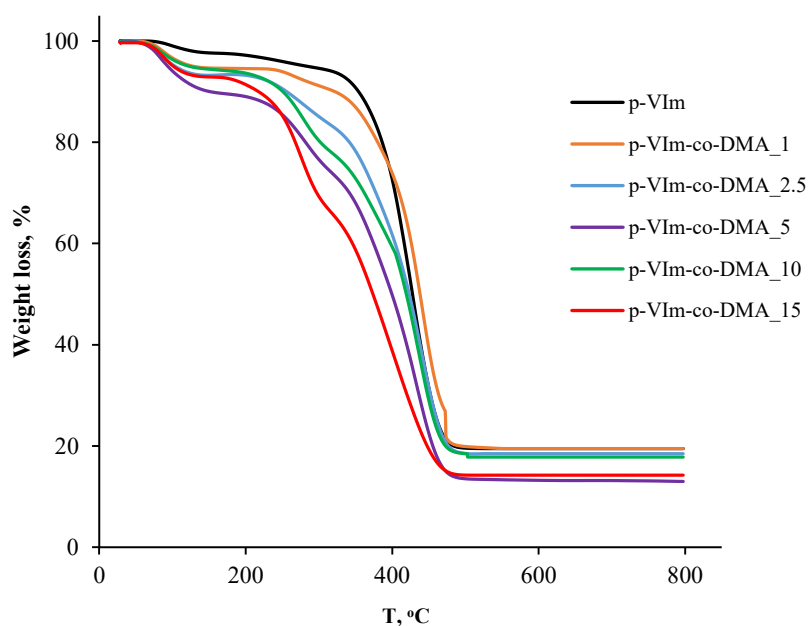


Figure 4. TG curves of the hydrogels

Table 2. The summary of TG analyses results

Sample	Process	Temperature range (°C)	Weight loss (%)	Ash amount at 800°C (%)
p-VIm	Losses of water and volatile compounds	80–140	2.3	19.7 [22]
	Decomposition step	310–480	74.8	
p-VIm-co-DMA_1	Losses of water and volatile compounds	60–140	5.2	19.5
	First decomposition step	235–300	3.4	
	Second decomposition step	300–510	69.9	
p-VIm-co-DMA_2.5	Losses of water and volatile compounds	55–140	6.7	18.8
	First decomposition step	200–300	8.1	
	Second decomposition step	300–515	66.4	
p-VIm-co-DMA_5	Losses of water and volatile compounds	50–140	9.5	14.4
	First decomposition step	150–300	13.5	
	Second decomposition step	300–515	62.6	
p-VIm-co-DMA_10	Losses of water and volatile compounds	50–165	5.5	14.7
	First decomposition step	175–330	17.6	
	Second decomposition step	330–530	60.7	
p-VIm-co-DMA_15	Losses of water and volatile	55–140	6.6	14.9

compounds		
First decomposition step	175–325	27.9
Second decomposition step	325–500	50.6

3.2. Swelling Behavior in Aqueous Solution

The swelling behavior of a hydrogel, which contains ionizable monomers such as VIm and DMA, can be affected by the nature of the polymer (i.e., the monomer composition and the content of cross-linking agent) and the environmental conditions such as pH, temperature and ionic strength of the swelling media. It was expected that the presence of ionizable monomers in the polymeric structure would enhance the water retention capacity of the hydrogel. In this study, the effect of changing the molar ratio of DMA/VIm on the swelling degree of the hydrogels was investigated at pH 6.0 and 25°C; the results are depicted in Figure 5. As seen in Figure 5, hydrogels showed a rapid water uptake, and the swelling degree increased with the increasing content of DMA in the copolymer structure.

Cabot et al. [25] determined the pK_a value of p-VIm as 4.9. At pH 6.0, p-VIm is neutral, while copolymeric hydrogels are positively charged because of the presence of DMA moieties whose pK_a value is about 8.4 [26]. For this reason, the positive charge intensity on the polymer chains of copolymeric hydrogels increases with increasing DMA content. So, repulsive forces exist between the neighboring ammonium groups on the polymeric backbone. These forces enhance the diffusion of water into the polymeric lattice resulting in an increased degree of swelling [22].

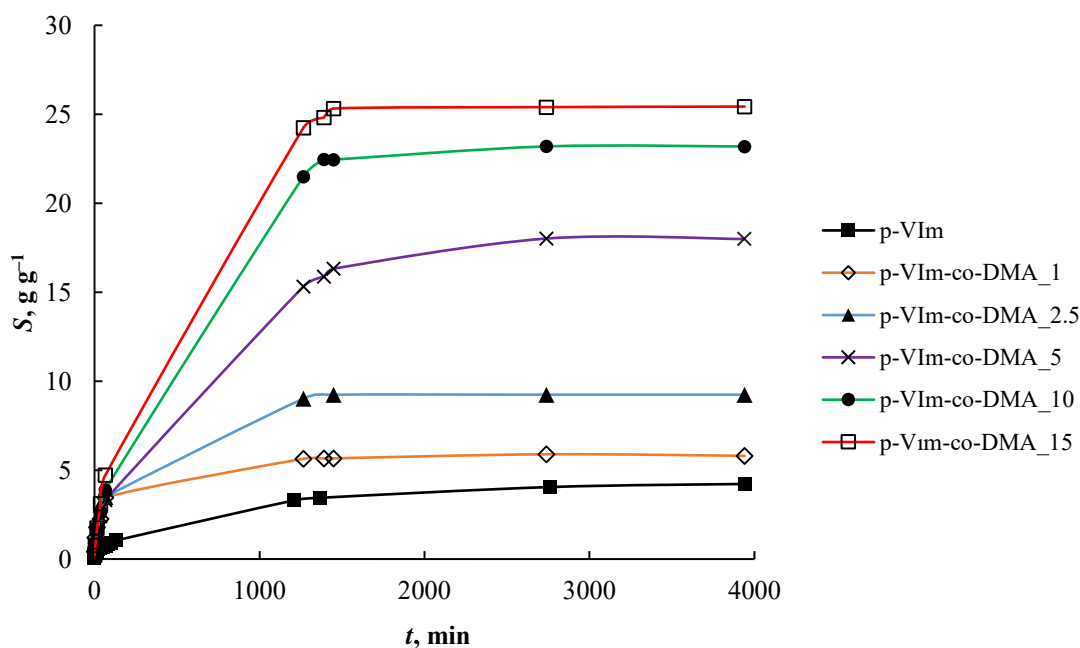


Figure 5. The swelling kinetic curves of the hydrogels in aqueous solution at pH 6.0 and 25°C

The experimental equilibrium swelling degrees of p-VIm, p-VIm-co-DMA_1, p-VIm-co-DMA_2.5, p-VIm-co-DMA_5, p-VIm-co-DMA_10 and p-VIm-co-DMA_15 are 4.20, 6.15, 9.88, 17.84, 23.07 and 25.64 $g\ g^{-1}$, respectively (see Figure 5). The percentage swelling (experimental) of p-VIm-co-DMA_15 increased up to 2564% while it was 420% for p-VIm. This means that the swelling degree increased by 610% with the presence of DMA. Uzum and Karadag [20] prepared some copolymeric hydrogels with acrylamide (AAm), *N*-vinylimidazole VIm and poly(ethyleneglycol) (PEG). They observed that the percentage swelling of AAm/VIm and AAm/VIm/PEG copolymeric hydrogels was higher than that of homopolymeric AAm hydrogel. In addition, a decrease in the percentage swelling

of AAm/VIm/PEG hydrogels was seen when PEG was added to the hydrogel systems. With AAm/VIm (containing 80 mg of VIm) and AAm/VIm/PEG (containing 80 mg of VIm), percentage swelling values were 4167% and 2574%, respectively. Isik and Dogantekin [1] also synthesized a series of AAm/VIm copolymeric hydrogels and their hydrogels exhibited a percentage swelling of approximately 1400% at pH 5 and 25°C and 1600% at pH 11 and 25°C. When the results obtained in this study with p-VIm-co-DMA_15 and p-VIm-co-DMA_10 at pH 6.0 (corresponding to percentage swelling of 2564% and 2307%, respectively) are compared with those of the AAm/VIm series, it can be clearly said that VIm/DMA hydrogels demonstrated better swelling performance. Moreover, in the study of Pekel and Guven [19], a percentage swelling of 450% was obtained with VIm/MA (maleic acid) containing 5.82% (w/w) MA at a pH of 6.0.

To test the swelling rate, the swelling process of the hydrogels was evaluated using Schott's second-order swelling kinetics model [27]. This model is expressed by Eq. 2:

$$\frac{dS}{dt} = k_s(S_\infty - S_t)^2 \quad (2)$$

where, k_s , S_∞ and S_t denote the swelling rate constant, and the swelling degree at a state of equilibrium and at time t , respectively. The integration of Eq. 2 gives the following equation (Eq. 3):

$$\frac{t}{S} = A + Bt \quad (3)$$

The constants $B = 1/S_\infty$ and $A = 1/k_s S_\infty^2 (= 1/(dS/dt)_0 = 1/r_0)$ can be calculated from the slope and intercept of Eq. 3. The plots of t/S versus t (Figure 6) show a good straight linear regression (with high R^2 values), indicating that the swelling process of the hydrogels followed Schott's second-order swelling model. The values of the kinetic parameters k_s , S_∞ and r_0 calculated from the slopes and intercepts, are tabulated in Table 3. It was shown that the swelling rate of the hydrogels was significantly influenced by the chemical composition of the structure, and that the values of r_0 increased with increasing DMA content in the copolymeric hydrogels. Furthermore, S_∞ values of the hydrogels were also increased up to a DMA content of 15%. These values are also similar to those of the experimental ones, suggesting that the kinetic model is in agreement with the swelling experiments. Higher swelling degree and enhanced swelling rate of the hydrogels with increasing content of DMA in the gel matrix are remarkable results.

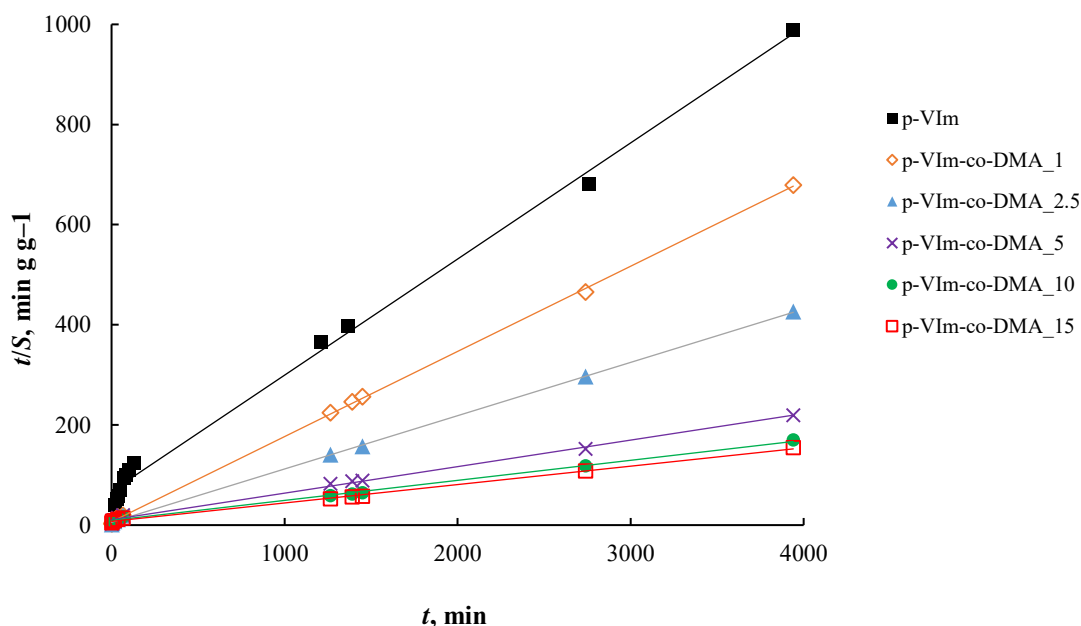


Figure 6. t/S versus t curves of hydrogels in aqueous solution at pH 6.0 and 25°C

Table 3. Swelling kinetic parameters of the hydrogels

Hydrogel	R^2	S_∞	r_0	k_s
p-VIm	0.9901	4.11	0.0177	0.00113
p-VIm-co-DMA_1	0.9997	6.08	0.1508	0.00167
p-VIm-co-DMA_2.5	0.9996	9.63	0.1817	0.00215
p-VIm-co-DMA_5	0.9996	17.96	0.1984	0.00334
p-VIm-co-DMA_10	0.9993	23.15	0.2234	0.00388
p-VIm-co-DMA_15	0.9991	25.51	0.2689	0.00437

4. CONCLUSIONS

In this study, p-VIm-based copolymeric hydrogels were synthesized at five different initial molar ratios via free radical solution polymerization in aqueous media, and characterization studies of them were carried out. FTIR, SEM and TGA were used for the structural, morphological and thermal characterization. The swelling behavior of the copolymers was also investigated. The following conclusions can be drawn:

- The additional bands (C=O stretching at 1720 cm^{-1} and asymmetric stretching of C–O–C at 1145 cm^{-1}) in the FTIR spectrum of p-VIm-co-DMA_15 confirm that the copolymer was successfully synthesized.
- All hydrogels have a spongy and porous morphology.
- p-VIm was thermally more stable than copolymeric analogues. p-VIm showed one thermal decomposition step, while copolymeric hydrogels displayed two steps.
- The swelling degree increased with increasing DMA content in the hydrogels. It was observed that this value reached 25.64 g g^{-1} (experimental) with p-VIm-co-DMA_15 at pH 6.0 and 25°C meaning that the swelling degree increased by 610% compared to that of p-VIm.
- The swelling kinetics of the hydrogels were fitted to the Schott's second-order swelling kinetic model with high linear regression values. The S_∞ values increased up to 25.51 g g^{-1} with the content of 15% DMA. r_0 and k_s values also increased with increasing DMA content in the hydrogels.

- Improved swelling degree and kinetics even at neutral pH values revealed that these type of VIm-based hydrogels could be useful for various applications involving the removal of some contaminants such as heavy metal ions, dyes and some organic pollutants from wastewater by adsorption.

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