

Copolymers of 2-Hydroxyethylmethacrylate and *N*-Maleoylglycine: Synthesis, Characterization, and Swelling Behavior

Manuel Jeria,¹ Guadalupe del C. Pizarro,¹ Oscar G. Marambio,¹ Margarita Huerta,¹ Paulina Valencia,¹ Bernabé L. Rivas²

¹Department of Chemistry, Tecnológica Metropolitana University, J. P. Alessandri 1242, Santiago, Chile

²Polymer Department, Faculty of Chemistry, University of Concepción, Casilla 160-C, Concepción, Chile

Received 3 June 2004; accepted 6 February 2005

DOI 10.1002/app.22258

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We synthesized copolymers based on 2-hydroxyethylmethacrylate and *N*-maleoylglycine by varying the monomer feed composition. The copolymers were characterized by Fourier transform infrared spectroscopy, elemental analysis, and thermogravimetry/differential scanning calorimetry as the thermal analysis method. The thermograms showed that the polymers degraded in a single-stage process. For the hydrogels of poly(2-hydroxyethylmethacrylate) and poly(2-hydroxyethylmethacrylate-*co*-*N*-maleoylglycine) [poly(HEMA-*co*-MG)], swelling behaviors were investigated by the immersion of the gels in solution at pH's of 3, 5, and 7. The swelling studies were performed

with and without ionic strength. The copolymer composition had a significant effect on the equilibrium swelling behavior of poly(HEMA-*co*-MG). With those soluble copolymer fractions, we obtained a low conversion (<30%); the monomer reactivity ratios were estimated by the Kelen-Tüdös linear method. The data indicated that poly(HEMA-*co*-MG) was a random copolymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1897–1902, 2005

Key words: radical polymerization; hydrophilic polymers; swelling; monomer reactivity ratios; differential scanning calorimetry (DSC)

INTRODUCTION

Hydrogels have received a considerable amount of attention for their use as absorbents and as support carriers in biomedical engineering.^{1–5} Superabsorbent polymers are crosslinked polyelectrolytes. Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving. These polymers can absorb many times their own weight in water, and their most common use is in disposable nappies and other absorbent products.

The commercially important superabsorbent polymers are sodium salts of crosslinked poly(acrylic acid) and graft copolymers of crosslinked poly(acrylic acid). In addition to their liquid–water absorption characteristics, superabsorbent polymers absorb water from the vapor state and, therefore, can be used to control

humidity. In fact, these products are more effective than silica gel and help to maintain constant humidity in vegetable and fruit storage buildings and can also help conserve water in agriculture and horticulture applications.^{6–12}

The swelling behavior of a copolymer depends on the nature of the polymer and the characteristics of the external solution and can be accounted for by Flory's theory.¹³ A polymer's nature involves factors including the density of crosslinking, strength of the hydrophilic group, and elasticity of the polymer network.

This aim of this study was to investigate the swelling behaviors of copolymer hydrogels from different monomer ratios of 2-hydroxyethylmethacrylate (HEMA) and *N*-maleoylglycine (MG) in deionized water and the effect of an ionic strength of 0.06M (NaNO₃) and pH on the swelling properties of the hydrogels.

EXPERIMENTAL

Reagents

HEMA was used as received (Merck-Schuchardt, Germany). MG was prepared according to a published method from maleic anhydride and glycine.¹⁴ Benzoyl peroxide (Merck-Schuchardt) was used as the initiator.

Correspondence to: G. del C. Pizarro (gpizarro2@yahoo.com).

Contract grant sponsor: Universidad Tecnológica Metropolitana.

Contract grant sponsor: Deutsche Gesellschaft für Technische Zusammenarbeit.

Contract grant sponsor: Deutsche Akademische Austauschdienst.

Preparation of the copolymers

The copolymerization reaction of HEMA and MG was carried out with several feed monomer compositions at 70°C and with 0.5 mol % benzoyl peroxide for 24 h in tetrahydrofuran as the solvent. The polymerization flasks were degassed three times with freeze cycles under nitrogen. The obtained copolymers were filtered off and washed with diethyl ether. They were collected and dried *in vacuo* until a constant weight was reached.

To determine the monomer reactivity ratios, copolymers at low conversion (<30%) were obtained.

Characterization

The copolymer composition was calculated from the N/C weight percentage ratio as determined by elemental analysis (EA):

$$\text{Swelling \%} = \left[\frac{\text{Weight of the swollen gel} - \text{Weight of the dried sample}}{\text{Weight of the dried sample}} \right] \times 100\% \quad (1)$$

To determine the swelling properties, the dried samples (100 mg) of the copolymers were placed in pure water (5 mL) and in an aqueous solution (5 mL) with an ionic strength of 0.06M. The molar ratio of copolymer and ionic strength were 1 : 1 (molar mass of the copolymer unit = 285 g/mol). The swelling studies were measured at different pH values (3, 5, and 7). The pH values of the external solution were adjusted by adding 0.1M HCl or 0.1M NaOH. Swollen gels were filtered and subsequently weighed each hour for 12 h at room temperature.

Measurement

EAs were carried out with a Carlo Erba 1108 analyzer (Italy). Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer model 1818 spectrometer (Perkin Elmer, Shelton, CT). Potentiometric titration was carried out on a Hanna 211 pH meter at room temperature with a 0.10M solution of NaOH. Thermal analysis was performed in a nitrogen atmosphere at a heating rate of 10°C/min and was determined with a Mettler Toledo thermal analyzer with an 822-DSC module (Spain). Thermogravimetric data were obtained with a PerkinElmer TGS-1 thermal analyzer.

RESULTS AND DISCUSSION

Synthesis and characterization of the copolymers

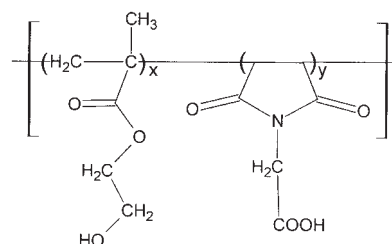
The radical copolymerization of HEMA and MG was conducted in tetrahydrofuran under several feed monomer compositions by radical polymerization.

ANAL. Calcd for copolymer 1: N, 5.776%; C, 49.674%; H, 4.869%. Found: N, 5.735%; C, 49.316%; H, 5.057%. Calcd for copolymer 2: N, 5.225%; C, 50.217%, H, 5.144%. Found: N, 5.159%; C, 49.583%; H, 5.288%. Calcd for copolymer 3: N, 3.881%; C, 51.543%; H, 5.812%. Found: N, 3.844%; C, 51.053%; H, 6.031%. Calcd for copolymer 4: N, 2.707%; C, 52.703%; H, 6.397%. Found: N, 2.714%; C, 52.847%; H, 6.711%.

Swelling study

An insoluble sample of poly(2-hydroxyethylmethacrylate-*co*-*N*-maleoylglycine) [poly(HEMA-*co*-MG); 100 mg] was weighed accurately as a granular polymer. The percentage of swelling was calculated from the ratio of the mass of fluid absorbed to the mass of dry polymer according to the following equation:

The general structure of the copolymers was as follows:



The copolymers were insoluble in water, methanol, acetone, and chloroform, and they swelled in water.

TABLE I
Experimental Conditions for the Copolymerization Reaction Carried Out for 24h and the Copolymer Compositions of Poly(HEMA-*co*-MG)

Copolymer	HEMA (mmol)	MG (mmol)	Yield (%)	N/C found	Copolymer composition (mol %) ^a
1	1.6	4.8	80.0	0.11627	40.2 : 59.8
2	2.1	4.2	80.2	0.10404	46.5 : 53.5
3	3.2	3.2	87.2	0.07530	61.3 : 38.7
4	4.2	2.1	88.2	0.05136	73.6 : 26.4

^a From EA.

$G = (m_1/m_2 - 1)/z$ and $F = (m_1/m_2)/z^2$; $z = \log(1 - \delta_1)/\log(1 - \delta_2)$; $\delta_1 = \delta_2 y / X_o$; $\delta_2 = \text{wt}\%(\mu + X_o)/(\mu + y)/100$; $\mu = \mu_2/\mu_1$; $y = m_1/m_2$; $X_o = M_1/M_2$; wt% = conversion; μ_1 and μ_2 are the molecular weights of monomer 1 and 2 respectively; M_1 and M_2 = initial composition of monomers in mol; $M_1 = \text{NPhMI}$ and $M_2 = \beta\text{MHI}$; m_1 and m_2 = correspond to the monomer composition in the copolymer for each monomer.

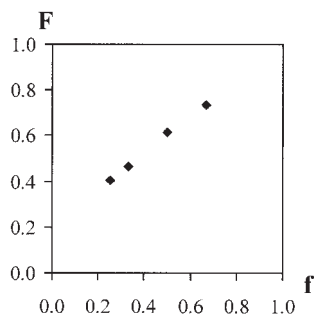


Figure 1 Relationship (moles) between HEMA in the feed (f) and HEMA incorporated into the copolymers (F).

The results of the copolymerization reaction are summarized in Table I.

The relationship (in moles) between the HEMA monomer unit in the feed and that in the copolymers is shown in Figure 1.

The weight ratios of acrylic derivatives to maleoylglycine in the copolymers were calculated from the N/C weight percentage ratio as determined by EA. The FTIR (KBr) spectra of copolymers 1–4 were basically the same. The presence of the most characteristic absorption bands at 3509 cm^{-1} ($-\text{OH}$, $-\text{COOH}$), 2998 cm^{-1} (CH), 1733 and 1706 cm^{-1} ($\text{C}=\text{O}$ from acid, ester, and imide), and 1427 cm^{-1} ($\text{C}-\text{N}$ from imide) and the absence of the absorption band of the double bond confirmed that copolymerization had occurred.

Determination of the monomer reactivity ratios

To determine the monomer reactivity ratio for HEMA (M_1) and MG (M_2), copolymers with low conversions were obtained. These values were determined from the monomer feed ratios and the copolymer composition by the Kelen-Tüdös (K-T) method for high conversion.¹⁵

Figure 2 shows $G/(r_1 + r_2/\alpha)(\eta) - F/(\alpha + F)(\xi)$ plots according to the K-T method, from which the monomer reactivity ratios were determined for the copolymers. r_1 and r_2 values were also determined according to equation:

$$\eta = (r_1 + r_2/\alpha)\xi \quad (1)$$

where η and ξ are mathematical functions of the monomers in the feed and in the copolymer, respectively, α is an arbitrary denominator with any positive value, which produces a more homogeneous distribution of data along $n - \xi$ axes.

The variable ξ can take any possible value in the 0 to 1 interval. A plot of η versus ξ gives a straight line, which on extrapolation to $\xi = 0$ and $\xi = 1$ gives $-r_2/\alpha$ and r_1 , respectively. $\alpha = (F_{\min} \times F_{\max})^{0.5}$, where F_{\min} and F_{\max} correspond to the smallest and largest frac-

tion in the copolymer (F) that are calculated, respectively.

The results, shown in Table II, give reactivity ratios for HEMA and MG of $r_1 = 1.155$ and $r_2 = 0.300$, respectively. The experimental data indicated that poly(HEMA-*co*-MG) was a random incorporation with homosegments of HEMA with some tendency to alternate, $r_1 \times r_2 = 0.34$.

Swelling degree of poly(2-hydroxyethylmethacrylate) [poly(HEMA)]

Poly(HEMA) was synthesized in the presence and absence of a crosslinking reagent (CR). The swelling behavior in $0.06M$ NaNO_3 was evaluated at different pH values for both homopolymers. The results show that swelling of the homopolymer without CR was higher than that of the homopolymer with CR (see Table III). This was attributed to the increase in the crosslinking of the polymer network, which promoted more stiffness in the polymer chains and decreased the swelling capacity.

Swelling degree of the copolymers

With these results considered, the synthesis of the copolymers was carried out without a CR. The swelling behavior was evaluated in pure water and in $0.06M$ NaNO_3 at different pH values and comonomer ratios.

Figure 3 shows the water absorption of the poly(HEMA-*co*-MG) system without a CR and with a $0.06M$ ionic strength and in deionized water as a function of pH. The swelling of the hydrogels increased in the pH 5–7 range with an ionic strength of $0.06M$, and the copolymers were rich in HEMA units, where the maximum extend of swelling (1200.5 – 1474.5% and 1426.0 – 1598.9% , respectively, see Table III) was observed. Moreover, the poly(HEMA-*co*-MG) with ionic strength swelled more than poly(HEMA-*co*-MG) in

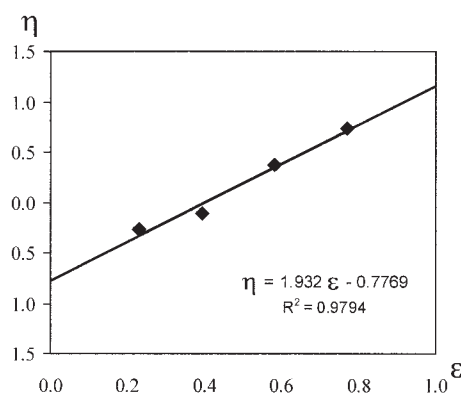


Figure 2 η versus ε representation of the K-T method copolymerization parameters for poly(HEMA-*co*-MG).

TABLE II
Comonomer Reactivity Ratios for Poly(HEMA-co-MG) by the Kelen Tüdös Method

M_2	m_2	Weight	X_o	y	δ_1	δ_2	z	F	G	ξ	η
75.00	59.82	30.0	0.33	0.67	0.495	0.246	2.423	0.114	-0.136	0.2302	-0.2727
66.67	53.53	20.2	0.50	0.87	0.288	0.166	1.873	0.248	-0.071	0.3927	-0.1118
50.00	38.74	27.2	1.00	1.58	0.340	0.215	1.716	0.537	0.339	0.5838	0.3682
33.33	26.43	28.2	2.00	2.78	0.315	0.226	1.475	1.280	1.210	0.7698	0.7275

$\mu = 1.1919$; $\alpha = 0.3827$. M_2 = monomer composition in the feed (mol %); m_2 = copolymer composition of M_2 (mol %); F = HEMA incorporated into the feed (mol).

pure water at pH 5 and pH 7 (see Table III). This behavior was attributed to the higher ionization of the carboxyl groups of these hydrogels at pH 7; as indicated by the potentiometric data, the amount of COOH ionized corresponded to 88.8%. Initially, when a polymer network is placed in an electrolyte solution, it absorbs water and ionizes. This leads to an influx of counterions. The protons are released from the ionized fixed carboxylic acid groups and are replaced by counterions. The transport of counterions contributes to the swelling.¹⁶ During the dynamic absorption in a gel containing weakly ionizable groups, the diffusion of mobile ions from the swelling medium into the polymer is necessarily coupled with ionization of fixed charges and penetrate diffusion as the polymer swells. In the hydrogel, each monomer unit of the copolymer has a portion that holds an electrical charge. The electrical charges on the polymer attract water molecules and bind them to the polymer. Each charge binds several water molecules, and each molecule of the polymer can bind a large volume of water.

The copolymer composition significantly impacted the equilibrium swelling behavior of the poly(HEMA-co-MG) gel, as shown in Figure 3. As the MG/HEMA ratio decreased, the swelling capacity increased. This could have been due to the increase of hydroxyl groups, that is, weakly hydrophilic groups, which may have subsequently produced hydrogen bonds between the comonomer units. Moreover, the swelling of the copolymers increased with the pH. This behavior could have been due to a weakening of the intramolecular hydrogen binding attraction forces of the chains, which was caused by an increase in the charges along the macromolecules when the pH was

increased. This led to an increase in the repulsion forces of the carboxylate groups when the carboxylic groups in the copolymer were dissociated. This promoted lateral chain of HEMA to occupy a larger volume, and the swelling process was increased when the water was adsorbed by hydrogen bonding with the hydrophilic groups. In all of the copolymer compositions, the maximum capacity of swelling occurred at pH values of 5 and 7, and this increased when the copolymer was richest in HEMA; there was a higher dissociation of the acid groups of MG at this pH range because the pK_a of poly(*N*-maleoylglycine) [poly(MG)] was 2.1.

The swelling studies showed a high absorption capacity at an ionic strength of 0.06M for copolymers 3 and 4. Copolymers 1 and 2, rich in MG units, were partially water soluble in the presence of an ionic strength of 0.06M and an alkaline pH after 6 h. Poly(MG) was water soluble¹³ for this reason, whereas when the content of MG in the copolymer was higher, it was partially water soluble.

Thermal behavior

The thermal behaviors of the four poly(HEMA-co-MG) copolymers were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis under nitrogen at a heating rate of 10°C/min.

The DSC curves showed the characteristic endothermic and exothermic peaks (see Fig. 4). Copolymers 1 and 2 showed endothermic transitions due to the melting process between 200 and 270°C. Copolymers 3 and

TABLE III
Swelling Percentage of Poly(HEMA) for a Period of 12 h as a Function of pH and Without and with a CR

pH	Swelling percentage (%)	
	No CA	0.3 mol % CA
3	62.3	49.6
5	73.7	59.4
7	101.1	79.8

Ionic strength = 0.06 M.

TABLE IV
Swelling Percentage of Poly(HEMA-co-MG) in Pure Water (PW) and 0.06M NaNO₃ for a Period of 12 h at Different pH's and Copolymer Compositions

Copolymer	pH 3		pH 5		pH 7	
	PW	IS	PW	IS	PW	IS
1	35.1	52.4	105.5	150.3	150.0	178.9
2	65.2	82.8	139.2	239.2	177.4	270.4
3	95.1	152.1	150.5	1200.5	180.5	1474.5
4	95.9	215.3	166.0	1426.0	190.9	1598.9

IS = ionic strength.

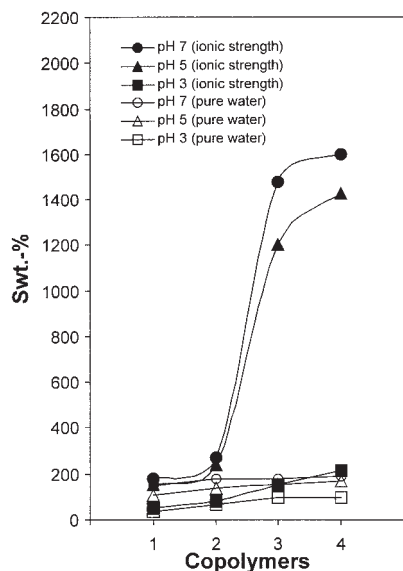


Figure 3 Swelling percentage (Swt %) in pure water and in an aqueous salt solution (0.06M NaNO₃) of poly(HEMA-*co*-MG) for a period of 12 h as function of pH and copolymer composition.

4 showed slight endothermic transitions due to the melting process between 170 and 280°C. Poly(MG) (curve 5) showed a slight endothermic transition due to the melting process between 240 and 280°C.

All of the copolymers showed endothermic transitions due to the decomposition reactions in the temperature range 290–400°C.

The obtained thermograms showed that the polymers degraded in a single-stage process that is characteristic of the thermal decomposition of a great number of macromolecular compounds, which provides evidence that no other preferred or competitive and simultaneous process occurred^{13,17–20} (see Fig. 5). Table V shows the values of the thermal decomposition temperatures (TDTs) for each copolymer. The TDT of

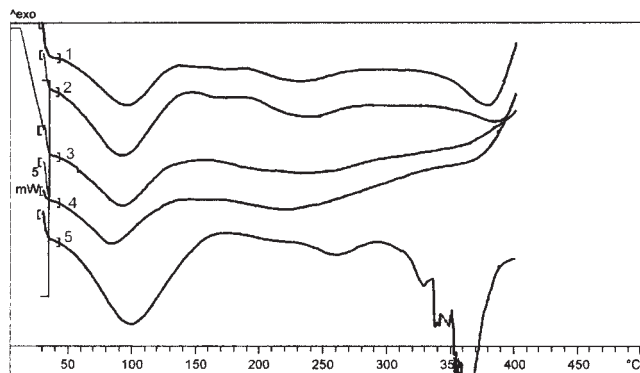


Figure 4 DSC curves of the copolymers (samples 1–4) and poly(MG) (5) with a heating rate of 10°C/min under nitrogen gas at a temperature range of 25–450°C.

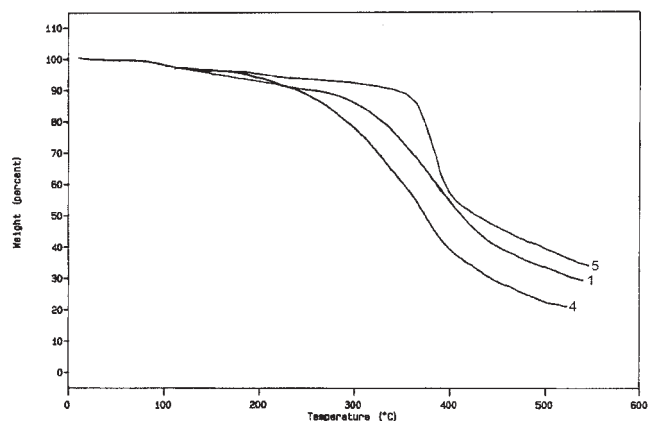


Figure 5 Thermogravimetric analysis curves of copolymers 1, 4, and 5 at a heating rate of 10°C/min under nitrogen gas at a temperature range of 25–450°C.

the copolymers ranged between 280 and 310°C. Thermal stability increased with increasing MG unit content in the copolymer, which was a consequence of the imide ring rigidity. The highest TDT values were found for copolymers 1 and 2, which contained higher amounts of MG co-units because of the more stable structure of the monomer. This behavior may have been related to the copolymer composition. In general, the poly(acrylic derivatives-*co*-*N*-maleoylglycine) with slight excesses of MG monomer units were most stable.¹⁶ The poly(HEMA-*co*-MG) copolymers 1 and 2 showed the highest thermal stabilities (see Table V). Higher contents of HEMA decreased the TDT. Copolymers 3 and 4 showed broad exothermic peaks over 280°C, which meant that a slower reaction of decomposition was carried out because poly(HEMA-*co*-MG) presented in its structure a high percentage of HEMA units (see Table V).

The copolymers presented a lower TDT than that of the poly(MG) (340°C; see Table V). This could have been because the poly(HEMA-*co*-MG) presented in its structure a high percentage of intramolecular crosslinking reactions due to a higher percentage of HEMA comonomer units.

CONCLUSIONS

All of the polymers obtained were insoluble in water and in some common organic solvents.

TABLE V
Thermal Behavior of the Poly(HEMA-*co*-MG)

Copolymer	Weight loss (%) at different temperatures (°C)					TDT (°C)
	100	200	300	400	500	
1	0.0	2.0	5.0	12.2	57.0	310
2	0.0	2.4	4.0	18.0	63.0	310
3	0.0	6.2	15.8	32.8	61.3	280
4	0.0	5.5	16.8	46.0	73.0	280

Heating rate = 10°C/min.

The experimental data indicated that the HEMA-*co*-MG systems were random copolymers. The swelling of the polymers in aqueous solutions with ionic strengths of 0.06M were evaluated at different pH values as the weight of absorbed water per 100 mg of dry polymer and ranged between 50 and 1600 wt %. The copolymers richest in HEMA units exhibited higher swelling capacities when the pH was increased up to 7. The absorption studies showed that not only the copolymer composition but also the pH and ionic strength of the solution played an important role in the absorption capacity of poly(HEMA-*co*-MG). The influence of water absorption at room temperature was strong at pH 5 and pH 7, with maximum absorptions between 1200 and 1600%, when the poly(HEMA-*co*-MG) was richest in HEMA monomer units.

The thermal stability decreased with increasing content of HEMA in the copolymer.

Higher contents of HEMA reduced the TDTs. The TDTs of poly(HEMA-*co*-MG) were influenced by the composition of the copolymer. A higher incorporation of MG increased the TDT values.

References

1. Sakiyama, T.; Chu, C. H.; Fujii, T.; Yano, T. *J Appl Polym Sci* 1993, 50, 2021.
2. Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. *J Appl Polym Sci* 1993, 47, 113.
3. Díaz-Peña, E.; Quijada-Garrido, I.; Barrales-Rienda, J. M. *Polym Bull* 2002, 48, 83.
4. Hogari, K.; Ashiya, F. *Advances in Superabsorbent Polymers*; American Chemical Society: Washington, DC, 1994.
5. Yoshinobu, M.; Morita, M.; Sakita, I. *J Appl Polym Sci* 1992, 45, 805.
6. Boyer, R. F. *J Chem Phys* 1945, 13, 363.
7. Sakurada, I.; Nakajima, A.; Aoki, H. *J Polym Sci* 1959, 35, 507.
8. Poh, B. T.; Adachi, K.; Kotaka, T. *Macromolecules* 1987, 20, 2563.
9. Adachi, K.; Nakamoto, T.; Kotaka, T. *Macromolecules* 1989, 22, 3106.
10. Lokhande, H. T.; Varadarjan, P. V.; Iyer, V. *J Appl Polym Sci* 1992, 45, 2031.
11. Issa, R.; Akehah, A.; Rehab, A.; Solaro, R.; Chiellini, E. *J. Controlled Release* 1990, 13(1), 1.
12. Lowe, T. L.; Virtanen, J.; Tenhu, H. *Polymer*. 1999, 40, 2595.
13. Flory, P. S. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
14. del C. Pizarro, G.; Marambio, O. G.; Jeria-O, M.; Geckeler, K. E. *Macromol Chem Phys* 2003, 204, 922.
15. Tüdös, F.; Kelen, T.; Turcsanyi, B. *J Polym Sci Polym Chem Ed* 1981, 19, 1119.
16. Peppas, N. A.; Khare, A. R. *Adv Drug Delivery Rev* 1993, 11, 21.
17. del C. Pizarro, G.; Marambio, O. G.; Rivas, B. L.; Geckeler, K. E. *Polym Bull* 1997, 39, 165.
18. Rivas, B. L.; del C. Pizarro, G.; Tagle, L. H. *Polym Bull* 1994, 33, 97.
19. Uhl, F. M.; Levchik, G. F.; Levchik, S. V.; Dick, C.; Ligat, J. J.; Snape, C. E.; Wilkie, C. A. *Polym Degrad Stab* 2001, 71, 317.
20. Díaz, V. N.; Tagle, L. H.; Gargallo, L.; Radic, D. *Eur Polym J* 2001, 37, 1753.