

Research Article

Study of Swelling Properties and Thermal Behavior of Poly(N,N-Dimethylacrylamide-co-Maleic Acid) Based Hydrogels

Sadjia Bennour and Fatma Louzri

Laboratory of Polymer Materials, Faculty of Chemistry, University of Sciences and Technology Houari Boumediene, BP 32, El Alia, 16111 Algiers, Algeria

Correspondence should be addressed to Sadjia Bennour; sadjiabennour@yahoo.fr

Received 9 April 2014; Revised 30 June 2014; Accepted 2 July 2014; Published 22 July 2014

Academic Editor: Alejandro Sosnik

Copyright © 2014 S. Bennour and F. Louzri. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Hydrogels copolymers N,N-dimethylacrylamide (DMA) and maleic acid (MA) were prepared by free-radical polymerization at 56°C in aqueous solution, using N,N-methylenebisacrylamide (NMBA) as cross-linking agent and potassium persulfate (KPS) as initiator. The effects of comonomer composition, cross-linker content, and variation of pH solutions on the swelling behavior of polymers were investigated. The obtained results showed an increase of the swelling of poly(N,N-dimethylacrylamide-co-maleic acid) (P(DMA-MAx)) as the content of maleic acid increases in the polymeric matrix, while they indicate a great reduction of the degree of swelling as the cross-linking agent ratio increases. It was also shown that the swelling of copolymer hydrogels increased with the increase of pH and the maximum extent was reached at pH 8.7 in all compositions. Fourier transform infrared spectroscopy (FTIR) revealed the existence of hydrogen bonding interactions between the carboxylic groups of MA and the carbonyl groups of DMA. Differential scanning calorimetry analysis (DSC) showed an increase of the glass-transition temperature (T_g) as concentrations of MA and NMBA increased. Thermogravimetric analysis (TGA) of copolymers was performed to investigate the degradation mechanism.

1. Introduction

Hydrogels are composed of hydrophilic homopolymer or copolymer network and can swell in the presence of water or physiological fluids. Chemical cross-links (covalent bonds) or physical junctions (e.g., secondary forces, crystallite formation, and chain entanglements) provide the hydrogels' unique swelling behavior and three-dimensional structure [1–3]. Volume changes in hydrogels occur in response to changing environmental conditions such as temperature [4–6], pH [7–9], solvent composition [10], and ionic strength [4, 11]. Hydrogels have been a topic of extensive research in the past decades and their properties as, for example, their high water content and the possible control over the swelling kinetics make them very attractive for biomedical applications [12–16]. The pH sensitive hydrogels containing pendant acidic or basic groups such as carboxylic acids, sulfonic acids, primary amines, or ammonium salts which change ionization in response to change in the pH have become the subject matter of major

interest for use as carriers in drug delivery research [17–19]. Poly(N,N-dimethylacrylamide) is a hydrophilic polymer, due to its remarkable properties, such as water solubility and biocompatibility, and it is very useful in the biomedical applications including polymer supports for protein synthesis, two-phase catalysts, and controlled drug delivery [20, 21]. Moreover, grafting of the N,N-dimethylacrylamide monomer onto substrates like poly(dimethyl-siloxane) produces a material with unique properties suitable for determining the diffusion characteristics of small molecule drugs, glucose, insulin, and albumin in vitro [22].

The present work was aimed to synthesize the cross-linked copolymers of N,N-dimethylacrylamide (DMA) with maleic acid (MA) and to investigate the swelling behavior of the copolymer composed of a nonionic monomer DMA and an ionizable monomer MA. In order to study the effects of comonomer composition and the cross-linker content on the swelling of polymers, the equilibrium swelling values of DMA homopolymer and DMA-MA copolymers in buffer

TABLE 1: Molar composition of the hydrogels.

DMA/MA mole ratio in feed	DMA/MA ^a mole ratio in copolymer	DMA (mmol)	MA (mmol)	KPS ^b (mol%)	NMBA ^b (mol%)	H ₂ O (mL)
100/0	100/0	40.4	0	0.036	0.32	4
91/9	92/8	36.4	3.45	0.036	0.32	4
82/18	85/15	32.3	6.89	0.036	0.32	4
73/27	71/29	28.3	10.35	0.036	0.32	4
64/36	67/33	24.3	13.79	0.036	0.32	4
54/46	62/38	20.2	17.24	0.036	0.32	4
91/9	92/8	36.4	3.45	0.036	0.16	4
91/9	92/8	36.4	3.45	0.036	0.48	4
91/9	92/8	36.4	3.45	0.036	0.64	4
91/9	92/8	36.4	3.45	0.036	1.28	4

^aDetermined by elemental analysis.^bmol% of the total mole number of monomers.

solutions with different pH values at room temperature were determined. The thermal stability of PDMA and P(DMA-MAx) was investigated by thermogravimetry.

2. Experimental

2.1. Materials. N,N-dimethylacrylamide (DMA) was supplied from Merck and purified with vacuum distillation prior to usage in order to remove the inhibitor. Maleic acid (MA, 99%) purchased from Fluka, N,N-methylenebisacrylamide (NMBA) from Fluka as a cross-linking agent, and potassium persulfate (KPS) from Merck as an initiator were used as received. Distilled water was used for the polymerization reactions and swelling studies.

The following pH-buffered solutions were used in order to examine the swelling behavior [23]: pH = 0.9, potassium chloride, $I = 0.14$ M; pH = 3.9, citric acid/phosphate, $I = 0.23$ M; pH = 6.9, citric acid/phosphate, $I = 0.49$ M; pH = 8.7, boric acid/NaOH, $I = 0.02$ M.

2.2. Synthesis of Hydrogels. Poly(N,N-dimethylacrylamide) (PDMA), poly(N,N-dimethylacrylamide-co-maleic acid) (P(DMA-MAx)) containing 8, 15, 29, 33, and 38 mol% of maleic acid, using NMBA (0.32 mol% of the total mole number of monomers) as cross-linking agent, and P(DMA-MA8) with varying compositions of NMBA (0.16, 0.48, 0.64, and 1.28 mol% of the total mole number of monomers) were synthesized by free-radical polymerization using KPS as initiator. The polymerization recipes are listed in Table 1.

Polymerization reactions were performed in glass tubes with the inner diameters of 1 cm and lengths of 10 cm. DMA and MA monomers with different molar ratios and cross-linker concentration were dissolved in water. After nitrogen bubbles for 20 min through the solution, the initiator KPS was added. Then, the polymerization was carried out at 56°C for 15 min. At the end of the reaction, the glass tubes were broken carefully without destroying the cylindrical hydrogels. The resulting hydrogels were sliced into small cylinders with lengths of 4 mm and then immersed in distilled water for

5 days, and the water was changed every 24 hours in order to remove the residual unreacted monomers. The resulting swollen gels were dried at room temperature for several days and then in a vacuum oven at 40°C until constant weight.

The compositions of the formed copolymer hydrogels were determined by elemental analysis for nitrogen (Microanalyzer CHNOS-932 LECO).

2.3. Characterization

2.3.1. FTIR Measurements. Hydrogels samples were prepared by grinding the dry hydrogels with KBr and compressing the mixture to form disks and then dried in vacuum oven at 70°C for several days. FTIR spectra of these hydrogels were recorded on a model Perkin Elmer spectrophotometer at room temperature with a resolution of 2 cm⁻¹ and were averaged over 60 scans.

2.3.2. DSC Measurements. The glass transition temperatures (T_g) of PDMA and P(DMA-MAx) hydrogels were determined with a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 10°C/min under a nitrogen atmosphere in the 50°C to 220°C temperature range.

2.3.3. Thermogravimetric Analysis. A thermogravimetric analysis of the hydrogels investigated was carried out on a TG SETARAM under nitrogen atmosphere from 25°C to 500°C at a heating rate of 10°C/min.

2.4. Swelling Measurements. Dried hydrogels were allowed to hydrate in buffer solutions with different pH values 0.9, 3.9, 6.9, and 8.7 at 16°C. After being fully hydrated, the samples were taken out and the excess water on their surface was gently removed by filter paper.

The weights of the hydrating samples were measured at timed intervals. The swelling ratio (SR) and equilibrium

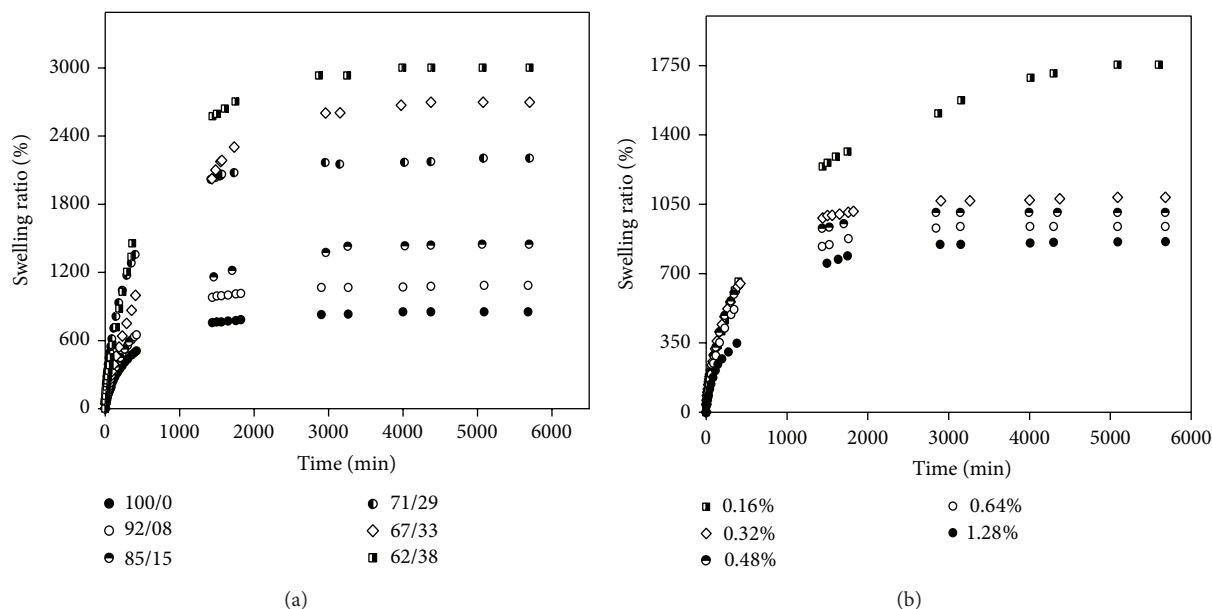


FIGURE 1: (a) Effect of maleic acid concentration on the dynamic swelling behavior of P(DMA-MAx) hydrogels in the media of pH 6.9 at 16°C (NMBA 0.32 mol% of monomers). (b) Effect of NMBA concentration on the dynamic swelling behavior of P(DMA-MA8) hydrogels in the media of pH 6.9 at 16°C.

swelling ratio (SR_e) are calculated by the following equations [14]:

$$SR(\%) = \left[\frac{W_s - W_d}{W_d} \right] \times 100, \quad (1)$$

$$SR_e(\%) = \left[\frac{W_e - W_d}{W_d} \right] \times 100,$$

where W_s is the weight of the swelled hydrogels at time t , W_d is the weight of the dried hydrogels, and W_e denotes the weight of the gels at equilibrium swelling.

3. Results and Discussion

3.1. Swelling Behavior

3.1.1. Effect of Maleic Acid Content. The effect of maleic acid composition on the swelling of the prepared P(DMA-MAx) hydrogels at different pHs (0.9, 3.9, 6.9, and 8.7) and at 16°C was investigated. For instance, the swelling curves of P(DMA-MAx) hydrogels with different compositions of MA at pH 6.9 are given in Figure 1(a). As seen in this figure, the swelling ratio increases with time, but, later, constant swelling values are observed. These swelling values can be considered as an equilibrium swelling ratio (SR_e).

It is well known that swelling is induced by the electrostatic repulsion of ionic charges present within the network. Thus, as the number of carboxylic groups increases on going from PDMA to P(DMA-MAx), the swelling increases too.

The values of equilibrium swelling ratio of DMA/MA hydrogels in different buffer solutions are reported in Table 2(a). As shown, the hydrophilic nature of the hydrogel

copolymer is enhanced by increasing the amount of maleic acid [24, 25].

3.1.2. Effect of Cross-linker Content. The effect of increasing the amount of the cross-linking agent NMBA on the swelling capacity of the P(DMA-MA8) in different buffer solutions (pH 0.9, 3.9, 6.9, and 8.7) was investigated.

It is well known that the cross-link density directly affects the mechanical deformation of hydrogels. As the ratio of the cross-linking agent NMBA varied from 0.16 to 1.28 mol% in P(DMA-MA8), the degree of swelling was greatly reduced (Figure 1(b)). It is expected that hydrogels with higher cross-link density would provide numerous water channels for the diffusion of water, but the water content decreases due to increased level of cross-linking [9, 26].

The values of equilibrium swelling ratio of P(DMA-MA8) hydrogels with different NMBA contents at different pHs are given in Table 2(b).

3.1.3. Effect of pH. Figure 2(a) represents pH dependence of the equilibrium swelling ratio for P(DMA-MAx) hydrogels at 16°C in buffer solution from pH 0.9 to 8.7. As shown in this figure, the equilibrium mass swelling percentage for pure PDMA is not affected by varying the pH of the swelling medium since PDMA is nonionic hydrogel and does not have any group that could be ionized in an aqueous solution. With the introduction of the MA groups into the main chain, the swelling ratios are enhanced as the pH values of buffer solutions are increased. The hydrogels exhibit lower swelling capability in an acid medium and higher degree in a basic medium. This is related to the fact that the carboxyl groups could accept or release protons in response to various pH

TABLE 2: (a) Equilibrium swelling ratios of P(DMA-MAx) hydrogels with different MA contents at different pH media. (b) Equilibrium swelling ratios of P(DMA-MA8) hydrogels with different NMBA contents at different pH media.

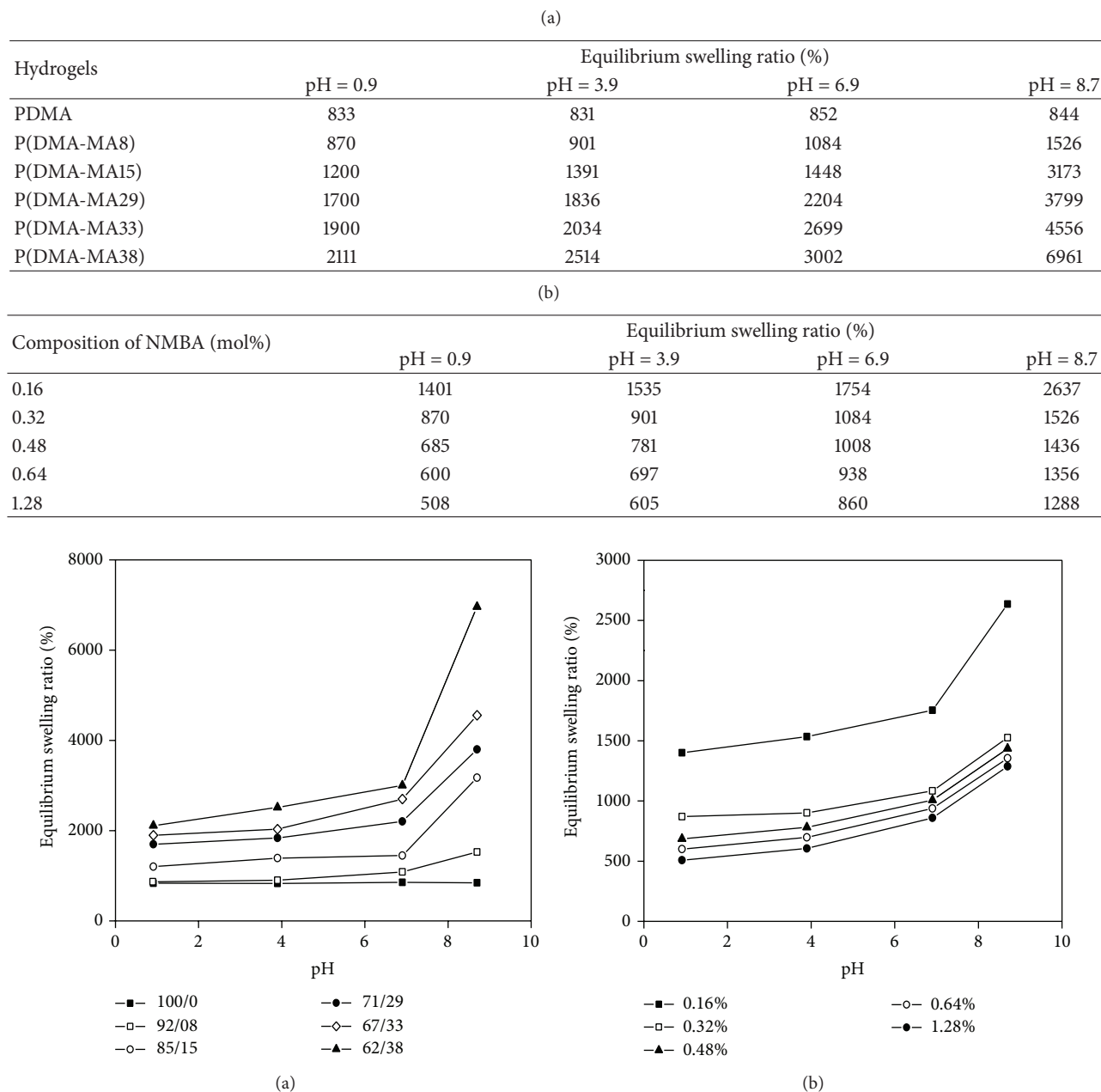


FIGURE 2: (a) Effect of pH on the equilibrium swelling ratio of P(DMA-MAx) hydrogels for different MA concentrations at 16°C (NMBA 0.32 mol% of monomers). (b) Effect of pH on the equilibrium swelling ratio of P(DMA-MA8) hydrogels for different NMBA compositions at 16°C.

aqueous media. At pH values lower than the pKa value of maleic acid, the first and second dissociation constants of MA are $pK_{a1} = 1.85$ and $pK_{a2} = 6.06$, respectively [27]; the carboxylic groups present within the network remain almost nonionized, thus imparting almost nonpolyelectrolyte type behavior to the hydrogel. This is ascribed to the fact that a lot of hydrogen bonds are formed due to the presence of carboxyl groups in the gel network. The hydrogen bond

interaction would restrict the movement or relaxation of the gel network chains. As a result, a compact hydrogel network is formed leading to a lower swelling ratio. On the contrary, when the pH of the swelling medium was above the pKa of the gel, the ionization of the carboxylic acid groups of the gel occurred. Consequently, hydrogen bonds are broken and an electrostatic repulsion is generated among polymer networks. This repulsive force would push the network chain segments

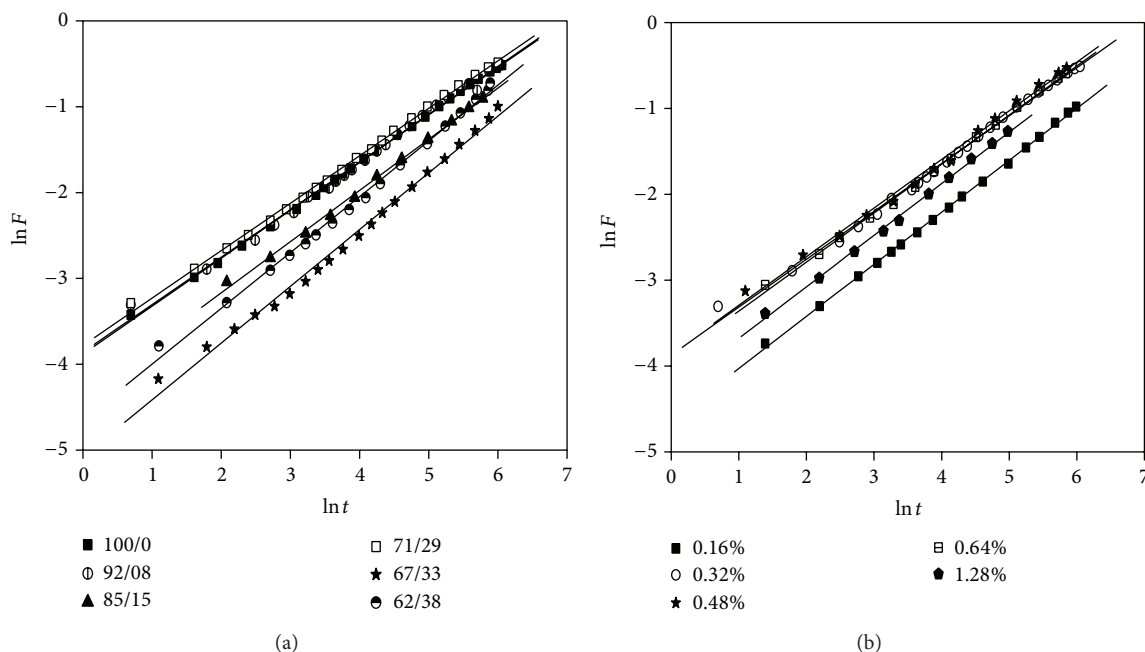


FIGURE 3: (a) Dependence of $\ln F$ on $\ln t$ of P(DMA-MAX) hydrogels in the media of pH 6.9 with different compositions of MA at 16°C. (b) Dependence of $\ln F$ on $\ln t$ of P(DMA-MA8) in the media of pH 6.9 with different compositions of NMBA at 16°C.

apart and thus attract more water into the hydrogels, so a higher swelling ratio is observed [28–31].

The percentage equilibrium swelling of P(DMA-MA8) is decreased with increasing cross-linking agent concentration (Figure 2(b)). The increasing cross-link density restricts the swelling of the hydrogels.

3.1.4. Diffusion Process at Different pH. Analysis of the mechanisms of water diffusion in swelling polymeric systems has received considerable attention in recent years, because of the important applications in biomedical, pharmaceutical, environmental, and agricultural engineering fields.

To determine the nature of water diffusion into hydrogels, kinetic modeling was conducted based on Fickian diffusion law for the onset stage of swelling (the model is valid only for the first 60% of the swelling) [14, 32]:

$$F = \frac{M_t}{M_\infty} = kt^n, \quad (2)$$

where M_t is the total amount of water intake at time t , M_∞ is the total amount of water intake at an equilibrium state which is determined by a gravimetric method, k is a swelling coefficient which is a parameter correlated with the polymeric network structures, and n is an exponent characteristic of the swelling which represents solvent diffusion modes inside hydrogels. For Fickian kinetics in which the rate of penetrate diffusion is rate limiting, $n = 0.5$, whereas values of n between 0.5 and 1 indicate the contribution of non-Fickian processes such as polymer relaxation.

For example, Figures 3(a) and 3(b) can be used to elucidate dependence of $\ln F$ on $\ln(t)$ for various hydrogels samples with different MA and NMBA contents at pH = 6.9,

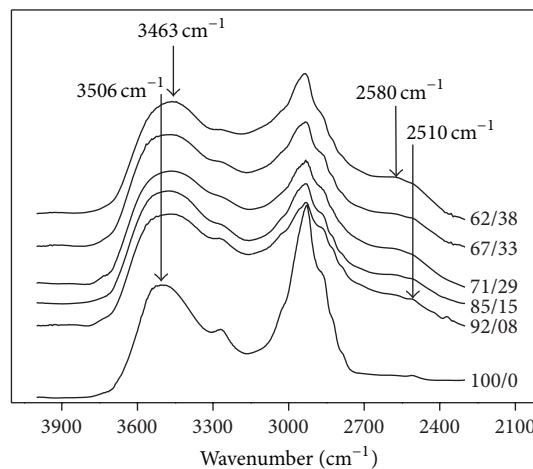


FIGURE 4: Scale-expanded infrared spectra of P(DMA-MAX) hydrogels in the hydroxyl region.

respectively. After having been fitted, the kinetic parameters k and n as well the correlation coefficient R^2 obtained are listed in Tables 3(a) and 3(b). The results indicate that the diffusion exponent for all samples ranges between 0.486 and 0.796, that is, non-Fickian or anomalous diffusion, and it occurs when the rate of permanent diffusion and the rate of polymer relaxation are comparable [32, 33].

3.2. FTIR Analysis. Figure 4 shows the scale-expanded infrared spectra of PDMA and P(DMA-MAX) recorded at room temperature in the 3900–2400 cm^{-1} region. The spectrum of pure PDMA shows a broad band at 3506 cm^{-1} , corresponded to hydrogen bonding between carbonyl groups

TABLE 3: (a) Swelling kinetic coefficients of P(DMA-MAx) hydrogels with different MA contents at different pH media. (b) Swelling kinetic coefficients of P(DMA-MA8) hydrogels with different NMBA contents at different pH media.

(a)				
Medium	Hydrogels	R^2	n	$\ln k$
pH = 0.9	PDMA	0.9997	0.576	-3.428
	P(DMA-MA8)	0.9996	0.487	-3.142
	P(DMA-MA15)	0.9996	0.486	-3.405
	P(DMA-MA29)	0.9984	0.636	-4.912
	P(DMA-MA33)	0.9969	0.684	-4.760
	P(DMA-MA38)	0.9991	0.584	-4.174
pH = 3.9	PDMA	0.9998	0.594	-3.997
	P(DMA-MA8)	0.9993	0.582	-3.762
	P(DMA-MA15)	0.9989	0.586	-4.209
	P(DMA-MA29)	0.9978	0.685	-5.263
	P(DMA-MA33)	0.9986	0.768	-5.242
	P(DMA-MA38)	0.9992	0.661	-4.615
pH = 6.9	PDMA	0.9997	0.559	-3.883
	P(DMA-MA8)	0.9975	0.553	-3.858
	P(DMA-MA15)	0.9985	0.582	-4.293
	P(DMA-MA29)	0.9990	0.553	-3.782
	P(DMA-MA33)	0.9968	0.661	-5.075
	P(DMA-MA38)	0.9980	0.650	-4.648
pH = 8.7	PDMA	0.9991	0.553	-3.819
	P(DMA-MA8)	0.9991	0.564	-3.711
	P(DMA-MA15)	0.9988	0.668	-4.748
	P(DMA-MA29)	0.9991	0.738	-5.745
	P(DMA-MA33)	0.9991	0.734	-5.680
	P(DMA-MA38)	0.9981	0.796	-5.316
(b)				
Medium	Composition of NMBA (mol%)	R^2	n	$\ln k$
pH = 0.9	0.16	0.9976	0.651	-4.617
	0.32	0.9996	0.487	-3.142
	0.48	0.9976	0.553	-3.665
	0.64	0.9964	0.564	-4.021
	1.28	0.9979	0.523	-3.555
pH = 3.9	0.16	0.9977	0.586	-4.675
	0.32	0.9993	0.582	-3.762
	0.48	0.9981	0.589	-4.081
	0.64	0.9985	0.575	-4.064
	1.28	0.9968	0.608	-4.410
pH = 6.9	0.16	0.9997	0.606	-4.633
	0.32	0.9975	0.553	-3.858
	0.48	0.9974	0.566	-3.858
	0.64	0.9989	0.571	-3.932
	1.28	0.9975	0.571	-4.191
pH = 8.7	0.16	0.9984	0.736	-4.974
	0.32	0.9991	0.564	-3.711
	0.48	0.9991	0.658	-4.333
	0.64	0.9971	0.631	-4.178
	1.28	0.9985	0.687	-4.429

and hydroxyl groups of water. When the MA groups are introduced into PDMA matrix, this later gradually shifts to

lower wavenumbers 3463 cm^{-1} , indicating the presence of hydrogen bonding interactions between carboxylic group of MA and carbonyl of amide. Moreover, the shoulder observed around 2510 cm^{-1} (shifted to 2580 cm^{-1}) is characteristic of COOH dimers.

In the carbonyl stretching $1780\text{--}1560\text{ cm}^{-1}$ region, the infrared spectrum of PDMA recorded at room temperature shows a broad band at 1640 cm^{-1} , assigned to the free carbonyl groups of the amide. With the incorporation of the MA groups within PDMA chain, a new band appears at 1735 cm^{-1} , attributed to free carboxylic groups. In addition, the band at 1640 cm^{-1} shifts to lower wavenumbers 1635 cm^{-1} , corresponding to the DMA carbonyl group that is directly hydrogen bonded to the MA hydroxyl group (Figure 5(a)).

The infrared spectra of P(DMA-MA8) with different NMBA compositions recorded at room temperature in the carbonyl region are illustrated in Figure 5(b). We should notice a gradual shift of the characteristic band of the carboxyl-carbonyl amide interactions to higher wavenumbers with increasing NMBA content. This behavior reveals that hydrogen bonding associations are favored with the lower amount of NMBA.

3.3. Thermogravimetric Analysis. The thermogravimetric (TGA) and derivative thermogravimetric (DTGA) curves for PDMA and P(DMA-MAx) containing 8, 15, 29, 33, and 38 mol% of MA are represented in Figure 6(a). It is seen that all studied hydrogels degrade in two main stages.

Parameters, such as temperature of maximum degradation (determined considering the derivative curves) and percentage of mass loss in each stage of degradation for all studied systems, are summarized in Table 4(a). As observed, the mass loss for PDMA in stage 1 is apparently associated with adsorbed water. The second stage from 366 to 475°C corresponds to the effective degradation of the polymer.

For P(DMA-MAx), the percentage of mass loss at the range $5\text{--}16\%$ in stage 1 can be assigned to the elimination of water adsorbed by the hydrophilic groups and probably to the elimination of hydroxyl groups due to the development of cyclic anhydride involving the liberation of water. Data from the literature indicated that with temperature increase (above 200°C), poly(styrene-co-maleic acid) with $42.8\text{ mol}\%$ of maleic acid shows absorption bands at 1779 cm^{-1} and 1854 cm^{-1} which are typically associated with cyclic anhydride formation [34]. In the second stage, at higher temperatures decomposition of anhydride rings takes place and it is overlapped with degradation of the main chain.

The onset temperature of the second main degradation stage as well as temperature of maximum degradation for copolymers decreases with acid composition. The amount of residual weight at the end temperature of degradation increases with increasing acid content in P(DMA-MAx). The reason for incomplete degradation of copolymers is probably the thermal cross-linking induced by heating the sample during thermogravimetric analysis.

TABLE 4: (a) Thermogravimetric parameters for P(DMA-MAx) hydrogels with different compositions of MA. (b) Thermogravimetric parameters for P(DMA-MA8) hydrogels with different compositions of NMBA.

(a)

Hydrogels	Stage 1		Stage 2		
	ΔT^a (°C)	Δm^b (wt%)	ΔT^a (°C)	T_{\max}^c (°C)	Residual weight (wt%)
PDMA	55–170	4	366–475	447	0
P(DMA-MA8)	55–219	5.7	312–488	440	4.38
P(DMA-MA15)	53–220	9	281–485	428	6.44
P(DMA-MA29)	55–230	11	262–471	409	7.72
P(DMA-MA33)	56–224	13	254–489	406	9.42
P(DMA-MA38)	54–223	16	241–472	397	11.6

^aTemperature range.

^bTotal weight loss percentage at the end of the step.

^cTemperature maximum values of DTGA curves.

(b)

Composition of NMBA (mol%)	Stage 1		Stage 2		
	ΔT^a (°C)	Δm^b (wt%)	ΔT^a (°C)	T_{\max}^c (°C)	Residual weight (wt%)
0.16	52–220	5	279–467	434	4.13
0.32	53–219	5.7	281–479	441	4.36
0.48	58–220	4.58	277–478	442	3.71
0.64	58–222	5.11	283–486	449	3.59
1.28	59–211	4.38	285–496	485	3.47

^aTemperature range.

^bTotal weight loss percentage at the end of the step.

^cTemperature maximum values of DTGA curves.

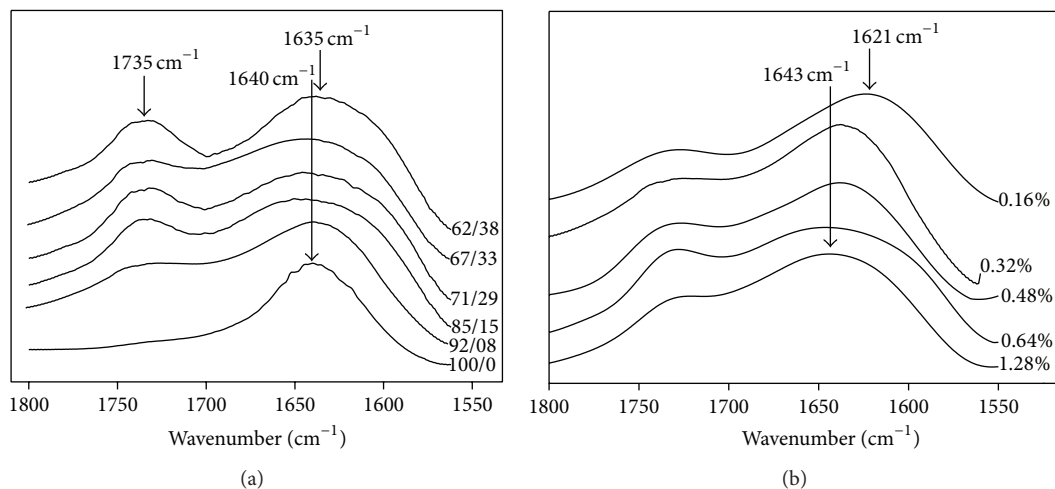


FIGURE 5: (a) Scale-expanded infrared spectra of P(DMA-MAx) hydrogels in the carbonyl region. (b) Scale-expanded infrared spectra of P(DMA-MA8) hydrogels with different compositions of NMBA in the carbonyl region.

The thermogravimetric (TGA) and derivative thermogravimetric (DTGA) curves for the copolymers P(DMA-MA8) with different amounts of NMBA are shown in Figure 6(b) while Table 4(b) summarizes their thermogravimetric parameters. The temperature of maximum degradation for these copolymers increases with NMBA content. This thermal stability is mainly due to an increase of the crosslink density.

3.4. DSC Analysis. Figure 7(a) shows thermograms of PDMA and P(DMA-MAx). The T_g values of PDMA and P(DMA-MAx) ($x = 8, 15, 29, 33$, and 38 mol%) are $126, 129, 136, 139, 143$, and 158°C , respectively. It is clear that the introduction of maleic acid species within PDMA backbone increases its T_g value. This fact is related to intermolecular hydrogen bonding between carboxyl and amide groups and intramolecular hydrogen bonding between carboxyl groups, which act as

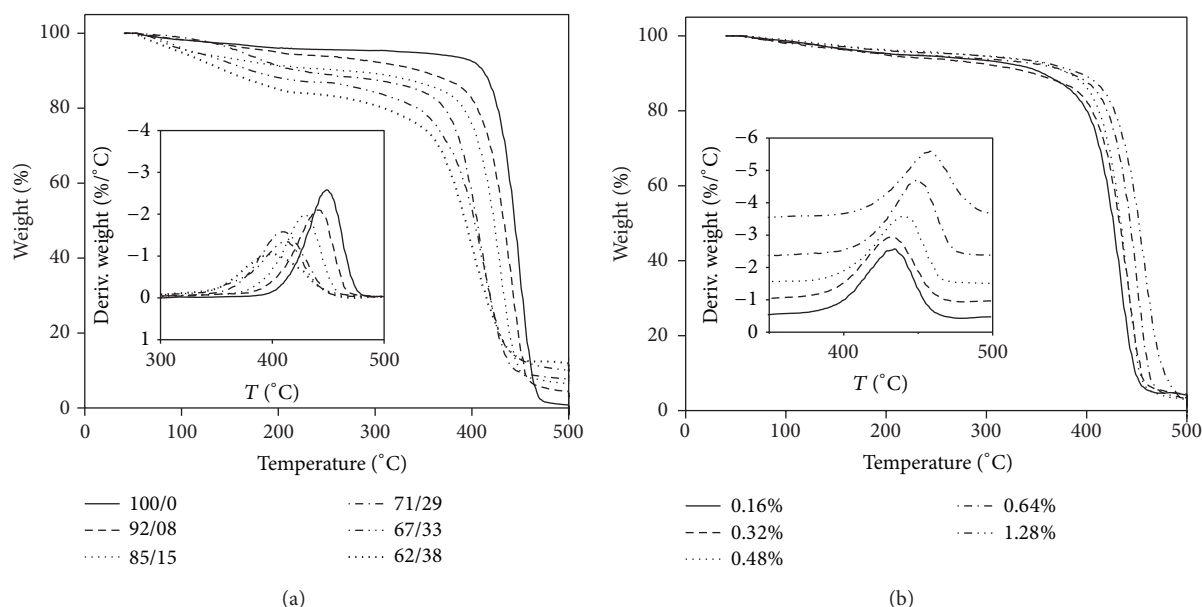


FIGURE 6: (a) TGA thermograms and DTGA curves of P(DMA-MAx) hydrogels. (b) TGA thermograms and DTGA curves of P(DMA-MA8) hydrogels with different compositions of NMBA.

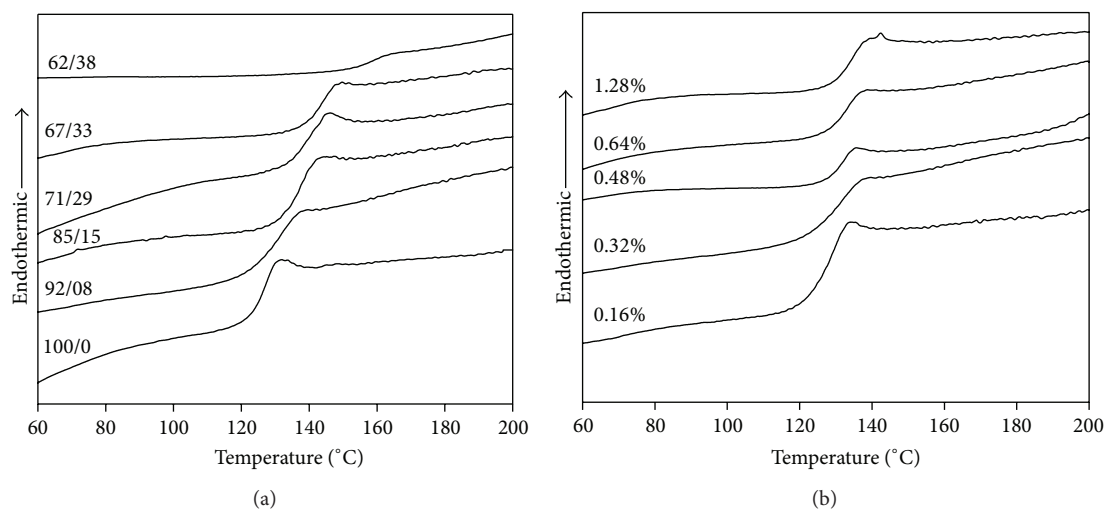


FIGURE 7: (a) DSC thermograms of P(DMA-MAx) hydrogels. (b) DSC thermograms of P(DAM-MA8) hydrogels with different compositions of NMBA.

additional cross-links, thus reducing subchain mobility and resulting in less flexible network.

The thermograms of P(DMA-MA8) with different amounts of NMBA are represented in Figure 7(b). The T_g values, in the range 127–134 °C, are increased with increasing cross-linking agent content. The high cross-link density restricts the movement of polymer segment.

4. Conclusion

A series of pH-sensitive P(DMA-MAx) hydrogels were synthesized by free-radical polymerization in water using NMBA as cross-linker.

The equilibrium swelling ratio of hydrogels increases with the increase of MA content but reduces with the increase of NMBA concentration. The hydrogels have apparent pH-sensitive character. With increase in pH value from 0.9 to 8.7, the swelling ratio increased accordingly. In the diffusion transport mechanism study, the results indicate that the swelling exponent n for PDMA and DMA-MA copolymeric gels is in the range from 0.486 to 0.796. This implies that the swelling transport mechanism is a non-Fickian transport. The thermal stability of the copolymers is essentially associated with the DMA monomer, losing stability when the percentage of MA in the copolymer system increases. The described pH-sensitive hydrogel might have great potential application in drug delivery system.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] A. S. Hoffman, "Hydrogels for biomedical applications," *Advanced Drug Delivery Reviews*, vol. 54, no. 1, pp. 3–12, 2002.
- [2] O. Wichterle and D. Lím, "Hydrophilic gels for biological use," *Nature*, vol. 185, no. 4706, pp. 117–118, 1960.
- [3] D. M. García, J. L. Escobar, Y. Noa, N. Bada, E. Hernáez, and I. Katime, "Timolol maleate release from pH-sensitive poly(2-hydroxyethyl methacrylate-co-methacrylic acid) hydrogels," *European Polymer Journal*, vol. 40, no. 8, pp. 1683–1690, 2004.
- [4] M. Şen, Ö. Kantoğlu, and O. Güven, "The effect of external stimuli on the equilibrium swelling properties of poly(N-vinyl 2-pyrrolidone/itaconic acid) poly-electrolyte hydrogels," *Polymer*, vol. 40, no. 4, pp. 913–917, 1999.
- [5] C. S. Brazel and N. A. Peppas, "Synthesis and characterization of thermo- and chemomechanically responsive poly(N-isopropylacrylamide-co-methacrylic acid) hydrogels," *Macromolecules*, vol. 28, no. 24, pp. 8016–8020, 1995.
- [6] B. Yıldız, B. Işık, and M. Kış, "Synthesis of thermoresponsive N-isopropylacrylamide-N-hydroxymethylacrylamide hydrogels by redox polymerization," *Polymer*, vol. 42, no. 6, pp. 2521–2529, 2001.
- [7] B. Singh, N. Sharma, and N. Chauhan, "Synthesis, characterization and swelling studies of pH responsive psyllium and methacrylamide based hydrogels for the use in colon specific drug delivery," *Carbohydrate Polymers*, vol. 69, no. 4, pp. 631–643, 2007.
- [8] S. P. Zhao, M. J. Cao, L. Y. Li, and W. L. Xu, "Synthesis and properties of biodegradable thermo- and pH-sensitive poly[(N-isopropylacrylamide)-co-(methacrylic acid)] hydrogels," *Polymer Degradation and Stability*, vol. 95, no. 5, pp. 719–724, 2010.
- [9] K. Wang, S. Z. Fu, Y. C. Gu et al., "Synthesis and characterization of biodegradable pH-sensitive hydrogels based on poly(ϵ -caprolactone), methacrylic acid, and poly(ethylene glycol)," *Polymer Degradation and Stability*, vol. 94, no. 4, pp. 730–737, 2009.
- [10] T. Çaykara and M. Doğmuş, "The effect of solvent composition on swelling and shrinking properties of poly(acrylamide-co-itaconic acid) hydrogels," *European Polymer Journal*, vol. 40, no. 11, pp. 2605–2609, 2004.
- [11] Y. Luo, K. Zhang, Q. Wei, Z. Liu, and Y. Chen, "Poly(MAA-co-AN) hydrogels with improved mechanical properties for theophylline controlled delivery," *Acta Biomaterialia*, vol. 5, no. 1, pp. 316–327, 2009.
- [12] S. K. Bajpai and S. Dubey, "In vitro dissolution studies for release of vitamin B₁₂ from poly(N-vinyl-2-pyrrolidone-co-acrylic acid) hydrogels," *Reactive and Functional Polymers*, vol. 62, no. 1, pp. 93–104, 2005.
- [13] B. Singh, N. Chauhan, and S. Kumar, "Radiation crosslinked psyllium and polyacrylic acid based hydrogels for use in colon specific drug delivery," *Carbohydrate Polymers*, vol. 73, no. 3, pp. 446–455, 2008.
- [14] Y. Huang, H. Yu, and C. Xiao, "pH-sensitive cationic guar gum/poly (acrylic acid) polyelectrolyte hydrogels: swelling and in vitro drug release," *Carbohydrate Polymers*, vol. 69, no. 4, pp. 774–783, 2007.
- [15] G. Ma, D. Yang, Q. Li et al., "Injectable hydrogels based on chitosan derivative/polyethylene glycol dimethacrylate/N,N-dimethylacrylamide as bone tissue engineering matrix," *Carbohydrate Polymers*, vol. 79, no. 3, pp. 620–627, 2010.
- [16] J. Kopeček, "Hydrogel biomaterials: a smart future?" *Biomaterials*, vol. 28, no. 34, pp. 5185–5192, 2007.
- [17] M. Sen and O. Güven, "Dynamic deswelling studies of poly(N-vinyl-2-pyrrolidone/itaconic acid) hydrogels swollen in water and terbinafine hydrochloride solutions," *European Polymer Journal*, vol. 38, no. 4, pp. 751–757, 2002.
- [18] A. Vashist, Y. K. Gupta, and S. Ahmad, "Interpenetrating biopolymer network based hydrogels for an effective drug delivery system," *Carbohydrate Polymers*, vol. 87, no. 2, pp. 1433–1439, 2012.
- [19] B. Singh, G. S. Chauhan, S. Kumar, and N. Chauhan, "Synthesis, characterization and swelling responses of pH sensitive psyllium and polyacrylamide based hydrogels for the use in drug delivery (I)," *Carbohydrate Polymers*, vol. 67, no. 2, pp. 190–200, 2007.
- [20] S. Kondo, N. Nakashima, H. Hado, and K. Tsuoa, "Poly(N,N-dimethylamide-co-styrene)s as a highly efficient catalysts for two-phase reactions," *Journal of Polymer Science A: Polymer Chemistry*, vol. 28, no. 8, pp. 2229–2232, 1990.
- [21] A. Valdebenito and M. V. Encinas, "Effect of solvent on the free radical polymerization of N,N-dimethylacrylamide," *Polymer International*, vol. 59, no. 9, pp. 1246–1251, 2010.
- [22] W. L. F. Santos, M. F. Porto, E. C. Muniz, L. Olenka, M. L. Baesso, and A. C. Bento, "Poly(ethylene terephthalate) films modified with N, N'-dimethylacrylamide: incorporation of disperse dye," *Journal of Applied Polymer Science*, vol. 77, pp. 269–282, 2000.
- [23] Alexeev, *Analyse Qualitative*, 4th edition, 1980.
- [24] E. Karadağ and D. Saraydin, "Swelling of superabsorbent acrylamide/sodium acrylate hydrogels prepared using multi-functional crosslinkers," *Turkish Journal of Chemistry*, vol. 26, no. 6, pp. 863–875, 2002.
- [25] E. Karadağ, Ö. B. Üzümlü, and D. Saraydin, "Swelling equilibria and dye adsorption studies of chemically crosslinked superabsorbent acrylamide/maleic acid hydrogels," *European Polymer Journal*, vol. 38, no. 11, pp. 2133–2141, 2002.
- [26] B. Yıldız, B. Işık, and M. Kış, "Synthesis and characterization of thermoresponsive isopropylacrylamide acrylamide hydrogels," *European Polymer Journal*, vol. 38, pp. 1343–1347, 2002.
- [27] R. C. Weast, *Handbook of Chemistry and Physics*, The Chemical Rubber, Cleveland, Ohio, USA, 53rd edition, 1972.
- [28] J. Zhang, L. Y. Chu, Y. K. Li, and Y. M. Lee, "Dual thermo- and pH-sensitive poly(N-isopropylacrylamide-co-acrylic acid) hydrogels with rapid response behaviors," *Polymer*, vol. 48, no. 6, pp. 1718–1728, 2007.
- [29] M. Şen and A. Yakar, "Controlled release of antifungal drug terbinafine hydrochloride from poly(N-vinyl 2-pyrrolidone/itaconic acid) hydrogels," *International Journal of Pharmaceutics*, vol. 228, no. 1–2, pp. 33–41, 2001.
- [30] S. Jin, M. Liu, F. Zhang, S. Chen, and A. Niu, "Synthesis and characterization of pH-sensitivity semi-IPN hydrogel based on hydrogen bond between poly(N-vinylpyrrolidone) and poly(acrylic acid)," *Polymer*, vol. 47, no. 5, pp. 1526–1532, 2006.
- [31] B. Taşdelen, N. Kayaman-Apohan, O. Güven, and B. M. Baysal, "Preparation of poly(N-isopropylacrylamide/itaconic acid) copolymeric hydrogels and their drug release behavior," *International Journal of Pharmaceutics*, vol. 278, no. 2, pp. 343–351, 2004.

- [32] P. L. Ritger and N. A. Peppas, "A simple equation for description of solute release I. Fickian and non-Fickian release from non-swellable devices in the form of slabs, spheres, cylinders or discs," *Journal of Controlled Release*, vol. 5, no. 1, pp. 23–36, 1987.
- [33] P. L. Ritger and N. A. Peppas, "A simple equation for description of solute release I. Fickian and Non-Fickian release from swellable devices," *Journal of Controlled Release*, vol. 5, no. 1, pp. 37–42, 1987.
- [34] M. Świtała-Zeliazkow, "Thermal degradation of copolymers of styrene with dicarboxylic acids—II: copolymers obtained by radical copolymerisation of styrene with maleic acid or fumaric acid," *Polymer Degradation and Stability*, vol. 91, no. 6, pp. 1233–1239, 2006.

