Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Adsorption Properties of Poly(N-vinylpyrrolidone-co-methacrylic acid) Hydrogels

Dilek Şolpan[a]; Zeynep Kölge[a]; Murat Torun[a]
[a] Department of Chemistry, Hacettepe University, Beytepe, Ankara, Turkey

To cite this Article Şolpan, Dilek , Kölge, Zeynep and Torun, Murat(2006) 'Adsorption Properties of Poly(N-vinylpyrrolidone-co-methacrylic acid) Hydrogels', Journal of Macromolecular Science, Part A, 43: 1, 129 — 152
To link to this Article: DOI: 10.1080/10601320500406024
URL: http://dx.doi.org/10.1080/10601320500406024

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:129–152, 2006
Copyright © Taylor & Francis LLC
ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320500406024

Adsorption Properties of Poly(N-vinylpyrrolidone-co-methacrylic acid) Hydrogels

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 for which the methacrylic acid composition is around 5, 10, and 15%. MAA and VP monomer mixtures have been irradiated in a ^{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. Poly(N-vinylpyrrolidone-co-methacrylic acid) P(VP/MAA) hydrogels have been used for the adsorption of some dyes such as Safranine-O, Methylene Blue from aqueous solutions. These hydrogels were swollen in distilled water and in aqueous solutions of dyes at pH 4.0, 7.0, and 9.0. P(VP/MAA)1 hydrogel which contains the higher methacrylic acid content showed the maximum % swelling at pH 9.0 in water and swelling increased in the order of Safranine-O > Methylene Blue. Diffusion of water and aqueous solution of dyes within hydrogels was found to be of non-Fickian character. Diffusion coefficients of water and aqueous dye solution in P(VP/MAA) hydrogels were calculated. In the dye adsorption experiments, the effects of pH, concentration of aqueous dye solution and the composition of hydrogels on adsorption process were investigated. When the pH and concentration of aqueous solutions of dyes and the MAA content in hydrogels increased, the adsorption increased as well. From the adsorption studies, the cationic dyes could be repeatedly adsorbed and desorbed with P(VP/MAA) hydrogel without significant loss in their adsorption capacity.*

Keywords gamma-irradiation, hydrogel, poly(N-vinylpyrrolidone-co-methacrylic acid), adsorption, Safranine-O, methylene blue

Introduction

Polyelectrolyte complexes can be of great interest for biomedical application due to their peculiar properties. Such complexes, which are named polysalts when water-insoluble, are generally obtained by ionic interaction between polyanion and polycation or by polymerizing a suitable monomer onto a preformed macromolecule (1). Polycarboxylic acids such as poly(methacrylic acid) or poly(acrylic acid) form molecular complexes with polyethylene(glycol), poly(N-vinylpyrrolidone), poly(ethyleneimine) and polycations under appropriate conditions of pH (2).

Received March 2005; Accepted June 2005.

Address correspondence to Dr. Dilek Şolpan, Hacettepe University, Department of Chemistry, Beytepe, 06532 Ankara, Turkey. Tel.: 00/90/312/2977990; Fax: 00/90/312/2992163; E-mail: solpan@hacettepe.edu.tr

The complex formation of poly(methacrylic acid) PMAA is an important field of study, and it may be utilized in various fields of polymer research and technology. Some recent examples are the studies on the template polymerization of N-vinyl imidazole along with PMAA in water, and the investigation of the complexation of poly(ether-ester) with PMAA. In the latter, polymers contain biologically active residues. The complexes of the PMAA network with PEO have been suggested to be used as carriers of enzymes or drugs for their controlled release (3).

The most studied interpolymer complexes of PMAA are those formed either with PEO or with poly(N-vinylpyrrolidone), PVP. Recently, properties of solid complexes of PMAA with PEO and PVP, respectively, have been studied by Usaitis et al. Hydrogels are water-swollen networks (crosslinked structure) of hydrophilic homopolymers or copolymers. They generate great interest due to the facility of the incorporation of different chelating groups into the polymeric networks. Such polymeric hydrogels are promising materials in the field of hydrometallurgical applications and water purification, due to their chemical stability especially hydrolytic and thermal stability.

In this work, poly(N-vinylpyrrolidone-co-methacrylic acid) P(VP/MAA) copolymer hydrogels were prepared by means of γ-rays, which induce homo and copolymerization as a clean and environment friendly source of initiation. The factors affecting the preparation and properties of hydrogels were investigated and the adsorbing capacity of the prepared hydrogels for some dyes was examined.

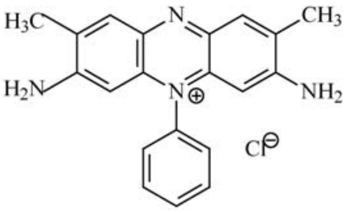
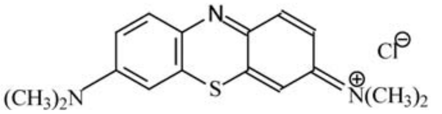
Experimental

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 was obtained from Aldrich. Hydrochloric acid and sodium hydroxide used to adjust 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 (0.1M 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 the preparation of hydrogels and in swelling and adsorption studies. Safranine-O (SO) and Methylene Blue (MB) dyes were obtained from Allied Chemical. Some properties of the dyes are given in Scheme 1.

Preparation of Hydrogels

The solutions of monomers of MAA and VP were prepared in three different compositions (MAA/VP mole ratios: 5/95, 10/90, 15/85). These solutions were placed in polyvinylchloride straws of 3 mm diameter and irradiated in air at 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 kGy h^{-1}. The hydrogels obtained in long cylindirical shapes were cut into smaller pieces. 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.

Name	Chemical Formula	Color Index (CI)	Molar Mass (gmol^{-1})	λ_{max} (nm)
Safranine-O		50240	350	517
Methylene Blue		52015	374	661

Scheme 1. Chemical formula and some properties of dyes.

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. Uncrosslinked polymer and residual monomer were removed from the gel structure. The amount of uncrosslinked MAA was determined by titration of extract against NaOH (0.05 M) to a phenolphthalein end point.

Swelling and Diffusion

Dried P(VP/MAA) hydrogels (2 mm thickness, 3 mm diameter) were weighed and left to swell in deionized water and 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:

$$\%\ \text{Swelling} = [(m_t - m_0)/m_0] \times 100 \tag{1}$$

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 characteristics, equilibrium water content, etc.) were calculated by using swelling data.

Spectroscopic Analysis of P(VP/MAA)-Dye Systems

Fourier transform infrared (FTIR) spectra of 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)-dye systems were characterized by comparing the FTIR spectra of P(VP/MAA)-dye systems and P(VP/MAA) hydrogels.

Adsorption Studies

Adsorption of the dyes from aqueous solutions was investigated in continuous adsorption equilibrium studies. The effect of the initial concentration, pH, effect of MAA content in hydrogel, and mass of hydrogel on the adsorption rate and capacity were studied. For adsorption studies, optimum mass of hydrogel was determined. The aqueous solution of dyes were prepared in the concentration 2.5–500 ppm (mgL^{-1}) range for Safranine-O, 2.5–500 ppm for Methylene Blue, respectively. Approximately 0.05 mg of P(VP/MAA) hydrogels containing 36%, 22%, 18% mole of MAA were transferred into 25 mL dye solution at different pH (4, 7, 9). The adsorption of hydrogel was allowed to reach equilibrium during four days at 25°C. The P(VP/MAA) hydrogels were removed from the adsorption medium after the adsorption was completed. The adsorption experiments were carried out spectrophotometrically. The amount of adsorbed dye per gram of the hydrogels was also determined. The amount of adsorption per unit mass of the P(VP/MAA) hydrogels was evaluated by using the following equation.

$$q_e = [(C_0 - C_e) \times V]/W \qquad (2)$$

where, q_e is the amount of dye adsorbed onto a unit dry mass of the P(VP/MAA) hydrogels (mg g^{-1}), C_0 and C_e are the concentrations of the dye in the initial solution and the aqueous phase after treatment for a certain period of time, respectively (mg L^{-1}), V is the volume of the aqueous phase (L) and W is the amount of dry P(VP/MAA) hydrogels used (g).

Results and Discussion

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 the copolymeric hydrogel system. An ionizing radiation process was used for the 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.

When the VP/MAA mixture was irradiated, a π-bond in the vinyl double bond of both monomers formed monomer radicals. The monomer radicals formed were combined together and poly(N-vinylpyrrolidone-co-methacrylic acid) copolymers were obtained. If the irradiation was continued, crosslinking reaction started, chains were crosslinked to each other, and gelation occurred in the system. In order to have

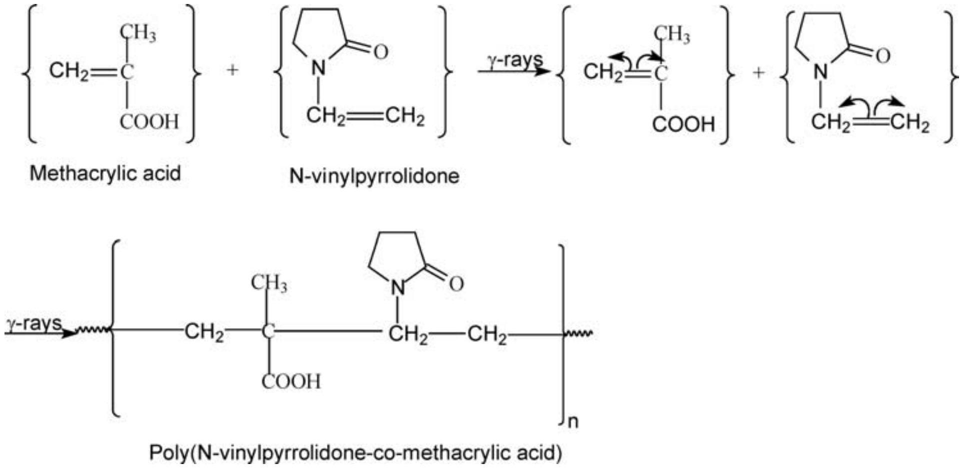


Figure 1. Possible copolymerization reaction of N-vinylpyrrrolidone with methacrylic acid.

high mechanical stability, hydrophilicity, and 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 higher crosslinking and percent gelation at lower doses. The VP/MAA mixtures were irradiated in the range between 0.4–20.0 kGy irradiation doses at 0.14 $kGyh^{-1}$ dose rate. MAA and VP monomer mixtures containing MAA initial compositions of 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 preliminary irradiations, ~80% gelation occurred for all mixtures in the range of 0.4–7.0 kGy 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 3.4 kGy irradiation dose, the hydrogels irradiated at 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 of 64/36, 78/22, 82/18, respectively. As can be seen from Figure 2, the percent gelation increased with the increasing irradiation dose. After the 6.0 kGy irradiation dose, the percent gelation started decreasing. It was observed that there is slight decrease in the % conversion for all initial mixtures after 6.0 kGy. This can be attributed to chain scission of system in the presence of oxygen. As can be seen from Figure 2, the effect of VP is much more dominant at a low irradiation dose and after 6.0 kGy, the percent conversion is also dependent on the amount of VP content.

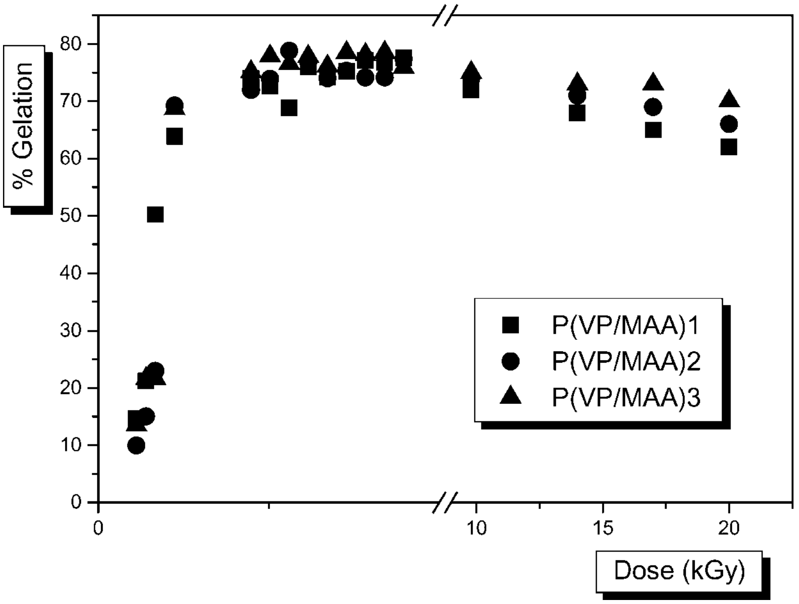


Figure 2. The effect of irradiation dose on the percent gelation of VP/MAA monomer mixtures containing 1% N,N-methylene-bis-acrylamide.

Initial mole percents of monomers in copolymeric gels and after removing uncrosslinked polymer and residual monomer with extraction from the gel structure were determined. To determine the composition of copolymers, the amount of crosslinked MAA was determined by titration of 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 in Table 1 lead to some interesting results. The reactivity ratios were calculated by using Q-e values of both monomers (4). 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 occurred in the range of 2.8–6.0 kGy irradiation doses, so, the hydrogel irradiated at 3.4 kGy irradiation dose was used and the ionic strength was 0.1 M during this study.

Table 1

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

Hydrogel	% mole of MAA in hydrogel	% mole 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

Spectroscopic Characterization

To determine the nature of the interaction between the dye and P(VP/MAA) hydrogel, FTIR spectra of P(VP/MAA), dye and P(VP/MAA)-dye systems are given for SO, MB, in Figures 3 and 4. In Figure 3, the FTIR spectrum of P(VP/MAA) hydrogel shows some bands revealing the presence of PMAA and PVP. The spectrum of P(MAA/VP) shows 1700, 1485, 1396 cm^{-1} bands, typical of the ν(C=O) of the cyclic groups and 1200, 1100 cm^{-1} bands, (CH_3) related to C and carboxylic group in PMAA. The band at 1690 cm^{-1} ν(C=O) of the carboxylic group and at 1436 cm^{-1} ν(C–C) stretching band of pyrrolidone ring, in addition to these bands, we can see the C–N absorption band at 1180 cm^{-1} in PVP. In Figure 3, FTIR spectra of SO and P(VP/MAA)-SO have the characteristic peaks at about 3400 cm^{-1} of the primary amine. The peaks observed in P(VP/MAA) in the range of 3600–3300 cm^{-1} are O-H bands. The peaks at 2900 cm^{-1} are C–H stretching vibrations in all structures. In the FTIR spectrum of P(VP/MAA)-SO, the absorbances at 1637 cm^{-1}, 1454 cm^{-1}, and 1342 cm^{-1} represent C=C stretching vibration in the aromatic rings of dye and aromatic C–N stretching bands of aromatic amine in dye, respectively. In Figure 4, in the spectra of P(VP/MAA)-MB, the peaks at 1450 and 1326 cm^{-1} are CH_3 connected to N in MB and the peak at 1700 cm^{-1} in P(VP/MAA) disappeared in P(VP/MAA)-MB in the range of 3600–3400 cm^{-1} indicative O–H and N–H bonds.

The relation between the nature of the copolymer P(VP/MAA) and their dye complexation behavior is generally complicated by many possible interactions. Oxygen in the carbonyl group of VP and MAA is responsible for the interaction of the dye with the hydrogel. Since the mobile π-electrons are pulled strongly towards oxygen, carbonyl carbon is electron deficient and carbonyl oxygen is electron rich. The dyes act

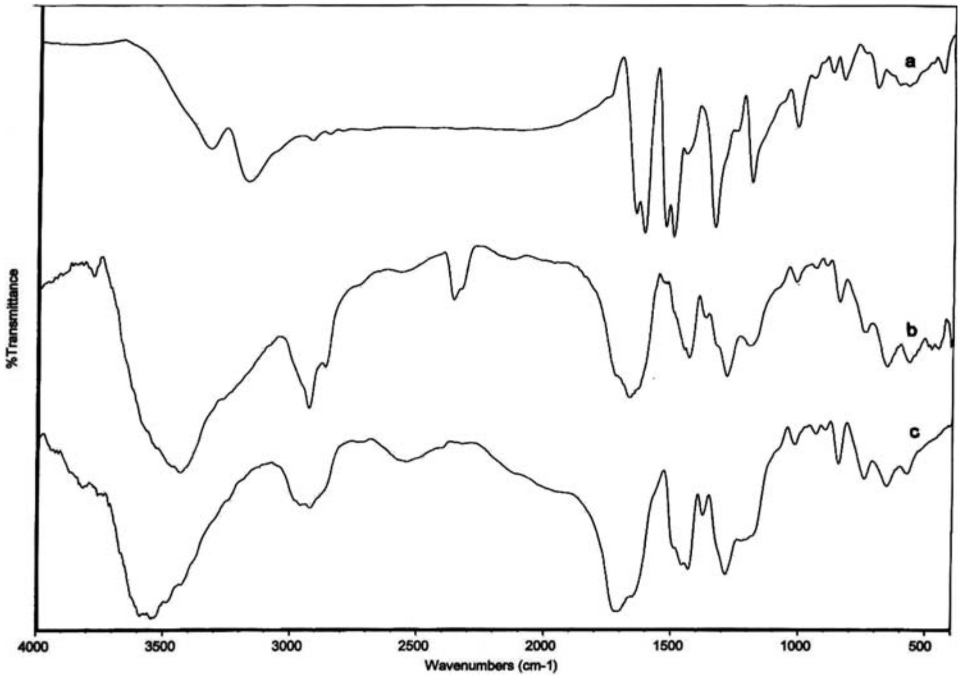


Figure 3. FTIR spectra of (a) Safranine-O (SO), (b) P(VP/MAA)-SO, (c) P(VP/MAA).

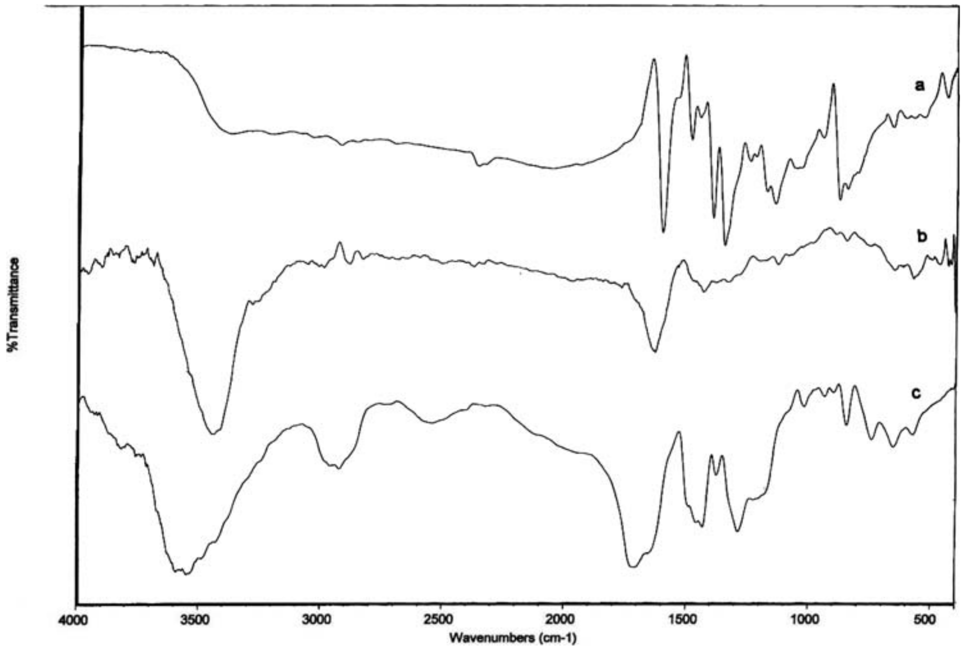


Figure 4. FTIR spectra of (a) Methylene Blue (MB), (b) P(VP/MAA)-MB, (c) P(VP/MAA).

as electron acceptors and are taken up by coordination to the donor oxygen of the carbonyl group. We can say that in FTIR spectra of P(VP/MAA)-dye systems, the interaction between P(VP/MAA) and dyes occurred on oxygen atom in MAA carbonyl group. It can be concluded that there is an ion-ion interaction between cationic groups of cationic dyes and carboxyl groups of hydrogels. These may occur between the negative charge of carboxyl group on the hydrogels and positive charge on the tertiary nitrogen atom on dye. Hydrogen bond can be expected to occur between nitrogen and hydrogen on the amine groups on the dye molecule and oxygen and hydrogen atom on the monomer units (5).

Swelling and Diffusion Studies

The effect of feed solution composition on the swelling of the prepared P(VP/MAA) copolymer hydrogel at different pH's and at 25°C, 0.1 M ionic strength was studied and the results are presented in Figure 5. The water uptake of initially dry hydrogels was 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 an ionic monomer such as methacrylic acid. Charged groups attached to the polymeric network structure played an essential role in swelling and adsorption properties (6).

The equilibrium swelling behavior of the P(VP/MAA) copolymer hydrogel was investigated as a function of pH. Figure 6 shows a typical behavior of a pH-sensitive copolymer hydrogel. The pH sensitivity of such hydrogel is fully dependent on its

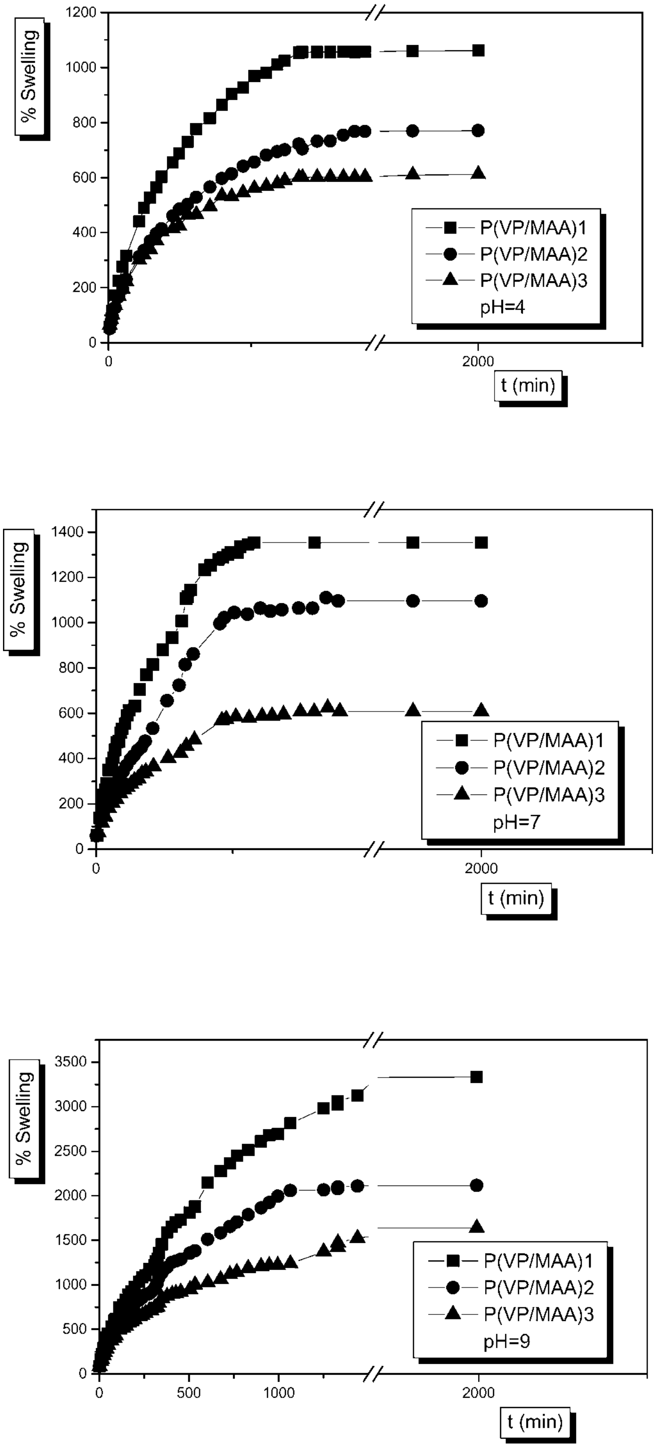


Figure 5. Effect of pH on swelling behavior of P(VP/MAA) hydrogels at 25°C. I: 0.1 M, total dose given: 3.4 kGy.

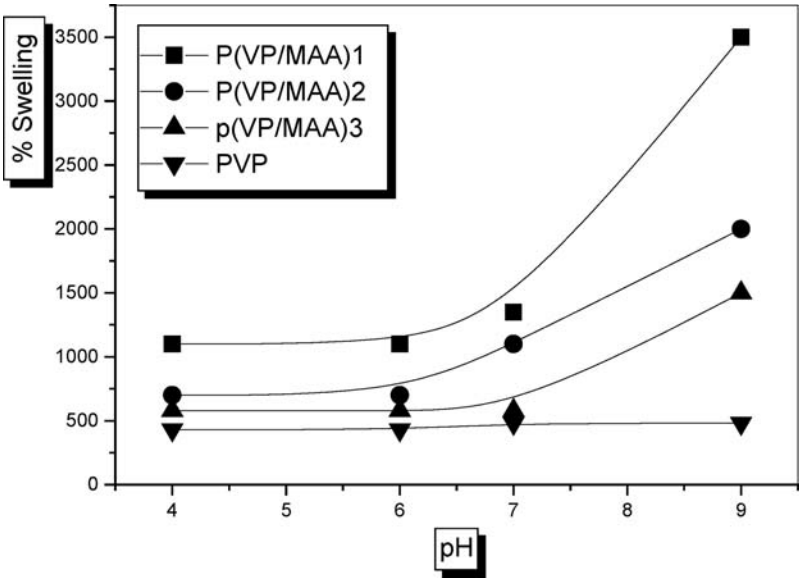


Figure 6. Effect of pH on swelling behavior of P(VP/MAA) copolymer hydrogels at 25°C. I: 0.1 M, total dose given: 3.4 kGy.

composition. All of the investigated copolymer hydrogels possess a change in the swelling degree at pH value around 6, which is approximately the pKa value of MAA (isobutyric acid repeating monomer unit, pKa = 4.83) ($Ka = 1.48 \times 10^{-5}$) (7, 8). At pH values lower than the pKa value, the carboxylic groups are completely disassociated and the swelling degree is very low. At pH values higher than the pKa value, the swelling degree increases due to the dissociation of the carboxylic groups and breakage of 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 (9).

$$F = M_t/M_\infty = kt^n \tag{3}$$

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. The exponents n and k were calculated from the slope and intercept of the lines and the results are given in Table 2. Diffusion coefficients were calculated from the relation (10).

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

where D is in $cm^2 min^{-1}$, t is the time at which the swelling is one-half the equlilibrium value ($V/V_o = 1/2$), and r is the radius of the swollen cylindirical sample. For the

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

	P(VP/MAA)3			P(VP/MAA)2			P(VP/MAA)1		
pH	$k \times 10^2$	n	$D \times 10^4$	$k \times 10^2$	n	$D \times 10^4$	$k \times 10^2$	n	$D \times 10^5$
4.0	1.5	0.64	4.64	1.6	0.57	5.07	1.7	0.49	5.16
7.0	1.9	0.65	4.75	1.6	0.57	5.31	1.8	0.49	5.68
9.0	2.2	0.58	4.94	1.6	0.52	5.79	2.1	0.50	7.98

D: $cm^2 min^{-1}$.

hydrogels, 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 2.07×10^{-4} to $7.98 \times 10^{-5}\,cm^2\,min^{-1}$. These diffusion coefficients lead to a higher water uptake rate with the higher pH. The exponents n of the hydrogels with the different hydrogel equilibrium water content, defined as the weight percent of water sorbed to that of hydrogels, exhibit 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 becomes more pronounced for samples at higher equilibrium water absorption (11).

The effect of dyes on the swelling capacity of P(VP/MAA) hydrogels was investigated. The aqueous solutions of cationic dyes were prepared in the desired concentrations, and 0.1 g of P(VP/MAA) hydrogels irradiated at 3.4 kGy were transferred into 25 mL of the synthetic aqueous solutions of dyes at various pH's and 25°C. The swelling curves of the hydrogel in the dye solutions are shown in Figures 7 and 8 for SO and MB, respectively. As seen from these figures, the swelling capacities of P(VP/MAA) hydrogels are in the range of 470–1330% in the aqueous solution of dyes at different pH values. These figures show that the swelling behaviors of P(VP/MAA) hydrogels in water and aqueous solution of dyes are similar to each other. The equilibrium swelling of P(VP/MAA)3 hydrogel whose MAA content is the lowest is lower than those of the other hydrogels but the equilibrium swelling of all the other the P(VP/MAA) hydrogels in water was higher than those of the aqueous solution of dyes.

To determine the nature of diffusion of the aqueous solution of dyes into hydrogels, Equations (3) and (4) were used. These equations were applied to the initial stages of swelling, and plots of $\ln F$ vs. $\ln t$ are presented in Figures 9 and 10 for SO and MB, respectively. F vs. $t^{1/2}$ graphs are given for aqueous dye solutions at various pH values in Figures 11 and 12 for SO and MB, respectively. The values of n, k, and diffusion coefficient, D are listed in Tables 3 and 4.

The equilibrium swelling of P(VP/MAA) hydrogels is low (470–1330%) in aqueous solutions of the cationic dyes, but high (580–3500%) in water. The dyes contain unpaired electrons of N and O. These atoms behave like a hydrophilic group and form hydrogen bonds with water. Since poly(N-vinylpyrrolidone) is a non-ionic polymer, ionizable groups on the polymer were increased by adding MAA to

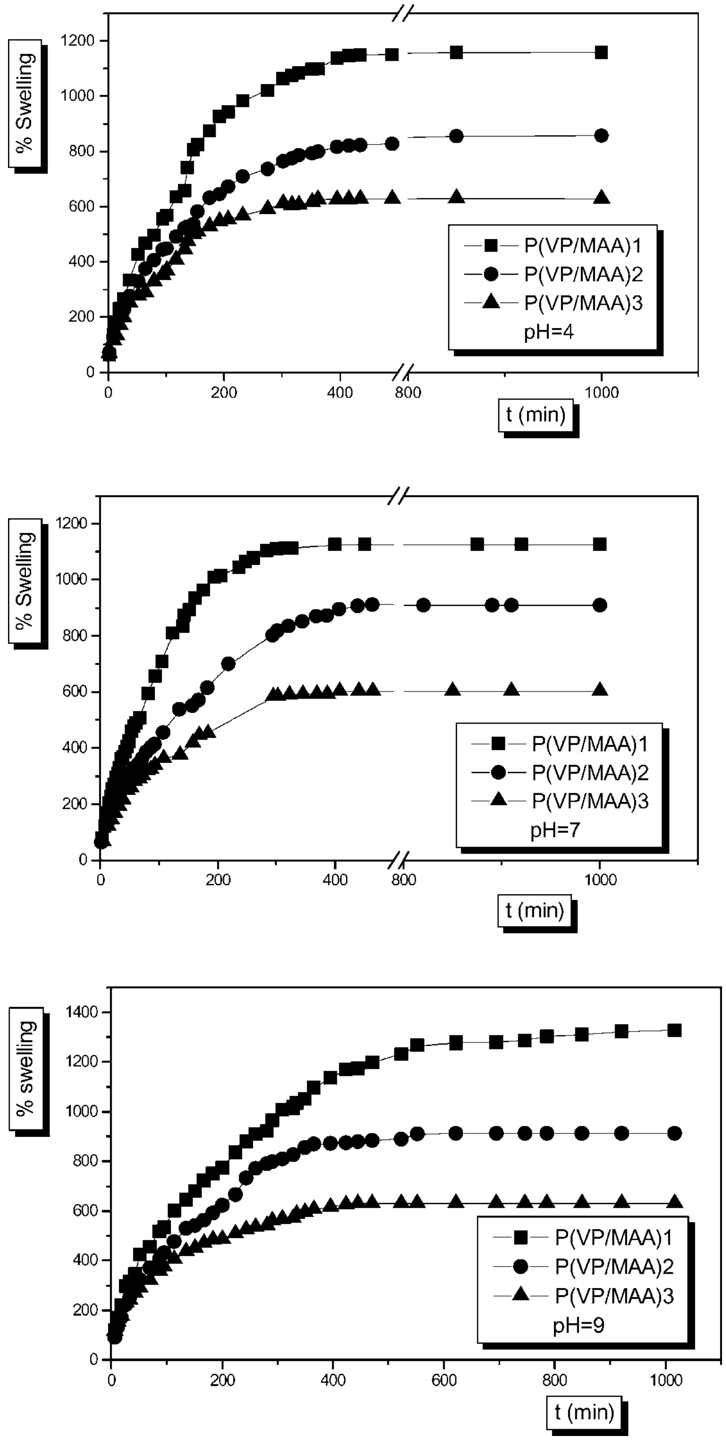


Figure 7. Effect of pH and hydrogel composition on swelling behavior of P(VP/MAA) hydrogels in 500 mg L^{-1} concentration of aqueous solution of Safranine-O at 25°C. I: 0.1 M, total dose given: 3.4 kGy.

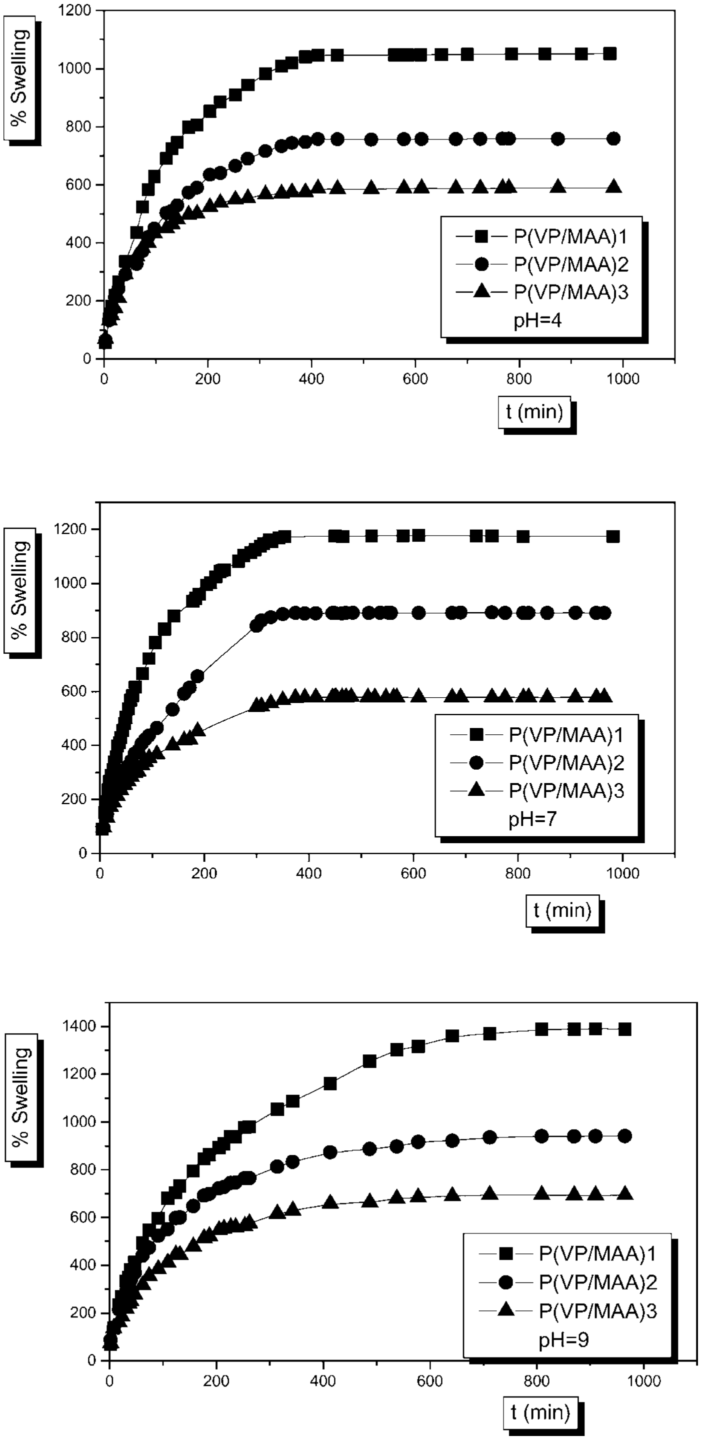


Figure 8. Effect of pH and hydrogel composition on swelling behavior of P(VP/MAA) hydrogels in 500 mg L^{-1} concentration of aqueous solution of Methylene Blue at 25°C. I: 0.1 M, total dose given: 3.4 kGy.

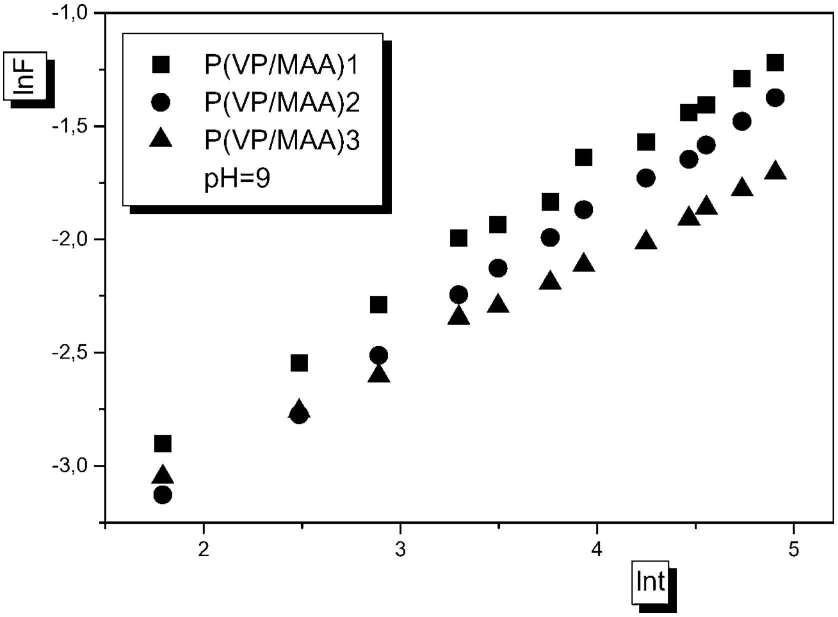


Figure 9. Plots of ln F vs. ln t of P(VP/MAA) hydrogels at 25°C in 500 mg L^{-1} concentration of aqueous solution of Safranine-O. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

N-vinylpyrrolidone monomer. So, these hydrogels have many carboxyl groups that can increase the interactions between the cationic groups of cationic dyes and carboxyl groups of hydrogels. The other types of interaction between hydrogels and dyes may be hydrophobic and hydrogen bonding. Hydrophobic effects are specifically aqueous solution interactions, which in the present case, will involve the aromatic rings and

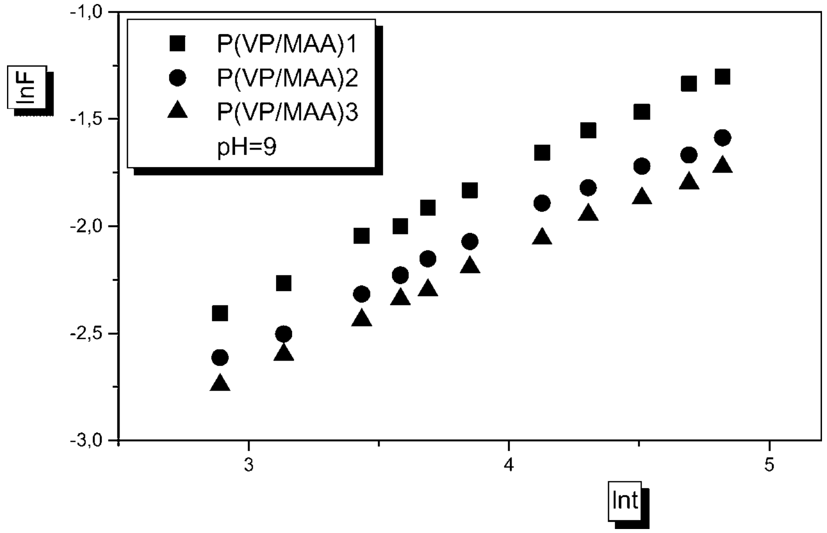


Figure 10. Plots of ln F vs. ln t of P(VP/MAA) hydrogels at 25°C in 500 mg L^{-1} concentration of aqueous solution of Methylene Blue. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

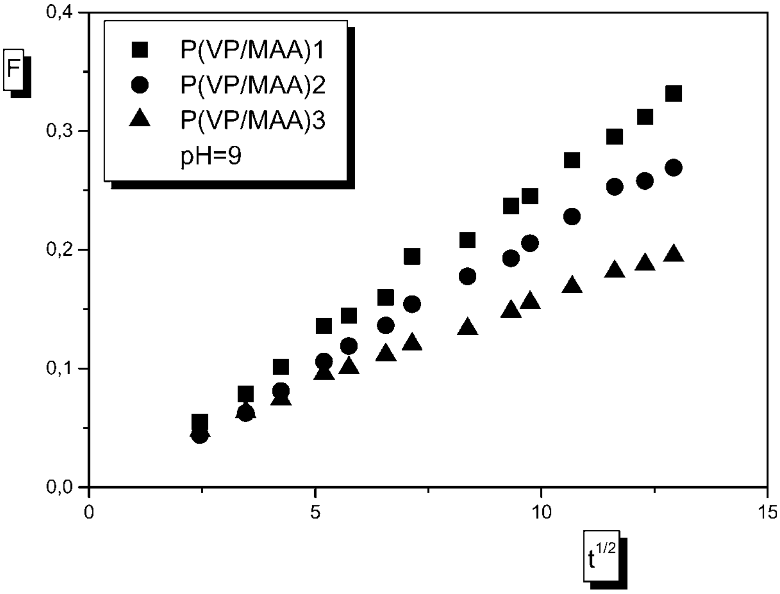


Figure 11. Plots of F vs. $t^{1/2}$ of P(VP/MAA) hydrogels at 25°C in 500 mg L^{-1} aqueous solution of Safranine-O. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

methyl groups on the dye molecules and the methylene groups on the hydrogel. Hydrogen bonding will be expected to occur between the nitrogen atom of amine group on the dye molecules and carbonyl groups on the two monomers, which form a hydrogel of crosslinked copolymer. However, electrostatic interactions between dye molecules and the hydrogel are dominant due to hydrophobic groups and hydrogen

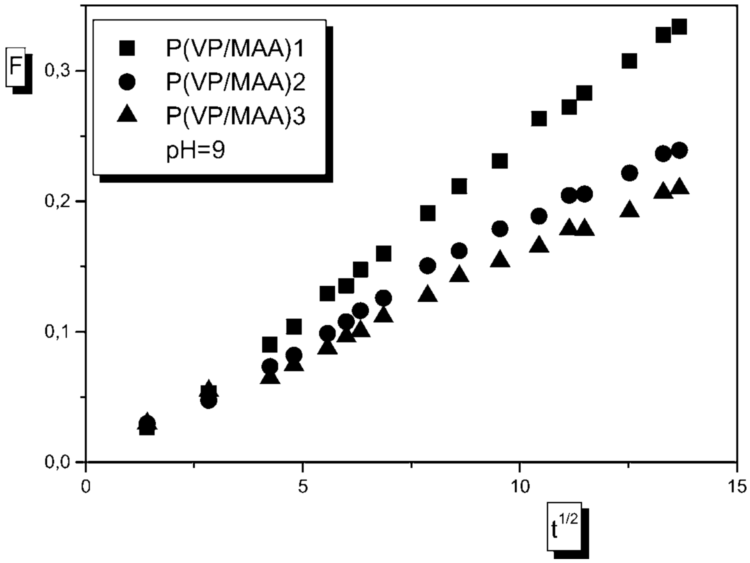


Figure 12. Plots of F vs. $t^{1/2}$ of P(VP/MAA) hydrogels at 25°C in 500 mg L^{-1} aqueous solution of Methylene Blue. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

Table 3
Swelling and diffusion parameters of P(VP/MAA) hydrogels in aqueous solution of Safranine-O at various pH and 25°C. I: 0.1 M, total dose given: 3.4 kGy

	P(VP/MAA)3			P(VP/MAA)2			P(VP/MAA)1		
pH	$k \times 10^2$	n	$D \times 10^4$	$k \times 10^2$	n	$D \times 10^4$	$k \times 10^2$	n	$D \times 10^5$
4.0	1.8	0.59	2.51	2.1	0.48	3.25	2.0	0.45	4.71
7.0	1.1	0.64	2.72	1.9	0.51	3.51	2.2	0.56	4.72
9.0	2.1	0.54	2.72	1.6	0.56	3.51	2.2	0.43	5.15

D: $cm^2 min^{-1}$.

bonding. At the end of these evaluations, according to swelling and diffusion parameters in Tables 3 and 4, the hydrogels in aqueous solutions were swollen in the following order at pH 9; water > SO > MB. In the experiments, the number that determines the type of diffusion n was found to be over 0.45. Hence, the diffusion of water and cationic dyes into P(VP/MAA) hydrogels was assumed to have a non-Fickian character (12). This is generally explained as being a consequence of the slow relaxation rate of the hydrogel matrix. The diffusion coefficients of water in the hydrogel are higher than the values of the dyes, so diffusion of dyes into the hydrogel is more difficult than those of the water, since the electrostatic interaction between the hydrogel and dye molecules is very dominant due to hydrophobic interaction and hydrogen bonds. These results are parallel to the results of swelling.

Adsorption Studies

The adsorption of Safranine-O, Methylene Blue, and Methyl Violet into P(VP/MAA) hydrogels of different compositions was investigated by batch equilibration method. In a batch adsorption system at equilibrium, total solute concentration (C_t, mol L^{-1}) is:

$$C_+ = C_b + C_e \tag{5}$$

where C_b is the equilibrium mole number of the solute on the adsorbent in per liter solution (bound solute concentration) and C_e is the equilibrium concentration of the solute in the solution in mol L^{-1} (free solute concentration). The value of the bound concentration

Table 4
Swelling and diffusion parameters of P(VP/MAA) hydrogels in aqueous solution of Methylene Blue at various pH and 25°C. I: 0.1 M, total dose given: 3.4 kGy

	P(VP/MAA)3			P(VP/MAA)2			P(VP/MAA)1		
pH	$k \times 10^2$	n	$D \times 10^4$	$k \times 10^2$	n	$D \times 10^4$	$k \times 10^2$	n	$D \times 10^5$
4.0	1.4	0.63	1.21	1.6	0.58	2.26	1.6	0.52	5.54
7.0	1.5	0.63	2.19	1.4	0.59	2.29	1.6	0.49	5.94
9.0	1.7	0.58	3.37	1.6	0.54	2.93	1.4	0.53	5.94

D: $cm^2 min^{-1}$.

may be obtained from the difference by using equation (5). For a fixed free solute concentration, C_b is proportional to the polymer concentration on binding system; the bound amount can therefore be conveniently expressed as the binding ratio, r, defined by

$$r = C_b/P \tag{6}$$

Thus, with C_b in mol L^{-1} and P in mol basis (moles of monomer units) per liter solution, r, then represents the average number of molecules of solute bound to each monomer unit at that free solute concentration.

The effect of pH, hydrogel composition and dye concentration on the uptake capacity of hydrogels for these dyes were examined. To determine the adsorption kinetics of dyes into P(VP/MAA) plots of the binding ratio (r) against time are shown in Figures 13 and 14 for SO and MB, respectively. Adsorption has increased with increasing time and reached equilibrium at 4 days. The binding ratio of cationic dyes into hydrogel systems gradually increased with increasing content of MAA in P(VP/MAA) because ionizable groups on the polymer were increased by adding MAA to VP monomer. Therefore, these hydrogels have many carboxyl groups that can increase the interaction between the cationic groups of dyes and carboxyl groups of VP and MAA in hydrogels.

For the adsorption of dyes into P(VP/MAA) hydrogels, the first order kinetics equation was tested, but the straight lines could not be plotted, then t/r vs. t graphs were plotted. These graphs are given in Figures 15 and 16 for SO and MB, respectively. The binding ratios of cationic dyes into P(VP/MAA) hydrogels is of second order. Rate constant; k, initial rate; r_i, the maximum binding ratio; r_{max} were calculated from the slope and intersection of these lines and are presented in Tables 5 and 6 for SO and

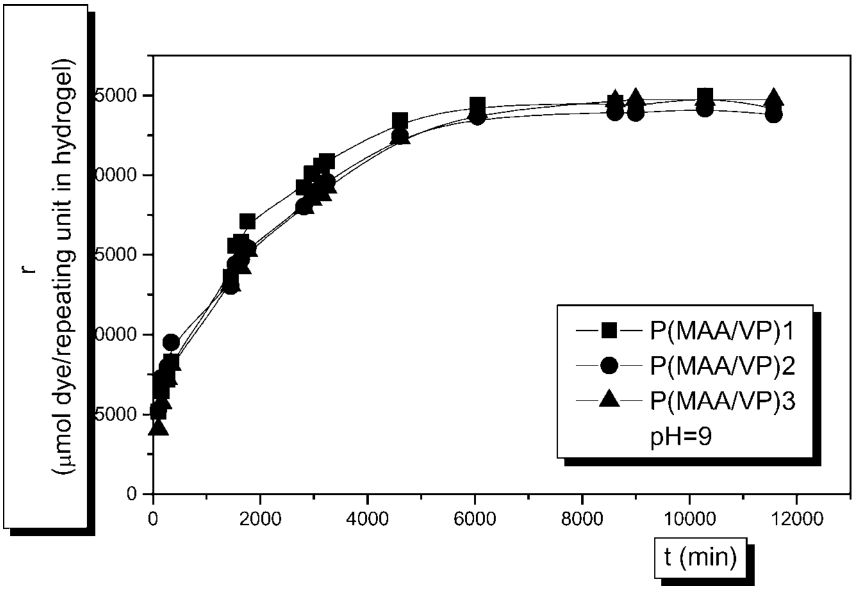


Figure 13. The variations of binding ratio (r) of P(VP/MAA)-dye systems with time at 25°C in 10 mg L^{-1} aqueous solution of Safranine-O. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

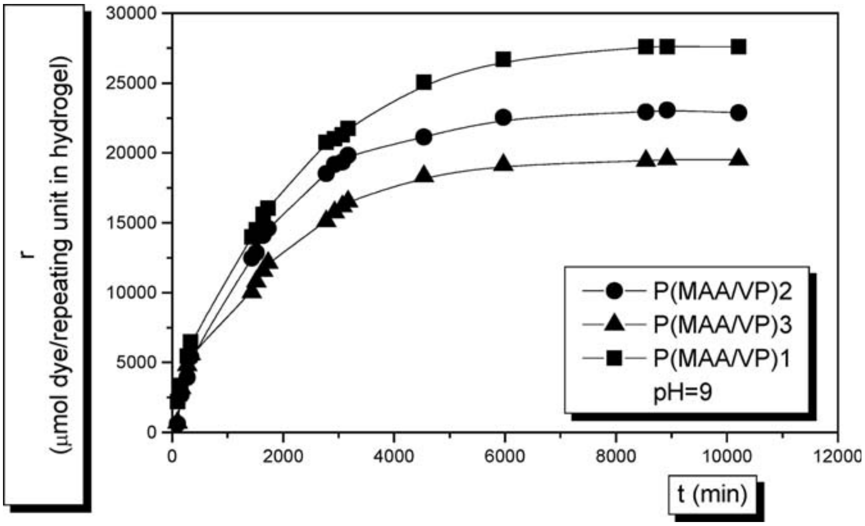


Figure 14. The variations of binding ratio (r) of P(VP/MAA)-dye systems with time at 25°C in 10 mg L^{-1} aqueous solution of Methylene Blue. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

MB, respectively.

$$dr/dt = k(r_{max} - r)^2 \tag{7}$$

$$t/r = 1/k\ r_{max} + t(1/r_{max}) \tag{8}$$

In Tables 5 and 6, it is shown that the values of r_{max} are increased with increasing MAA content in P(VP/MAA) hydrogels and pH of the medium in the order

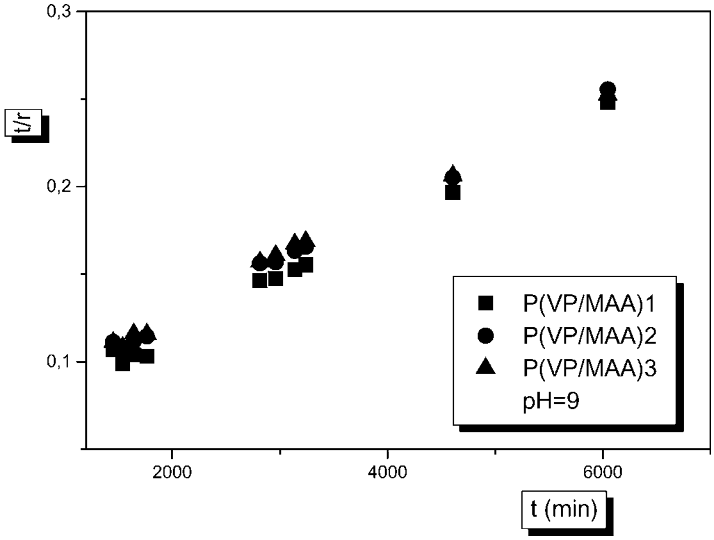


Figure 15. Adsorption kinetics of P(VP/MAA)-dye systems in 10 mg L^{-1} concentration aqueous solutions of Safranine-O at 25°C. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

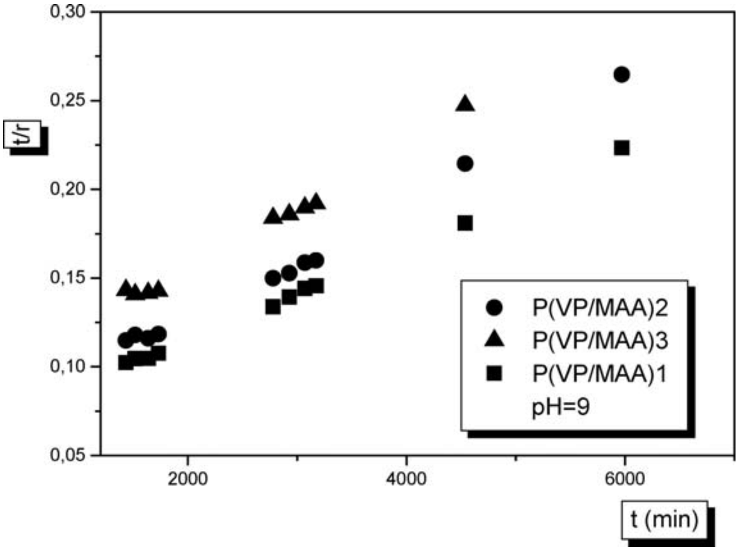


Figure 16. Adsorption kinetics of P(VP/MAA)-dye systems in 10 mgL^{-1} concentration of aqueous solutions of Methylene Blue at 25°C. pH: 9.0, I: 0.1 M, total dose given: 3.4 kGy.

of MB > SO. The reason for this order depends on the molecular structures of the dyes. MV may have more cationic groups than the other cationic dyes. For this reason, interaction between hydrophilic groups of dye and carboxyl groups of hydrogel occurs easily. The increase in rate constants are parallel to the r_{max} values.

The adsorption of P(VP/MAA) hydrogel of different compositions was investigated towards SO, MB by the batch equilibrium method. The amounts of dyes adsorbed and adsorption % by different hydrogels at various pH's are given in Tables 7 and 8 for SO and MB, respectively. From the table, the amount of dye uptake increases with increasing MAA content. MAA-rich compositions possess higher dye uptake than that at a lower degree of swelling at low pH values of dye feed solutions, which prevent the diffusion of the dye molecules inside the hydrogel to reach the adsorbing functional groups of the hydrogel. The optimum composition of the hydrogel was (82/18 mol%) P(VP/MAA) at which time the MAA possess the lowest pH sensitivity and minimize the ability of the hydrogel for dye uptake. As seen from these tables, for all investigated dyes, the adsorption increases with increasing pH value of the medium. This increment in dye adsorption could be attributed to the increase in the degree of swelling, which increases the diffusion of the dye molecules into the hydrogels to reach adsorbing and interacting sites. The results also show that the optimum pH was found to be 9.0 for all the dye molecules. The results showed that the ability of adsorption of P(VP/MAA) hydrogels decreases in order of MB > SO. These results are in very good agreement with relative size and their functional groups.

Effect of Concentration of Dye Solution and pH on Adsorption

To determine the effect of concentration of dye solution on adsorption plots of the binding ratio (r, mol dye/mol monomeric unit of hydrogel) against the free

Table 5
The variations of adsorption kinetics parameters of P(VP/MAA) hydrogels in 10 mg L^{-1} aqueous solution of Safranine-O with pH at 25°C. I: 0.1 M, total dose given: 3.4 kGy

	P(VP/MAA)3			P(VP/MAA)2			P(VP/MAA)1		
pH	$r_{max} \times 10^3$	$r_i \times 10^5$	$k \times 10^2$	$r_{max} \times 10^3$	$r_i \times 10^5$	$k \times 10^2$	$r_{max} \times 10^3$	$r_i \times 10^5$	$k \times 10^2$
4.0	12.53	7.98	1.00	18.90	5.29	0.44	19.50	3.39	0.31
7.0	18.28	5.47	1.17	25.71	3.89	0.97	26.99	3.35	1.09
9.0	26.53	3.77	1.26	26.04	3.84	1.28	27.32	3.26	0.92

Table 6
The variations of adsorption kinetics parameters of P(VP/MAA) hydrogels in 10 mg L^{-1} aqueous solution of Methylene Blue with pH at 25°C. I: 0.1 M, total dose given: 3.4 kGy

	P(VP/MAA)3			P(VP/MAA)2			P(VP/MAA)1		
pH	$r_{max} \times 10^3$	$r_i \times 10^5$	$k \times 10^2$	$r_{max} \times 10^3$	$r_i \times 10^5$	$k \times 10^2$	$r_{max} \times 10^3$	$r_i \times 10^5$	$k \times 10^2$
4.0	7.87	12.7	1.15	12.11	8.26	0.64	15.02	6.66	0.35
7.0	13.21	7.57	0.84	20.62	4.85	0.61	27.47	3.64	0.46
9.0	26.46	3.78	0.76	28.57	4.43	0.74	32.79	3.05	0.61

Table 7

Values of binding ratio (r), % adsorption, and q_e for P(VP/MAA) hydrogels in 10 mgL^{-1} concentration of aqueous solution of Safranine-O at various pH values and 25°C. I: 0.1 M, total dose given: 3.4 kGy

	P(VP/MAA)3			P(VP/MAA)2			P(VP/MAA)1		
pH	r	q_e	%ads	r	q_e	%ads	r	q_e	%ads
4.0	11232	2.28	46.06	15295	2.85	66.14	21949	3.61	70.76
7.0	16754	2.76	66.95	23456	3.13	82.86	21024	4.35	86.46
9.0	24173	4.31	89.43	23789	3.25	92.60	24750	4.19	94.22

r: μmol dye/repeating unit of monomer.
q_e: mg dye/g hydrogel.

concentrations of the dyes in the solutions (C, μmol dye L^{-1}) are shown in Figures 17 and 18 for SO and MB at pH 9.0 and 25°C, respectively. Figures 17 and 18 show that adsorption of dye into P(VP/MAA) hydrogels corresponds to type L (Langmuir type) adsorption isotherms in the Giles classification system for adsorption of a solute from its solution (13). In this type of adsorption isotherm, the initial curvature shows that when more sites in the substrate are filled, it becomes increasingly difficult for a bombarding solute molecule to find a vacant site available. This implies either that the adsorbed solute molecule is not vertically orientated or that there is no strong competition from the solvent.

As can be seen from Tables 7 and 8, the values of coverage of P(VP/MAA) hydrogels by the cationic dyes increase by the following order:

$$\mathrm{MB} > \mathrm{SO}$$

From these adsorption studies, it is seen that P(VP/MAA) hydrogels may be used as an adsorbent for removal of cationic dyes from water which is a serious problem in the textile industry.

Table 8

Values of binding ratio (r), % adsorption, and q_e for P(VP/MAA) hydrogels in 10 mgL^{-1} concentration of aqueous solution of Methylene Blue at various pH values and 25°C. I: 0.1 M, total dose given: 3.4 kGy

	P(VP/MAA)3			P(VP/MAA)2			P(VP/MAA)1		
pH	r	q_e	%ads	r	q_e	%ads	r	q_e	%ads
4.0	7104	2.71	21.70	10022	4.01	41.20	11289	5.76	57.87
7.0	11542	2.97	46.88	17258	4.31	64.08	22153	5.78	70.76
9.0	27873	4.71	91.43	19525	4.16	94.54	27583	5.82	96.73

r: μmol dye/repeating unit of monomer.
q_e: mg dye/g hydrogel.

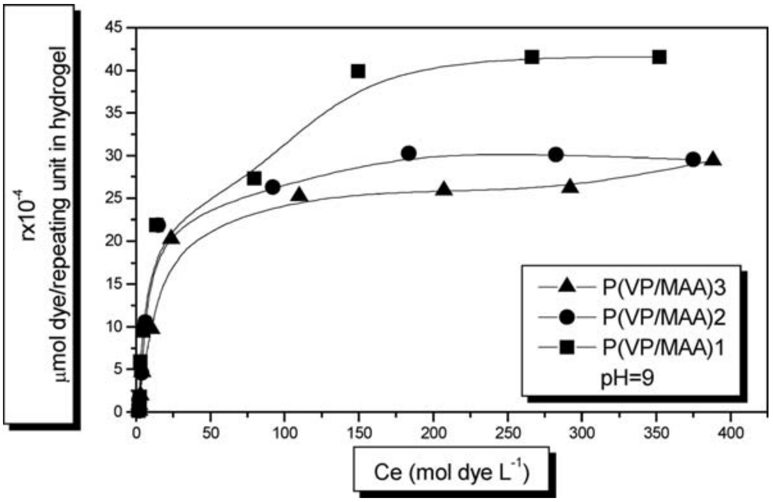


Figure 17. The variations of binding ratio (r) of P(VP/MAA) hydrogels-dye systems with the equilibrium concentration, in aqueous solution of Safranine-O at pH 9.0 and 25°C. I: 0.1 M, total dose given: 3.4 kGy.

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 was performed at 3.4 kGy dose.
- Percent composition of hydrogels was found by titration with NaOH.

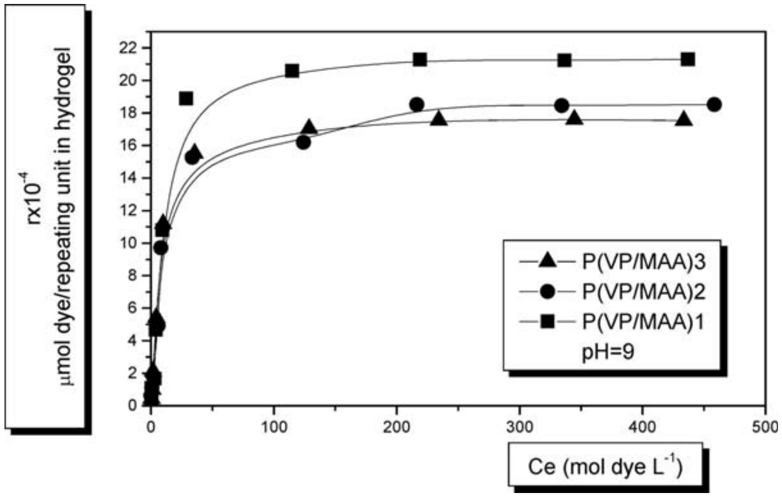


Figure 18. The variations of binding ratio (r) of P(VP/MAA) hydrogels-dye systems with the equilibrium concentration, in aqueous solution of Methylene Blue at pH 9.0 and 25°C. I: 0.1 M, total dose given: 3.4 kGy.

- Spectroscopic analyses were achieved to explain the interactions between the copolymer and dye.
- P(VP/MAA) hydrogel containing the high MAA, showed maximum % swelling in distilled water and aqueous solution of dye at basic medium due to electrostatic repulsions between the carboxylic acid in hydrogel and on dye. Swelling increased in the order of SO > MB in basic medium.
- Diffusion of water and the aqueous solution of dyes within hydrogels was found to be of non-Fickian character.
- Diffusion coefficients were calculated for P(VP/MAA) hydrogel in water and aqueous solution of SO and MB.
- Swelling kinetics of P(VP/MAA) hydrogel in distilled water and aqueous solution of dye 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 swell in basic medium and collapse in acidic medium.
- Adsorption kinetics of P(VP/MAA) hydrogels was found to be of second order.
- Adsorption capacities of P(VP/MAA) hydrogels were changed with pH values of aqueous dye solution.
- Adsorption capacity of P(VP/MAA) hydrogels were changed in the order of MB > SO.
- P(VP/MAA) hydrogels can be easily regenerated with HCl. This characteristic of the possibility for reusing the reactive polymer several times makes it economically suitable for use.

References

1. Cerrai, P., Guerra, G.D., Maltinti, S., and Tricoli, M. (1994) *Macromol. Rapid. Commun.*, 1: 983–990.
2. Osada, Y. (1979) *J. Polym. Sci. Polym. Chem.*, 17: 3485–3498.
3. Usaitis, A., Mannu, S.L., and Tenhe, H. (1997) *Eur. Polym. J.*, 33 (2): 219–223.
4. Brundup, J. and Immergut, E.H. (2000) *Polymer Handbook*, Third Edn.; Interscience Publishers, John Wiley, Inc.: NewYork; Vol. II, 268–269.
5. Hwang, M.C. and Chen, K.M. (1993) *J. Appl. Polym. Sci.*, 49 (6): 975–989.
6. Vazquez, B., Gurruchaga, M., Goni, F., and Roman, S. (1997) *J. Biomaterials*, 18: 521–526.
7. Marinsky, J.A. and Anspach, W.M. (1975) *The Journal of Physical Chemistry*, 79 (15): 439–444.
8. Travers, C. and Marinsky, J.A. (1974) The Complexing of Ca(II), Co(II), and Zn(II) by Polymethacrylic Acid and Polyacrylic Acid. *J. Polymer Sci. Symposium No.*, 47: 285–297.
9. Buckley, J.D., Berger, M.J., and Poller, D. (1962) *J. Polym. Sci.*, 56: 175–188.
10. Li, Y. and Tanaka, T. (1990) *J. Chem. Phys.*, 92: 1365–1372.
11. Shiaw-Guang, Hu D. and Jium-Nan, Chou K. (1996) *Polymer*, 37 (6): 1019–1025.
12. Peppas, N.A. and Franson, N.M. (1983) *J. Polym. Sci. Phys., Ed.*, 21: 983–997.
13. Giles, C.H., MacEwan, T.H., Nakhwa, S.N., and Smith, D. (1960) *J. Chem. Soc.*, 74: 3973–3993.