

Synthesis and Swelling Characteristics of Acid-Containing Poly(Vinyl Alcohol) Hydrogels

J. RUIZ, A. MANTECÓN, V. CÁDIZ

Universitat Rovira i Virgili, Departament de Química Analítica i Química Orgànica, Facultat de Química, Plaça Imperial Tàrraco 1, 43005 Tarragona, Spain

Received 19 July 2000; accepted 17 October 2000

ABSTRACT: Poly(vinyl alcohol) (PVA) was modified with phthalic and succinic anhydrides to produce vinyl alcohol-vinyl ester copolymers that contain free carboxylic acid or carboxylate groups. These half-esters were then crosslinked using the diglycidylether of 1,4-butanediol. Low crosslinker/carboxylic acid ratios were used to obtain low degrees of crosslinking, so that the capacity to absorb water of the resulting hydrogel was high. Water absorption was determined gravimetrically as a function of time at room temperature. The swelling behavior was significantly different in both ionic and nonionic polymers. The water uptake of the former was high enough for products to be considered superabsorbents. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1444–1450, 2001

Key words: poly(vinyl alcohol); hydrogel; superabsorbent

INTRODUCTION

In recent years, interest in developing new biodegradable materials for different applications has increased considerably. For example, several natural polymers have been modified and used as hydrogels^{1–3} and membranes,⁴ and to control the release of biologically active compounds.⁵ Poly(vinyl alcohol) (PVA) is a synthetic and biocompatible polymer that can be used in a similar way, as it undergoes chemical reactions of typical polyhydric alcohols. It can be crosslinked by difunctional agents that condense with hydroxyl groups.⁶ In addition, these groups can undergo various chem-

ical reactions, so that new specific or more reactive functional groups can be introduced. Thus, the scope of the crosslinking reaction is extended to other difunctional crosslinkers that do not directly react with hydroxyl groups.

The chemistry of PVA is largely concerned with ester formation by reaction with acid chlorides or acid anhydrides. When the anhydride is a cyclic carboxylic group, it is incorporated into the resulting polymer. PVA that contain a different number of carboxylic groups are of great interest in several industrial fields.⁷ These carboxylic groups also enable tridimensional networks to be obtained in a further step. The aim of this study is to obtain hydrogels from PVA with pendant monosuccinate or monophthalate groups. In a previous study,⁸ we reported the synthesis of these half-esters which in a second step reacted with diglycidyl aromatic compounds to provide highly crosslinked materials. The present study focuses on obtaining networks with hydrogel properties; thus, a lower crosslinking and an ali-

Correspondence to: A. Mantecon (E-mail: mantecon@quimica.urv.es).

Contract grant sponsor: Comisión de Investigación Científica y Tecnológica (CICYT); Contract grant number: MAT 99-1113; Contract grant sponsor: Comissió Interdepartamental de Recerca i Innovació Tecnològica (CIRIT); Contract grant number: 1998 SGR 00097.

Journal of Applied Polymer Science, Vol. 81, 1444–1450 (2001)
© 2001 John Wiley & Sons, Inc.

phthalic crosslinker have been used to attain a greater degree of swelling.

EXPERIMENTAL

Materials

PVA (Fluka) had a degree of hydrolysis of 86–89% and an average degree of polymerization of 300. Phthalic anhydride (Fluka) and succinic anhydride (Fluka) were purified by recrystallization. 1,4-Butanedioldiglycidylether (Aldrich), pyridine (Pan-reac), 4-dimethylaminopyridine (DMAP) (Fluka), benzyltrimethylammonium chloride (BTMA) (Aldrich), tetrahydrofuran (THF), sodium dodecyl sulfate (SDS), and dimethylsulfoxide (DMSO) (SDS) were used as received.

Esterification Reaction

PVA (0.05M of hydroxyl group) was dissolved by stirring in dimethylsulfoxide (DMSO) (50 mL) at room temperature. Different ratios of carboxylic anhydride (OH/acyl group 1/0.5, 1/0.35, and 1/0.2) and pyridine (pyr/acyl group 1.2/1) were added at room temperature and stirred for 3 days. The polymer was obtained by precipitation into aqueous HCl (0.1M). These products were purified as follows: dissolving in 0.1M NaOH and precipitation with 0.1M HCl (3 times). When the final products were ionic derivatives, the last precipitation took place in dioxane. The least modified vinylalcohol-vinylsuccinate copolymer was precipitated in diethylether. All polymers were dried under vacuum at room temperature to constant weight.

Crosslinking With 1,4-Butanediol Diglycidylether

The acidic polymer (5 mmol of acid group) was dissolved in the minimum amount of DMSO (15 mL), and BTMA (20 mol %) was added at room temperature. The diglycidylether compound was slowly added in a COOH/glycidyl group ratio of 10:1 or 5:1. The reaction mixture was then stirred for as long as possible (3–10 days). The crosslinked polymers were repeatedly washed with water. The filtered products were dried with phosphorus pentoxide under vacuum at room temperature until their weight stopped changing. The crosslinking of ionic polymers was carried out in a similar way at 60°C for 1 day using water as solvent.

Water Absorption Measurements

The dynamic water absorption of the samples was measured by two gravimetric procedures. First, a polymer sample of 100 mg was placed in a desiccator over P₂O₅ to establish constant weight. The sample was accurately weighed and then placed in a closed chamber containing a saturated aqueous solution of potassium nitrate which provided a relative humidity of 93% (16 mmHg water vapor pressure in the atmosphere). The experiments were carried out at room temperature (25°C). The samples were weighed at different time intervals until the hydrated weight was constant. Absorbency was calculated as grams of water per gram of dry polymer. Second, a polymer sample that had been weighed accurately was immersed in distilled water at room temperature and left until equilibrium was attained. Once the swelling had terminated, the surface was dried and the weight gain was measured. Equilibrium was reached after an immersion time of about 24 h. The water absorption by immersion was also expressed as the swelling ratio (SR): weight of swollen gel/weight of dry polymer.

Instrumentation

¹H- and ¹³C-NMR spectra were obtained using a Gemini 300 spectrometer with DMSO-d₆ as solvent. IR spectra were recorded on a MIDAC GRAMS/386 FTIR spectrometer. Elemental analyses were carried out using a Carlo Erba 1106 device. Glass transition temperature (*T_g*) data were evaluated on a Mettler DSC-30 thermal analyzer, using modified PVA samples of known weight (~5 mg) in covered aluminum pans under nitrogen atmosphere at a heating rate of 20°C/min.

The equilibrium absorption of water of all the samples was measured at room temperature using an electronic microbalance (Mettler AB204) with an accuracy of ±10⁻⁴ g. Reported values of equilibrium water uptakes are averaged over 9 measurements and, for each type of sample, water absorption was replicated three times.

RESULTS AND DISCUSSION

Esterification Reaction

PVA was dissolved in dimethylsulfoxide (DMSO) in the presence of pyridine and esterified with phthalic and succinic carboxylic acid anhydrides in a homo-

Table I Characterization of Vinyl Alcohol-Vinyl Ester Copolymers With Acid and Carboxylate Groups

	PVA-PA33	PVA-PA22	PVA-PA14	PVA-SA38	PVA-SA27	PVA-SA15
Ratio OH/acyl group	1/0.5	1/0.35	1/0.2	1/0.5	1/0.35	1/0.2
d.m. (%) NMR ^a	33	22	14	35–40	25–30	12–17
d.m. (%) EA ^b	32	20	11	38	27	15
d.m. (%) NMR ^c	32	22	12	39	29	16
Yield (%) ^d	86/82	71/70	60/63	65/62	62/59	60/60

^a d.m. (%) NMR: degree of modification (with regard to 100 copolymer units) calculated from NMR, vinyl alcohol-vinyl ester copolymers with acid groups.

^b d.m. (%) EA: degree of modification (with regard to 100 copolymer units) calculated from EA, vinyl alcohol-vinyl ester copolymers with acid groups.

^c d.m. (%) NMR: degree of modification (with regard to 100 copolymer units) calculated from NMR, vinyl alcohol-vinyl ester copolymers with carboxylate groups.

^d Yield (%): vinyl alcohol-vinyl ester copolymers with acid and carboxylate groups, respectively.

geneous medium, using different amounts of anhydride, as has been previously described.⁸ Using the ratios specified in the experimental part, phthalic derivative polymers with a modification degree of 33 phthalic units (PVA-PA33), 22 phthalic units (PVA-PA22) and 14 phthalic units (PVA-PA14) per 100 total units were obtained. Likewise, succinic derivative polymers with a degree of modification of 38 succinic units (PVA-SA38), 27 succinic units (PVA-SA27) and 15 succinic units (PVA-SA15) per 100 total units were obtained. The degrees of modification did not coincide with the ratio of the reagents in the feed. The polymers were precipitated in water acidified with HCl to obtain free carboxylic acid derivatives, whereas a NaOH solution was used to obtain ionic derivatives (marked with a negative superscript). Yields were calculated by taking into account the degree of modification reached. The results showed that yields increased with the degree of modification, probably because it makes them more insoluble in the precipitation mixture making more efficient the isolation of the product. These values are summarized in Table I. The degree of substitution was calculated by elemental analysis and ¹H-NMR spectra and both results were very close.

IR spectroscopy showed the expected carbonyl bands of ester and acid that overlap at 1760 cm⁻¹ and COOH stretching that appears at 3200–2400 cm⁻¹ in nonionic polymers. In ionic polymers COO⁻ stretching is observed at 1584 and 1430 cm⁻¹. All the spectra showed the vibration of OH at 3340 cm⁻¹ because of the partial esterification.

Nuclear magnetic resonance (NMR) spectroscopy confirmed the structure of all polymers. Copolymers of vinyl alcohol-vinyl succinate and vinyl alcohol-vinyl phthalate showed the same sig-

nals as previously reported,⁸ but with different intensity, depending on the esterification degree. For the ionic analogous polymers ¹H and ¹³C-NMR spectra showed the expected signals. As an example, Figure 1 shows the ¹H-NMR spectrum of PVA-SA27⁻ recorded in D₂O. Signals caused by the methine protons linked to ester are centered at 5.0 ppm and partially overlap with the solvent signal. The signal from the methine protons linked to hydroxylic group appear between 4.0–3.5 ppm. The methylene protons of the succinate moiety appear between 2.7–2.4 ppm and the acetate methyl and the methylenes of the main-chain appear between 2.2–1.4 ppm. The degrees of modification were determined by comparing the integrals of the succinate methylenes or aromatic protons to the integrals of the methylenes of the main-chain plus acetate methyl (unvariable signal for all polymers).

The hydroxyl groups are highly interconnected by hydrogen bonding, which contributes to a high *T_g* (41°C in the initial PVA). The introduction of other functional groups breaks this bonding and the resulting *T_g* value is affected by both the

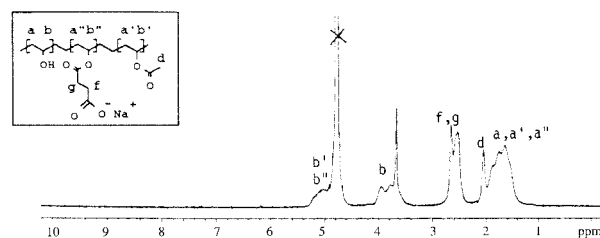
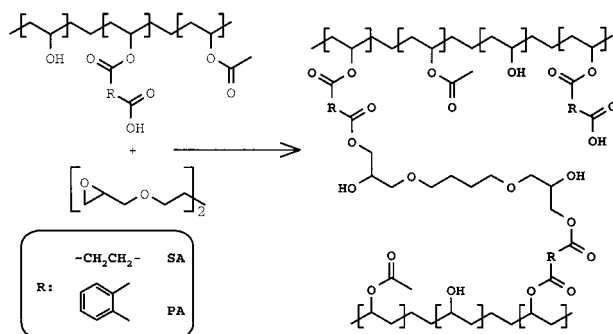


Figure 1 ¹H-NMR spectrum of vinyl alcohol-vinyl succinate copolymer with carboxylate groups (PVA-SA27⁻) recorded in D₂O.



degree of modification and the character of the substituent. So, the T_g values of vinylalcohol-vinylphthalate copolymers with free carboxylic groups were higher than the T_g value of starting PVA (43–56°C) and they increased as more phthalate groups were introduced according to the rigidity introduced. The T_g values of the vinylalcohol-vinylsuccinate copolymers were close to one another, but lower than PVA (31–34°C), due to the flexible chains introduced. The same trend was followed by the analogous ionic derivatives, but their T_g values were higher for phthalate derivatives (55–65°C) and succinate derivatives (42–45°C) than those of the corresponding acidic derivatives.

Crosslinking Reaction

In order to obtain crosslinked polymers, 1,4-butanedioldiglycidylether was reacted with all copolymers. Diglycidyl compounds react with the free acid or carboxylate groups in the modified PVA to give a network with different polar groups (Scheme I).

The reaction of epoxy compounds with simple alcohols in presence of quaternary ammonium salts can lead to the expected ethers,⁹ but not always with satisfactory results, and few examples of analogous polymer reactions are found in literature. However, a partial modification of PVA with epoxy compounds is recently reported,¹⁰ but in drastic conditions (at 200 °C) and reaching only low degrees of modification (10%). Therefore, under our reaction conditions, the remaining hydroxyl groups of PVA do not have to be competitive with carboxylic groups.

Reactions were carried out in DMSO at room temperature (in the case of polymers with free acid groups) or in water at 60°C (for polymers with carboxylate groups), using BTMA as the cat-

alyst. The COOH/glycidyl group ratio was 10:1 for copolymers with a greater modification degree and 5:1 for copolymers PVA–PA14 and PVA–SA15. The reaction mixture was stirred until a gel was formed. Products were insoluble in all the solvents tested which confirmed that crosslinking had occurred.

Gels in D₂O were obtained from all copolymers and were suitable for recording ¹³C-NMR spectra. In spite of the poor resolution of these spectra, the most significant signals were recognized. As an example the crosslinked vinylalcohol-vinylsuccinate copolymer with carboxylate groups (PVA–SA27⁻) is shown in Figure 2. Carbonylic carbons at 179 and 174 ppm are assignable to the carboxylate and ester, respectively. At 72–60 ppm, main-chain methine, crosslinker methine, and methylene signals overlap. Main-chain methylene carbons are present at 46–37 ppm and the succinate and glycidylic methylene signals appear at 30 and 25 ppm, respectively. At ~20 ppm, the methyl carbon of the acetate moiety can also be observed.

Swelling is the most significant property of hydrogels and is a practical consequence of the affinity of its chemical structure to water. The water absorption of the polymer sample was determined gravimetrically as a function of time using two different methods: by immersing the sample in deionized water or by exposing the sample to a relative humidity of 93%.¹¹ The ability of crosslinked PVA derivatives and linear polymer precursors to absorb water was evaluated and compared to that of the starting PVA. This comparison was only possible when the water absorption measurements were calculated at a relative humidity of 93% because PVA is partially soluble by immersion at 24 h.

Figures 3 and 4 show the results obtained by the relative humidity method for the free acid and

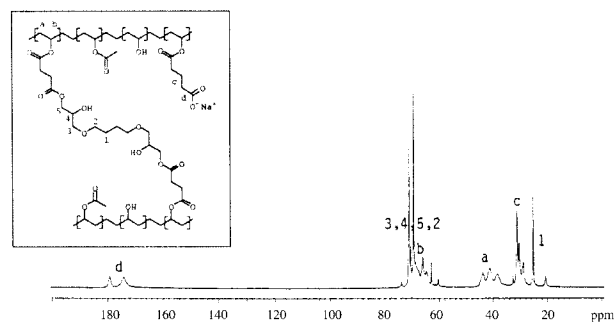


Figure 2 ¹³C-NMR spectrum of crosslinked vinyl alcohol-vinyl succinate copolymer with carboxylate groups (PVA–SA27⁻ + Digl.)

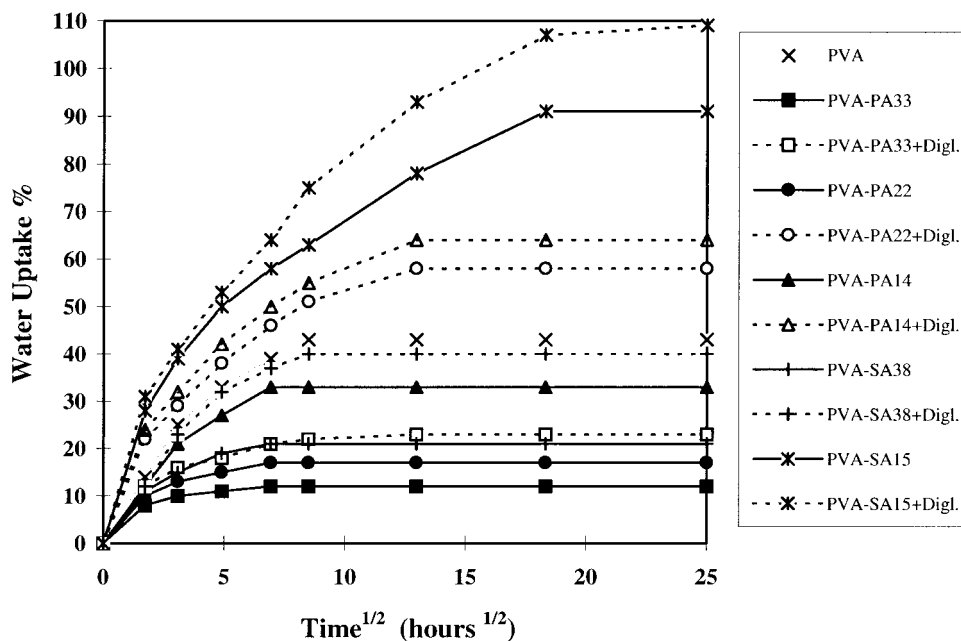


Figure 3 Water uptake as a function of time for vinyl alcohol–vinyl ester copolymers with acid groups.

ionic derivatives, respectively. As can be seen, succinates in general have a higher water uptake than that of phthalates and the absorption capacity of the crosslinked polymers is approximately double that of their linear precursors. PVA-SA15 had a higher absorption because it was not completely acidified. Figure 4 does not plot the ab-

sorption curves of the linear polymers because they are soluble (the sample lost its shape and its gravimetric measurement was inaccurate).

Table II shows data about the water absorption of acidic derivatives using both methods. After immersion in water, the samples readily reached the equilibrium hydration degree, but no signifi-

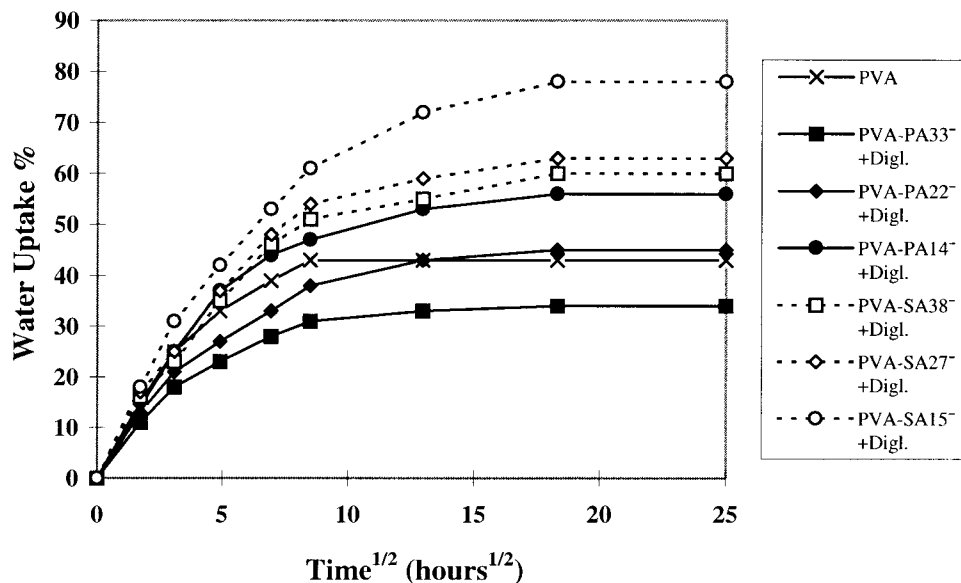


Figure 4 Water uptake as a function of time for vinyl alcohol–vinyl ester copolymers with carboxylate groups.

Table II Water Absorption of Acidic Derivatives in Equilibrium

	Relative Humidity 93% (Water Uptake %)	Immersion (Water Uptake %)
PVA-PA33 + Digl.	23	30
PVA-PA22 + Digl.	58	63
PVA-PA14 + Digl.	64	75
PVA-SA38 + Digl.	40	44
PVA-SA15 + Digl.	109	230

cant differences were observed in their water uptake. An exception was the PVA-SA15, which shows a higher capacity of absorption when immersed. This is because of the partially ionic character of the sample. The swelling of polymer networks that behave as hydrogels, but contain ionizable groups, is complex. It depends on the degree of ionization of the groups. This is particularly the case in carboxylic groups.¹² When such polymers are introduced into a high dielectric constant medium, the ionic units are dissociated and cause a charge density to go along the chains and a high concentration of ions into the gel. This ionic character produces new forces that influence the swelling process since the different ionic concentration into the gel and the external solution produces an osmotic pressure that can only be reduced by diluting the charge density of the network, i.e., by swelling. In addition, this charge density produces electrostatic repulsions between segmental chains and this causes the network to expand and therefore to swell.

Table III presents data concerning the water absorption of ionic derivatives using both methods. It can be seen that there is a considerable difference between the water absorption between the two methods. This is because only immersion produces an effect sufficient to reduce the osmotic pressure and increase the hydrodynamic volume;

Table III Water Absorption of Carboxylate Derivatives in Equilibrium

	Immersion (SR)	Immersion (Water Uptake %)
PVA-PA33 ⁻ + Digl.	85	8400
PVA-PA22 ⁻ + Digl.	42	4100
PVA-PA14 ⁻ + Digl.	14	1300
PVA-SA38 ⁻ + Digl.	78	7700
PVA-SA27 ⁻ + Digl.	38	4700
PVA-SA15 ⁻ + Digl.	17	1600

these factors, according to literature, explain the great absorption capacity polyelectrolytes.¹³ However, when absorptions were measured in a relative humidity of 93% the values obtained were similar for both nonionic and ionic polymers, which indicates that the above-mentioned effect does not act in these conditions.

Modification of PVA with different amounts of carboxylic or carboxylate moieties and further crosslinking allow to obtain a set of hydrogels with a wide range of water absorptions that can be compared with those of other reported alternative hydrogel materials. Hydrogels with carboxylic moieties, with a moderate absorption, can be compared with other hydrogels synthesized by our group¹⁴ and to a hydrogel based on poly(vinyl pyrrolidone) crosslinked with methyl methacrylate macromonomers.¹⁵ Hydrogels with a low content of carboxylate moieties (PVA-PA14⁻ + Digl and PVA-SA15⁻ + Digl) are comparable to reported interpenetrating polymer network composed of poly(vinyl alcohol) and poly(acrylic acid),¹⁶ to a semi-interpenetrating composed of crosslinked chitosan with glutaraldehyde and polyether¹⁷ or to a copolymer of *N*-isopropylacrylamide and *N,N'*-dimethylaminopropylmethacrylamide.¹⁸ Hydrogels with a medium content of carboxylate moieties (PVA-PA22⁻ + Digl and PVA-SA27⁻ + Digl) are comparable to reported methacrylic based hydrogel with polyethylene glycol¹⁹ or to a polyethylene oxide based superabsorbents.²⁰ Hydrogels with a high content of carboxylate moieties (PVA-PA33⁻ + Digl and PVA-SA38⁻ + Digl) are comparable to a reported protein-based polymer crosslinked with glutaraldehyde²¹ or to an acrylic acid and acrylamide-based superabsorbent polymers.²²

In summary, the results presented show that the water absorption is dependent on either crosslinking ratio or ionic content and similar absorptions can be reached from polymers with very different structures. Thus, as mentioned

above, a moderate absorption, by example, can be achieved with nonionic polymers with a low crosslinking or with an ionic polymer with a higher crosslinking degree.

REFERENCES

1. van Dijk-Wolthuis, W. N. E.; Hoogeboom, J. A. M.; van Steenberg, M. J.; Tsang, S. K. Y.; Hannink, W. E. *Macromolecules* 1997, 30, 4639.
2. de Oliveira, W.; Glasser, W. G. *J Appl Polym Sci* 1996, 61, 81.
3. Zhou, W.-J.; Wilson, M. E.; Kurth, M. J.; Hsieh, Y.-L.; Krochta, J. M.; Shoemaker, C. F. *Macromolecules* 1997, 30, 7063.
4. Chen, R. H.; Hua, H.-D. *J Appl Polym Sci* 1996, 61, 749.
5. Arranz, F.; Sanchez-Chaves, M. *Reactive Funct Polym* 1995, 28, 69.
6. Peppas, N. A. *Hydrogels in Medicine and Pharmacie*; Peppas, N. A., Ed.; CRC Press: Boca Raton, FL, 1988.
7. Maruhashi, M. *Polyvinylalcohol Developments*; Finch, C. A., Ed.; John Wiley & Sons: New York, 1992; Chapter 6.
8. Giménez, V.; Mantecón, A.; Ronda, J. C.; Cádiz, V. *J Appl Polym Sci* 1997, 65, 1643.
9. Shechter, I.; Wynstra, J. *Ind Eng Chem* 1956, 48, 86.
10. Haralabalopoulos, A. A.; Tsiourvas, D.; Paleos, C. M. *J Appl Polym Sci* 1996, 62, 1597.
11. Tirrell, D.; Grossman, S.; Vogl, O. *Macromol Chem* 1979, 180, 721.
12. Kálal, J. *Chemistry and Technology of Water-Soluble Polymers*; Finch, C. A., Ed.; Plenum Press: New York, 1983.
13. Lin, Z. S.; Rempel, G. L. *J Appl Polym Sci* 1997, 64, 1345.
14. Giménez, V.; Mantecón, A.; Cádiz, V. *Acta Polym* 1998, 49, 502.
15. Michálek, J.; Vacík, J.; Küdelková, J.; Jezová, N. *Angew Makromol Chem* 1996, 239, 151.
16. Lee, Y. M.; Kim, S. H.; Cho, C. S. *J Appl Polym Sci* 1996, 62, 301.
17. Yao, K. D.; Peng, T.; Goosen, M. F. A.; Min, J. M.; He, Y. Y. *J Appl Polym Sci* 1993, 48, 343.
18. Park, T. G.; Hoffman, A. S. *J Appl. Polym Sci* 1992, 46, 659.
19. Podual, K.; Doyle, F. J. III; N. A. Peppas, *Polymer* 2000, 41, 3975.
20. Smith, P. B.; Cutié, S. S.; Henton, D. E.; Powell, C.; Kosman, J.; Howell, B. A. *J Polym Sci* 1996, 62, 1285.
21. Hwang, D.-C.; Damodaran, S. *J Appl Polym Sci* 1996, 62, 1285.
22. Liu, Z. S.; Rempel, G. L. *J Appl Polym. Sci* 1997, 64, 1345.