Preparation and Characterization of Poly(N-Vinylpyrrolidone-co-Methacrylic Acid) Hydrogels

Dlek Şolpan[a]; Zeynep Kölge[a]; Murat Torun[a]

[a] Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

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DİLEK ŞOLPAN, ZEYNEP KÖLGE, AND MURAT TORUN

Hacettepe University, Department of Chemistry, Beytepe, Ankara, Turkey

In this study, N-vinylpyrrolidone (VP)/methacrylic acid (MAA) copolymers have been prepared at three different mole percents, the methacrylic acid composition being around 5, 10, 15%. MAA and VP monomer mixtures have been irradiated in ^{60}Co-γ source at different irradiation doses and percent conversions have been determined gravimetrically. ∼80% conversion of monomers into hydrogels were performed at 3.4 kGy irradiation dose. These hydrogels were swollen in distilled water at pH 4.0, 7.0, and 9.0. P(VP/MAA) hydrogel which contains 5% methacrylic acid showed the maximum % swelling at pH 9.0 in water. Diffusion of water was found to be of non-Fickian character. Diffusion coefficients of water in P(VP/MAA) hydrogels were calculated. Initial swelling rates of P(VP/MAA) hydrogels increased with increasing pH and MAA content in hydrogels. Swelling kinetics of P(VP/MAA) hydrogels was found to be of second order. Thermal behavior of PMAA, PVP and P(VP/MAA) hydrogel were investigated by thermal analysis. P(VP/MAA) hydrogel gained new thermal properties and the temperature for maximum weight loss and temperature for half-life of P(VP/MAA) hydrogel were determined.

Keywords gamma-irradiation, hydrogel, poly(N-vinylpyrrolidone-co-methacrylic acid), adsorption

Introduction

Hydrogels can be defined as three-dimensional networks of polymers which have the ability to swell the dry network mass several hundred times when in contact with water or aqueous solutions. Gel properties depend strongly on the degree of crosslinking, the chemical composition of the polymer chains, and the interactions of network and surrounding liquid. The liquid prevents the polymer network from collapsing into the compact mass and the network prevents the liquid from running off (1).

In recent years, much attention has been directed at hydrogels that undergo large volume changes in response to a small variation in external stimuli such as pH and temperature. Temperature and pH have been the solution variables that change in typical physiological, biological and chemical systems. Temperature and/or pH-sensitive hydrogels have been suggested for use in a variety of novel applications including controlled drug

delivery, immobilized enzyme reactors and separation process. In the recent past, much work has been carried out on the synthesis and characterization of pH- and temperature-sensitive hydrogels by copolymerization and crosslinking (2).

Poly(N-vinylpyrrolidone) (PVP) has unusual complexing and collodial properties and is physiologically inert. Aqueous solutions of PVP, when heated with strong bases such as sodium metasilicate and trisodiumphosphate, form a precipitate but, when PVP aqueous solutions are submitted to high energy radiation, hydrogels with high absorption are obtained. The water absorption capacity is directly related to the degree of crosslinking which depends to a great extent on the radiation dose, the type of high-energy radiation (electron beams, γ-rays, fast protons, X-ray, etc.), and to a smaller extent, on the dose rate and temperature (3).

In this work, poly(N-vinylpyrrolidone-co-methacrylic acid) P(VP/MAA) copolymer hydrogels were prepared by means of γ-rays inducing homo and copolymerization as a clean and environment friendly source of initiation. The factors' effect on the preparation and properties of the hydrogels were investigated.

Experimental

Materials

The monomers used in this study, N-vinyl-2-pyrrolidone (VP) and methacrylic acid (MAA), were obtained from Merck, N,N-methylene-bis-acrylamide was used as a crosslinking agent, and it was obtained from Aldrich. Hydrochloric acid and sodium hydroxide, used to adjust the pH of the medium, were obtained from Merck. The pH of the adsorption medium was changed between 4.0 and 9.0 by using different buffer systems (0.1 M CH_3COONa-CH_3COOH for pH 4.0–6.0, 0.1 M K_2HPO_4-KH_2PO_4 for pH 7.0 and 0.1 M NH_4OH-NH_4Cl for pH 9.0). Deionized water was used for preparation of hydrogels and in swelling.

Preparation of Hydrogels

The solutions of monomers of MAA and VP were prepared at three different compositions (MAA/VP mole ratios: 5/95, 10/90, 15/85). These solutions were placed in polyvinylchloride straws, 3 mm in diameter, and irradiated in air at an ambient temperature in a Gammacell 220 type γ irradiator. Doses of 0.4–20.0 kGy were applied at a fixed dose rate of 0.14 kGyh^{-1}. The hydrogels obtained in long cylindirical shapes were cut, these polymer pieces were then washed in distilled water to remove the unreacted monomers (if any) and dried in air and in vacuum and stored for later evaluations. The percent gelation was determined gravimetrically. ∼80% gelation was performed for all mixtures at 3.4 kGy dose.

Determination of Percent Gelation

The obtained poly(N-vinylpyrrolidone-co-methacrylic acid) P(VP/MAA) hydrogels were cut into pieces ≈ 2mm long. The prepared gels were immersed in deionized water for a week to remove the uncrosslinked polymer and low molecular weight substances. Extracted gels were dried again in a vacuum oven at room temparature to a constant weight. Percent conversion of these hydrogels as an insoluble network was determined by dividing the weight of this hydrogel to its initial weight. The percent gelation of P(VP/MAA) hydrogels was calculated as follows:

$$\% \text{ Gelation} = (\text{weight of dry gel}/\text{weight of initial polymer}) \times 100 \qquad (1)$$

Composition of Hydrogels

The irradiated monomer mixtures were dried in a vacuum oven until a constant weight and subjected to extraction with deionized water as solvent. The uncrosslinked polymer and residual monomer were removed from the gel structure. The amount of uncrosslinked MAA was determined by titration of the extract against NaOH (0.05 M) to a phenolphthalein end point.

Swelling Studies

Dried P(VP/MAA) hydrogels (2 mm thickness, 3 mm diameter) were weighed and left to swell in deionized water and a dye solution of desired pH (4, 7, 9) at an ambient temperature. Periodically, the P(VP/MAA) hydrogels were withdrawn from the solution and weighed after removing the excess surface water. The measurements were continued until the weight of P(VP/MAA) hydrogels reached a constant value. The percent swelling of each P(VP/MAA) hydrogel was calculated from the following relation:

$$\% \text{ Swelling} = [(m_t - m_0)/m_0] \times 100 \tag{2}$$

where m_t is the mass of swollen P(VP/MAA) at time t, and m_0 is the initial mass of dry P(VP/MAA). Some parameters (diffusion characters, equilibrium water content, etc.) were calculated by using swelling data.

Spectroscopic and Thermal Analysis

Fourier Transform Infrared (FTIR) spectra of the homopolymers, P(VP/MAA) hydrogels, dyes and P(VP/MAA) hydrogels, which contain dyes, were recorded between $4000-400\,cm^{-1}$ on a Nicolet 520 FTIR spectrometer as KBr pellets. The P(VP/MAA) hydrogels were characterized by comparing the FTIR spectra of homopolymers and P(VP/MAA) hydrogels. A Dupont 910 model thermogravimetric analyzer was used for determination of the thermal stabilities of homopolymers and P(VP/MAA) hydrogels. Samples weighing $5-10\,mg$ were heated in a dynamic nitrogen atmosphere from $20°C$ to $800°C$ at a heating rate of $10°C\,min^{-1}$.

Results and Discussion

Synthesis and Characterization

Poly(N-vinylpyrrolidone) and its copolymers are widely used in the textile, food, pharmaceutical and cosmetics industries, and for the finishing of paper. In spite of the large amount of work denoted to a study of polymerization and copolymerization of N-vinylpyrrolidone (VP), both initiation with the aid of initiators and by γ-radiation (3–9). Polymerization of methacrylic acid and acrylic acid in the presence of poly(vinyl pyrrolidone) has been described in many papers (10–14), and it has been shown that in both cases polymerization proceeds as a template process. In this study, to raise the water-uptake capacity of the N-vinylpyrrolidone (VP), methacrylic acid (MAA) having hydrophilic groups and N-vinylpyrrolidone are used to prepare a copolymeric hydrogel system. An ionizing radiation processing was used for preparation of poly(N-vinylpyrrolidone-co-methacrylic acid) P(VP/MAA) hydrogels. A possible free radical polymerization reaction of N-vinylpyrrolidone with methacrylic acid by γ-rays is shown in Figure 1.
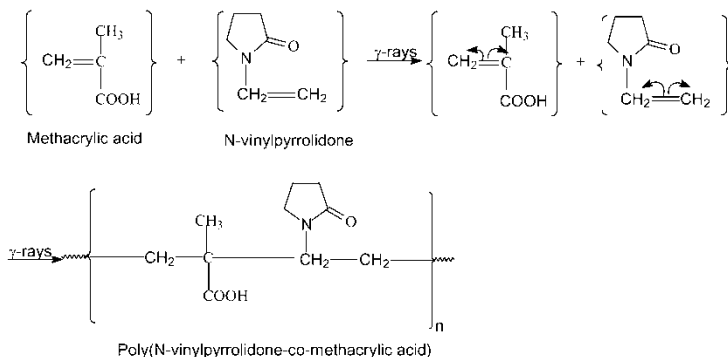
Figure 1. Possible copolymerization reaction of N-vinylpyrrrolidone with methacrylic acid.

When the VP/MAA mixture was irradited, π-bond in the vinyl double bond of both monomers were formed into monomer radicals. The monomer radicals formed were combined together and poly(methacrylic acid-co-vinyl pyrrolidone) copolymers were obtained. If the irradiation was continued, crosslinking reaction started, chains were cross-linked to each other, and gelation occurred in the system. In order to have high mechanical stability, hydrophilicity, and the ability to adsorb cationic species, the MAA was added to N-vinylpyrrolidone (VP). 1% N,N-methylene-bis-acrylamide was added to the VP/MAA initial mixtures to form more stable hydrogels and to provide more crosslinking and percent gelation at lower doses. The VP/MAA mixtures were irradiated in the range between 0.4 and 20.0 kGy irradiation doses at 0.14 kGyh^{-1} dose rate. MAA and VP monomer mixtures, which contain MAA initial compositions 5, 10, 15% by mole basis were used. After the preparation of hydrogels, they were cut, then these hydrogels were put into water and the swollen hydrogels were dried.

Composition of Hydrogels

The percent gelation of P(VP/MAA) hydrogels is given in Figure 2. At the end of prelimi-nary irradiations $\approx$80% gelation occurred for all mixtures in the range of 0.4–7.0 kGy
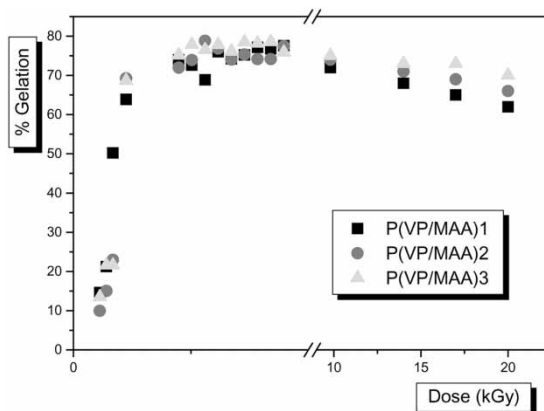

Figure 2. The effect of irradiation dose on the percent gelation of VP/MAA monomer mixtures containing 1% N,N-methylene-bis-acrylamide.

irradiation doses. It is well known that degrees of conversion and crosslinking greatly depend on the irradiation dose. The higher exposure dose means longer exposure time, which consequently prolongs the propagation step of the process of copolymerization leading to higher degrees of conversion and crosslinking. It is obvious that a decrease in gelation is a result of chain scission occurring in the polymer chain, thus decreasing the probability of crosslinking and degree of percent gelation. Since the gelation reached maximum extent at a 3.4 kGy irradiation dose, the hydrogels irradiated at the 3.4 kGy irradiation dose were used in this study. P(VP/MAA)1, P(VP/MAA)2, P(VP/MAA)3 have been used for three different compositions of P(VP/MAA) hydrogels which contain VP/MAA monomer mixtures at three different mole percents, which are 64/36, 78/22, 82/18, respectively. As can be seen from Figure 2, the percent gelation increased with the increasing irradiation dose. After a 6.0 kGy irradiation dose, the percent gelation started decreasing. A slight decrease in the % conversion for all initial mixtures after 6.0 kGy was observed. This can be attributed to chain scission of the system in the presence of oxygen. As can be seen from Figure 2, the effect of VP is more predominant at a low irradiation dose and after 6.0 kGy, the percent conversion is also dependent on the amount of VP content.

Initial mole percents of monomers in copolymeric gels were determined after removing uncrosslinked polymer and residual monomer with extraction from the gel structure. To determine the composition of the copolymers, the amount of crosslinked MAA was determined by titration of the extract against NaOH to phenolphthalein end point. The mole percents of monomers in the hydrogel systems are given in Table 1. Feed composition and corresponding copolymer compositions were evaluated and the results (Table 1) lead to some interesting results. The reactivity ratios were calculated by using Q-e values of both monomers (15). The results of relatively high r_1 (44.66) and low r_2 (3.38) values explain that MAA has the ability to polymerize with itself and the other monomer rather poorly and the composition of MAA in the hydrogel system is higher than those of feed composition. The highest percent gelation occured in the range of 2.8–6.0 kGy irradiation doses, so, the hydrogel irradiated at 3.4 kGy irradiation dose were used and the ionic strength was kept as 0.1 M during this study.

Spectroscopic Characterization

To ascertain structurally the formation of the poly(N-vinylpyrrolidone-co-methacrylic acid) P(VP/MAA) hydrogels, a FTIR analysis was carried out on P(VP/MAA) hydrogel, PMAA and PVP homopolymers. As shown in Figure 3, in the FTIR

Table 1

Composition of MAA and VP in the gel systems and % gelation at 3.4 kGy irradiation dose

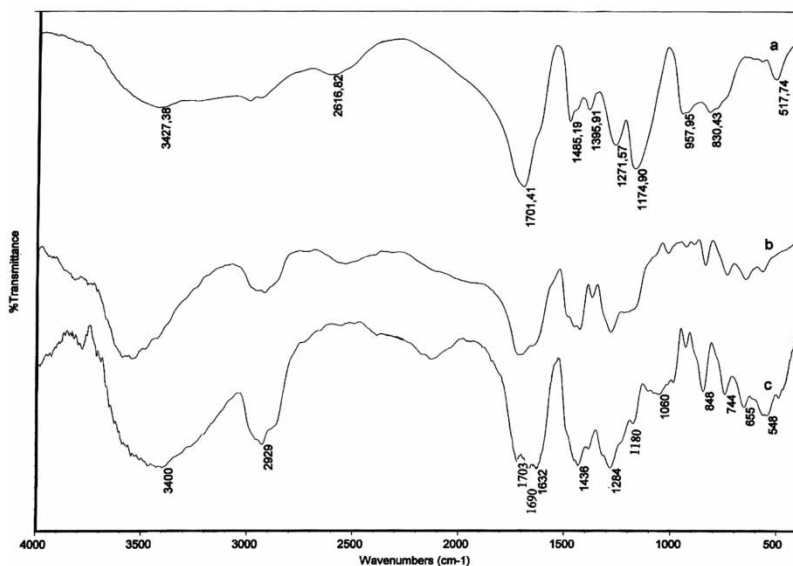| Hydrogel	% Mol of MAA in hydrogel	% Mol of VP in hydrogel	% Gelation
P(VP/MAA)1	35.7	64.3	77.0
P(VP/MAA)2	21.9	78.1	77.0
P(VP/MAA)3	17.5	82.5	76.0

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Figure 3. FTIR spectra of (a) PMAA, (b) P(VP/MAA)3, (c) PVP.

spectra of PVP, PMMA and P(VP/MAA) hydrogel, the absorbances are given in the following:

PVP
$1100-1200\,cm^{-1}$	C–N absorption bonds
$2900\,cm^{-1}$	C–H stretching vibrations
$1396\,cm^{-1}$	–CH$_2$– groups on the chain
$1703\,cm^{-1}$	C=O stretching band peak
$1436\,cm^{-1}$	C–C stretching band of pyrrolidone ring

The band at $1690\,cm^{-1}$ corresponds to stretching vibrations of the C=O bond in the free PVP carbonyl groups (16).

PMAA
$3000-3500\,cm^{-1}$	O–H band
$2900\,cm^{-1}$	C–H stretching vibrations
$1396\,cm^{-1}$	–CH$_2$– groups on the chain
1485, 1396 and $1700\,cm^{-1}$	COOH
$1100\,cm^{-1}$, $1200\,cm^{-1}$	CH$_3$ related to C and carboxylic group

The infrared bands of α-branched carboxylic acid are at $612\,cm^{-1}$ and $535\,cm^{-1}$, this may be due to a torsional vibration of the methyl group (17–20).

P(VP/MAA)
1700, 1485, $1396\,cm^{-1}$	ν(C=O) of the cyclic groups
1200, $1100\,cm^{-1}$	(CH$_3$) bands related to C and carboxylic group in PMAA.
$1690\,cm^{-1}$	ν(C=O) of the carboxylic group
$1436\,cm^{-1}$	ν(C–C) stretching band of pyrrolidone ring
$1180\,cm^{-1}$	C–N absorption band at in PVP

The bands that belong to both components can be seen in the FTIR spectrum of P(VP/MAA) hydrogel. These results indicate that the MAA monomer copolymerized with VP monomer. The FTIR spectrum of P(VP/MAA) hydrogels at different compositions are shown in Figure 4. The most important peaks appeared at 1690 and 1436 cm^{-1}. These peaks at 1690 cm^{-1} $\nu(C{=}O)$ of the carboxylic group and at 1436 cm^{-1} $\nu(C{-}C)$ stretching band of pyrrolidone ring increased gradually with increasing VP percent in the hydrogels.

Thermal Characterization

In order to investigate the thermal behavior of PMAA, PVP, P(VP/MAA) hydrogels, their thermograms were recorded. The TGA data furnished in Figure 5 show the general nature of the thermograms of the homopolymers, PMAA and PVP, and copolymer hydrogel. The thermal stability of the homopolymers and copolymer was assessed by comparing the weight loss in the temperature range 25°C–800°C. Figure 5 shows the effect of PVP or PMAA in the copolymer hydrogel on its thermal stability. Pure PVP shows high thermal stability that starts to decompose at 400°C, whereas pure PMAA shows its famous two degradation steps at 200 and 400°C, which are due to the anhydride formation and decarboxylation (19–22). It is known that PMAA decomposes at 200°C. Figure 5(b) also shows that the prepared copolymer hydrogel P(VP/MAA)3 possesses high thermal stability, which is almost similar to that of pure PVP. It was observed that when a less stable species combined with a species of higher thermal stability, this hydrogel gained new thermal characteristics. The temperature for maximum weight loss (T_{max}) for P(VP/MAA)3 is 415°C and the temperature for half-life ($T_{1/2}$) is 450°C. P(VP/MAA)3 gives $\sim$5% residue at 700°C.
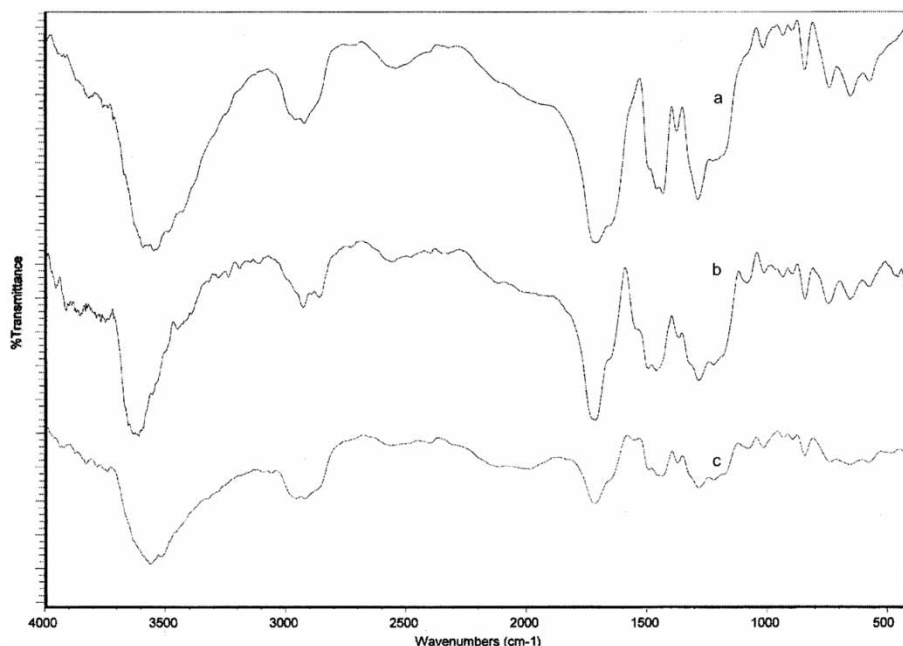

Figure 4. FTIR spectra of (a) P(VP/MAA)1, (b) P(VP/MAA)2, (c) P(VP/MAA)3.
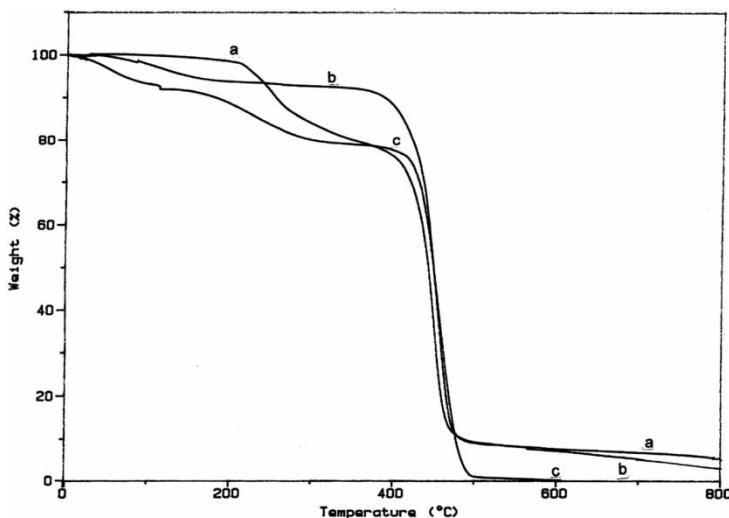
Figure 5. The thermograms of (a) PMAA, (b) P(VP/MAA)3, (c) PVP.

Swelling and Diffusion Studies

The most important property of a hydrogel is its ability to absorb and hold an amount of solvent in its network structure. The equilibrium swelling of a hydrogel is a result of the balance of osmotic forces determined by the affinity to the solvent and network elasticity (23). The two most important factors controlling the extent of swelling are the hydrophilicity of polymer chains and the crosslink density. Hydrogel properties depend strongly on the degree of crosslinking, the chemical composition of the polymer chains, and the interactions of the network and surrounding liquid. Swelling properties of hydrogels are very important parameters for assessing their applicability as controlled released systems, super absorbent materials etc.

The effect of feed solution composition on the swelling of the prepared P(VP/MAA) copolymer hydrogel at different pHs, at 25°C temperature and at 0.1 M ionic strength was studied. The obtained results are presented in Figure 6(a,b,c). The water uptake of initially dry hydrogels are followed for a long period of time. All of the hydrogels showed similar swelling behavior. Swelling of hydrogels was found to increase with pH and time. The measurements were continued until a constant weight was reached for each sample. This constant weight corresponds to equilibrium swelling of polymer for a given gel sample swollen to equilibrium in water. pH-Sensitive copolymers can be prepared by using ionic monomer such as methacrylic acid. Charged groups attached to the polymeric network structure played an essential role in swelling and adsorption properties (24). It can be seen that the swelling behavior of the copolymer is greatly influenced by its composition. Figure 7 gives the effect of the MAA content in hydrogels on the swelling behavior of P(VP/MAA) copolymer hydrogel at different pHs, at 25°C and 0.1 M ionic strength. At low pH value (pH 4), the swelling degree increases as the VP content in the copolymer gel increases. Whereas, at high pH value (pH 9), the swelling degree is higher than the other pH values. These results could be explained as follows: at low pH value, the MAA rich copolymer hydrogels possess a low swelling degree due to the association of the carboxylic groups and the intermolecular hydrogen bonding. As the VP content increases the number of the associated groups decreases and consequently, the
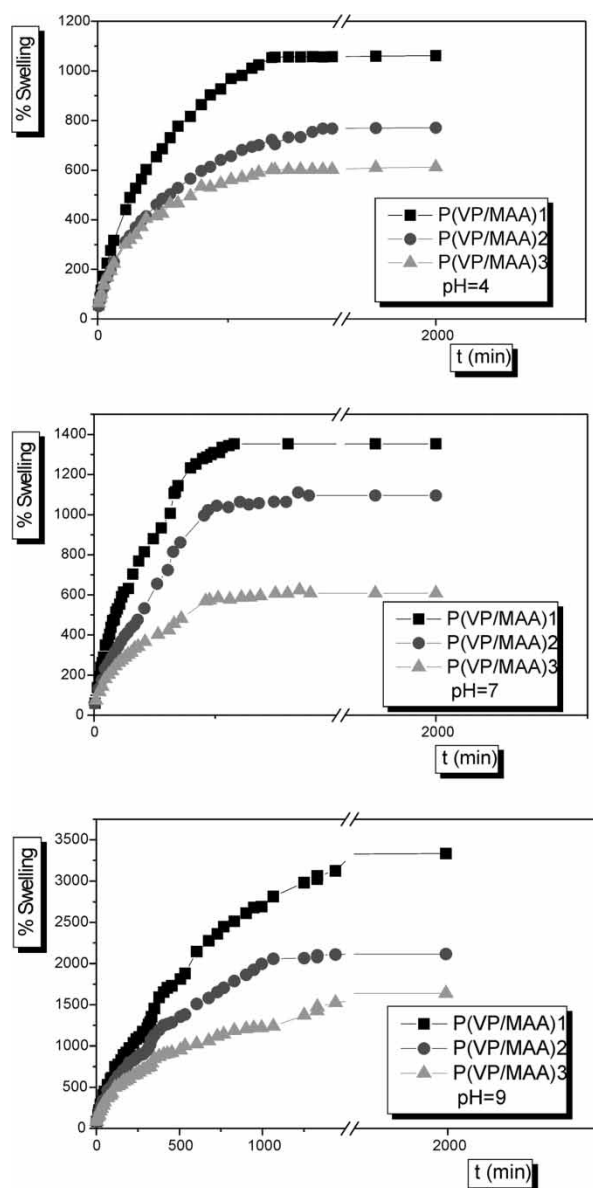
Figure 6. Effect of pH on swelling behavior of P(VP/MAA) hydrogels at 25°C I:0.1 M, total dose given: 3.4 kGy.

intermolecular hydrogen bonding also decreases but the intermolecular hydrogen bonding between VP and H_2O molecules increases which give a space for the PVP chain to swell freely in water. In contrast, at a high pH value (pH 9), the MAA rich copolymer gels possess high swelling degree that the carboxylic groups are completely dissociated. The swelling values reach its maximum value because of the intermolecular repulsion between the carboxylate groups. As the PVP content increases, the number of carboxylate groups decreases and although the intermolecular repulsion forces
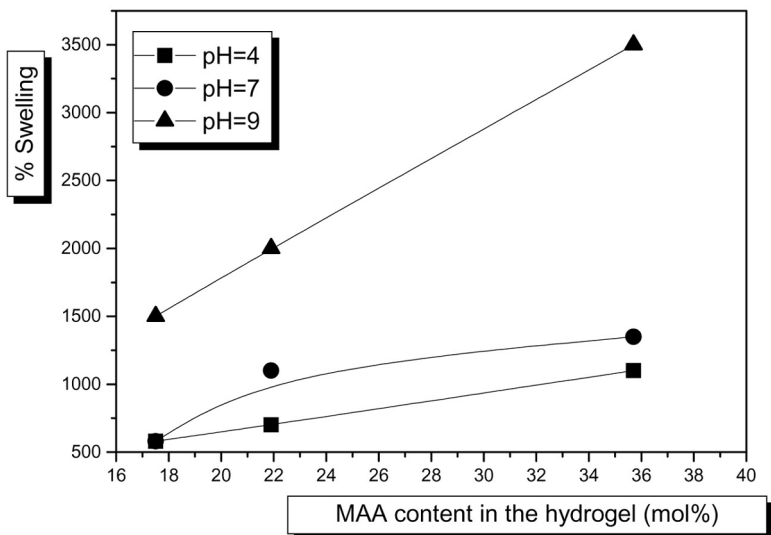
Figure 7. The effect of MAA content on the swelling behavior of P(VP/MAA) hydrogels at different pH's and 25°C. I: 0.1 M, total dose given: 3.4 kGy.

decreases, the intermolecular hydrogen bonding between VP and H_2O molecules continue to dominate, resulting in the increasing in the free spaces valid for swelling.

The equilibrium swelling behavior of P(VP/MAA) copolymer hydrogel was investigated as a function of pH. Figure 8 shows the typical behavior of a pH-sensitive copolymer hydrogel. The pH sensitivity of such a hydrogel is fully dependent on its composition. All of the investigated copolymer hydrogels possess change in the swelling degree at a pH value around 6, which is the approximately the pKa value of MAA (isobutyric acid repeating monomer unit, pKa = 4.83) ($Ka = 1.48 \times 10^{-5}$) (25, 26). At pH values lower
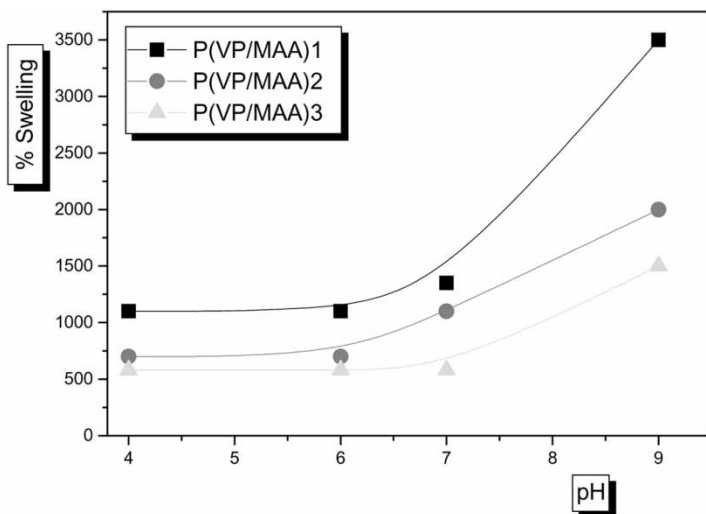
Figure 8. Effect of pH on swelling behavior of P(VP/MAA) copolymer hydrogels at 25°C, I: 0.1 M, total dose given: 3.4 kGy.
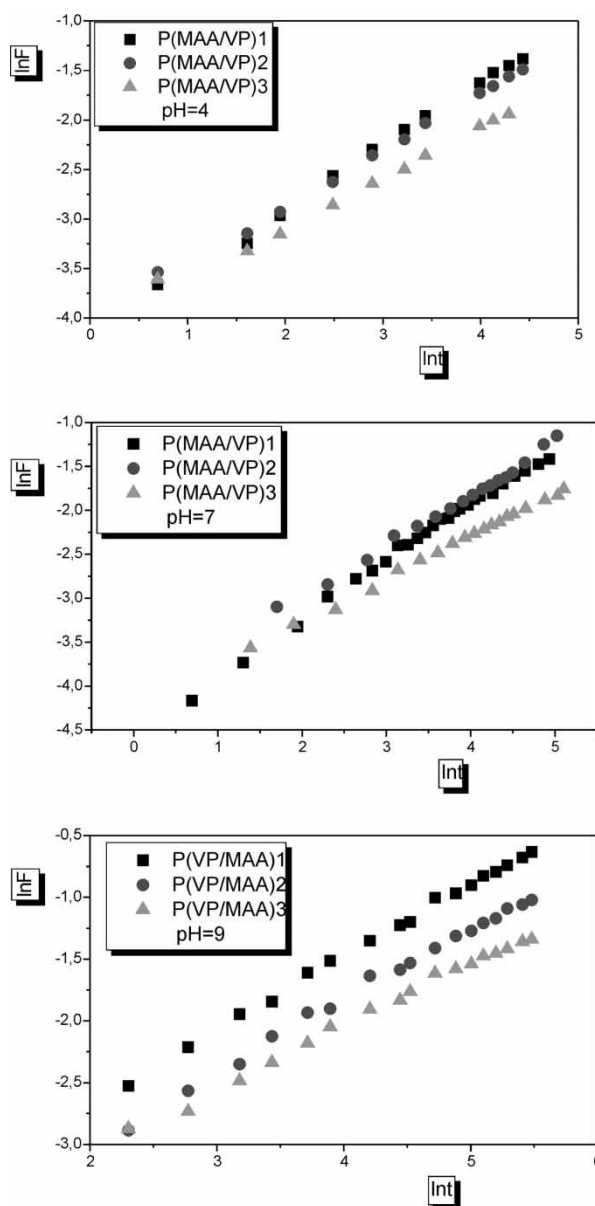
Figure 9. Plots of ln(F) vs. ln(t) of P(VP/MAA) hydrogels at various pH and 25°C. I: 0.1 M, total dose given: 3.4 kGy.

than the pKa value, the carboxylic groups are completely undissociated and the swelling degree is very low. At pH values higher than the pKa value, the swelling degree increased due to the dissociation of the carboxylic groups and broke the hydrogen bonding. The increase in the MAA content in the hydrogel leads to the increment in the carboxylate groups and consequently, increases the electrostatic repulsion which results in the expansion of the network structure.

In order to study the diffusion phenomena in P(VP/MAA) hydrogels, the swelling curves of P(VP/MAA) hydrogels were used to determine the nature of the diffusion of water into hydrogels by the following equation (27).

$$F = M_t/M_\infty = kt^n \qquad (3)$$

where M_t and M_∞ denote the amount of solvent diffused into the gel at time t and infinite time (at equilibrium), respectively. k is a constant related to the structure of the network, and the exponential n is a number used to determine the type of diffusion. This equation was applied to the initial stages of swelling. Plots of ln(F) vs. ln(t) are shown in Figure 9(a,b,c). The exponents (n) and k were calculated from the slope and intercept of the lines and the results were given in Table 2. Diffusion coefficients were calculated from the relation (28)

$$D = 0.049/(t/4r^2)^{1/2} \qquad (4)$$

where D is in $cm^2 min^{-1}$, t is the time at which the swelling is one-half the equlilibrium value (V/Vo = 1/2), and r is the radius of the swollen cylindirical sample. For the hydrogels, F vs. $t^{1/2}$ curves were given in Figure 10(a,b,c). Slope of the lines of F vs. $t^{1/2}$ give the diffusion coefficients. Diffusion coefficients are also listed in Table 2. Table 2 shows the diffusion coefficients (D) and the index (n), for P(VP/MAA) hydrogels at various pH's. Diffusion coefficients of P(VP/MAA) hydrogels varied from 4.6×10^{-4} to $7.98 \times 10^{-5} cm^2 min^{-1}$. These diffusion coefficients lead to a higher water uptake rate with higher pH. The exponents n of the hydrogels with different hydrogel equilibrium water content, which was defined as the weight percentage of water sorbed to that of hydrogels, exhibit a greater departure from 0.5 which is the characteristic of a non-Fickian transport. The information from Table 2 reveals that the coupling between molecular transport and stress relaxation during hydrogels swelling become more pronounced for samples at higher equilibrium water absorption (29).

Swelling Kinetics

To investigate extensive swelling of P(VP/MAA) hydrogels, the following equation can be used (30, 31):

$$t/s = A + Bt \qquad (5)$$

where $B = 1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A = 1/k_s S_{eq}^2$ is the reciprocal of the initial swelling rate of the gel and k_s is the swelling rate constant, t is

Table 2

The variation of the swelling and diffusion parameters of P(VP/MAA) hydrogels in water with pH at 25°C. I: 0.1 M, total dose given: 3.4 kGy

| pH | P(VP/MAA)1 | | | P(VP/MAA)2 | | | P(VP/MAA)3 | | |
	$k \times 10^2$	n	$D \times 10^5$	$k \times 10^2$	n	$D \times 10^4$	$k \times 10^2$	n	$D \times 10^4$
4.0	1.7	0.49	5.16	1.6	0.57	5.07	1.5	0.64	4.64
7.0	1.8	0.49	5.68	1.6	0.57	5.31	1.9	0.65	4.75
9.0	2.1	0.50	7.98	1.6	0.52	5.79	2.2	0.58	4.94
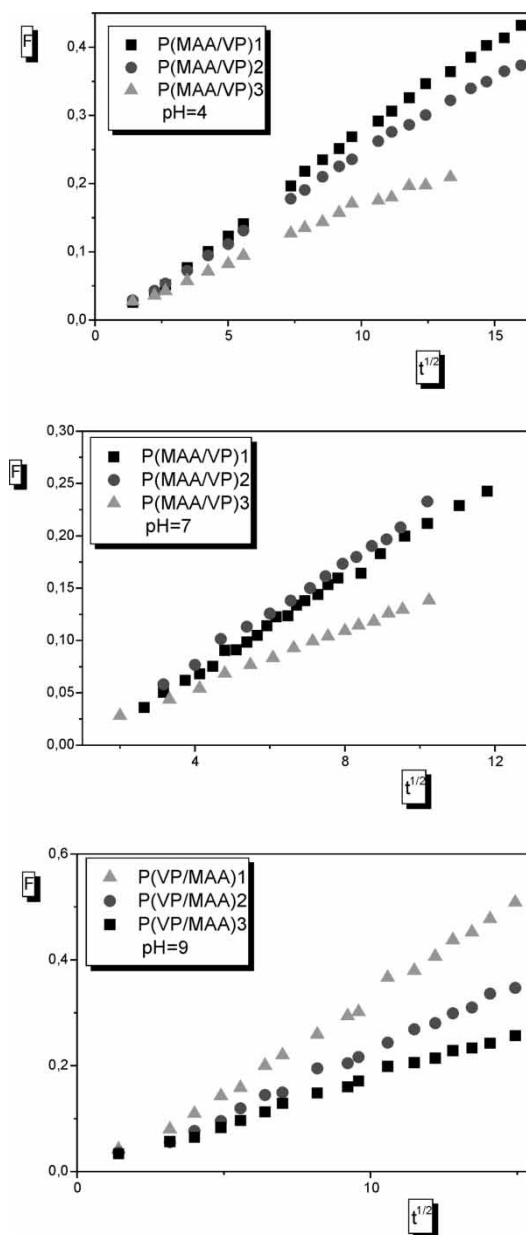
Figure 10. Plots of F vs. $t^{1/2}$ of P(VP/MAA) hydrogels at various pH and $25°C$. I: 0.1 M, total dose given: 3.4 kGy.

time and S is swelling of the hydrogels. This relation represents second order kinetics (30). Figure 11 shows the linear regression of the swelling curves obtained by means of Equation (5) for P(VP/MAA) hydrogels. The initial swelling rate (r_i), swelling rate (k_s) constant and theoretical equilibrium swelling (S_{eq}) of P(VP/MAA) hydrogels were calculated from the slope and intersection of the lines and were presented in Table 3.
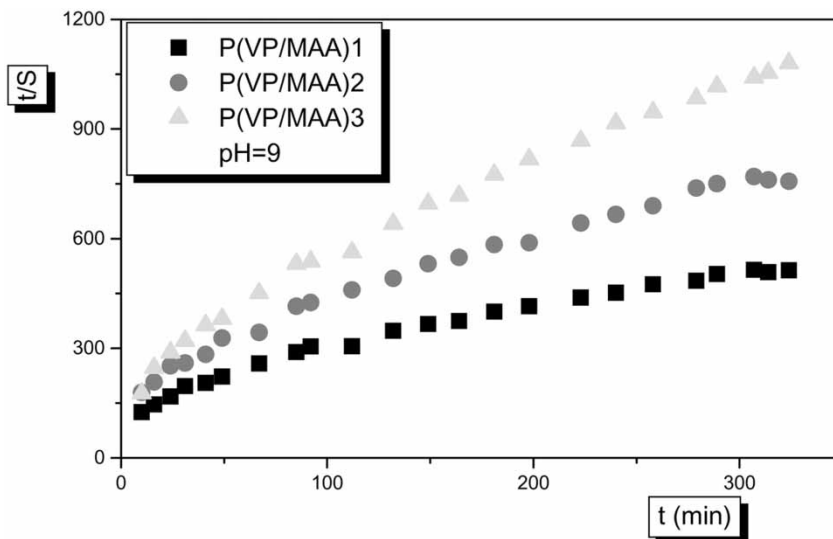
Figure 11. Swelling kinetics curves of P(VP/MAA) hydrogels in water at pH 9.0 and 25°C. I: 0.1 M, total dose given: 3.4 kGy.

Table 3 shows S_{eq} as a function of pH. In general, the swelling process is quicker (higher S_{eq} and higher r_i) at higher pH values. This behavior could be explained by dipole–dipole and hydrogen bonding specific interactions between hydroxylic groups in the water and carboxylic groups of MAA. These interactions become stronger as the hydroxyl group concentration of the medium increases favoring the swelling of the hydrogels. As can be seen, the behavior of S_{eq} depends on the pH range. In fact, all the studied hydrogels exhibit a similar tendency at acid and neutral pH.

It is very interesting to compare the swelling capacity at equilibrium, S_{eq}. Figure 8 showed the variation of this magnitude as a function of pH. The swelling at equilibrium increases as pH increases, for the same reasons as given for S_{eq}. In our opinion, and taking into consideration the chemical structure of both monomers, the possibility of stabilization of the hydrogel by hydrogen bonding increases and so the differences due to MAA monomer become more negligible.

Conclusions

P(VP/MAA) copolymers have been prepared at three different mole percents and irradiated in ^{60}Co-γ source at different irradiation doses.

Percent conversion of monomer mixtures into hydrogels increases with increasing irradiation dose ~80% conversion of monomer into hydrogel were performed at 3.4 kGy dose.

Percent composition of hydrogels was found by titration with NaOH.

Spectroscopic analysis of homopolymer and copolymers were done to explain the interactions between monomers.

The thermal property of P(VP/MAA) hydrogel was found between the homopolymers.

Table 3

The variation of the swelling kinetics parameters of P(VP/MAA) hydrogel in water with pH at 25°C. I: 0.1 M, total dose given: 3.4 kGy

pH	P(VP/MAA)1			P(VP/MAA)2			P(VP/MAA)3		
	$k_s \times 10^{-2}$	$r_i \times 10^2$	$S_{eq} \times 10^{-2}$	$k_s \times 10^{-2}$	$r_i \times 10^2$	$S_{eq} \times 10^{-2}$	$k_s \times 10^{-2}$	$r_i \times 10^2$	$S_{eq} \times 10^{-2}$
4.0	4.94	0.56	0.60	7.01	0.42	0.54	26.26	0.21	0.30
7.0	10.13	0.58	0.44	7.00	0.45	0.67	42.29	0.26	0.30
9.0	12.28	0.61	0.85	7.33	0.45	0.55	18.00	0.39	0.37

r_i: (g water/g hydrogel)/min.
k_s: (g hydrogel/g water)/min.
S_{eq}: g water/g hydrogel.
D: $cm^2 min^{-1}$.

P(VP/MAA) hydrogel containing the high MAA, showed maximum % swelling in distilled water at basic medium due to electrostatic repulsions between the carboxylic acid in hydrogel and hydroxyl ions.

Diffusion of water within hydrogels was found to be of a non-Fickian character.

Diffusion coeffcients were calculated for P(VP/MAA) hydrogel in water.

Swelling kinetics of P(VP/MAA) hydrogel in distilled water was found to be of second order.

Initial swelling rate increased with pH and MAA content in hydrogel.

P(VP/MAA) hydrogels are pH-sensitive hydrogels. They swelled in basic medium and collapse in acidic medium.

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