Physicochemical Characterization of Hydrogels Based on Polyvinyl Alcohol–Vinyl Acetate Blends

J. V. CAUICH–RODRíGUEZ,[1] S. DEB,[2] R. SMITH[3]

[1] Centro de Investigación Científica de Yucatán A.C., Apdo. Postal 87, Cordemex 97310, Mérida, Yucatán, Mexico

[2] Department of Dental Biomaterials, Guys Kings and St Thomas Dental Institute, 17th Floor Guy's Hospital, London Bridge, London SE1 9RT, United Kingdom

[3] IRC in Biomedical Materials, Queen Mary and Westfield College, Mile End Road, London E1 4NS, United Kingdom

ABSTRACT: Hydrogels made of polyvinyl alcohol–vinyl acetate and its blends with water soluble polymer were studied in terms of swelling behavior, microstructure, and dynamic mechanical properties. Hydrogels prepared by blending polyvinyl alcohol–vinyl acetate with either polyacrylic acid or poly(4-vinyl pyridine) exhibited a strong pH dependency. When poly(vinyl pyrrolidone) was used for blending, an unusual pH dependency was observed. An increase in the equilibrium water content in all systems resulted in an increase in the freezable water as determined by DSC. Critical point drying led to a striated surface on polyacrylic acid–polyvinyl alcohol–vinyl acetate hydrogels, whereas a porous structure was observed on the freeze-dried poly(vinyl pyrrolidone)–polyvinyl alcohol–vinyl acetate gels. Hydrogels with elevated storage modulus were obtained when either polyvinyl alcohol–vinyl acetate alone or polyacrylic acid–polyvinyl alcohol–vinyl acetate blends were thermally treated at high temperatures (i.e., 150°C). Low storage modulus was observed for both poly(vinyl pyrrolidone) and poly(4-vinyl pyridine)-containing hydrogels. Temperature dependency of storage modulus from 20 to 60°C was observed only for poly(4-vinyl pyridine)–polyvinyl alcohol–vinyl acetate hydrogels. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 3578–3590, 2001

Key words: polyvinyl alcohol–vinyl acetate; polyacrylic acid; poly(vinyl pyrrolidone); poly(4-vinyl pyridine); hydrogels

INTRODUCTION

Hydrogels are hydrophilic, three-dimensional networks that possess the ability to swell in aqueous media without dissolution. These polymeric networks are increasingly being used in a variety of biomedical applications because of their similarity to living tissue. Like living tissue, they have a soft rubbery nature and allow the permeation of low molecular weight species. Hydrogels usually exhibit different degrees of swelling, depending on their composition and molecular structure. In addition, there is a growing interest in the group of hydrogels that are responsive to changes in their environment such as pH, temperature, or ionic strength. Hydrogels showing a significant variation in swelling as a result of external changes such as pH and temperature

---

have been investigated for a wide range of applications including, for example, controlled release, pH-specific membrane separations, purification of pharmaceutical products, solute separation, and solvent recovery. A glucose-sensitive insulin-release device, an osmotic insulin pump, and a site-specific drug release in the gastrointestinal tract are some important uses of environmentally sensitive hydrogels.[1] pH-sensitive hydrogels are commonly prepared by addition of anionic monomers such as acrylic or methacrylic acid,[2] cationic monomers such as vinyl pyridine or aminoethyl methacrylates,[3] and ampholytic monomers such as acrylamide and sodium styrene sulfonate.[4] Temperature-sensitive hydrogels are obtained from crosslinked polymers of isopropyl acrylamide, which exhibit lower critical solution temperature (LCST).[5,6] Hydrogels sensitive to both pH and temperature have been prepared by copolymerization of N-isopropyl acrylamide and methacrylic acid,[7] by preparing an interpenetrating network (IPN) of N-isopropyl acrylamide and acrylic acid[8] or by graft copolymerization of acrylic acid onto amino-terminated poly(N-isopropyl acrylamide).[9]

In this study, we set out to prepare pH-sensitive hydrogels by blending polyvinyl alcohol–vinyl acetate (PVAA) with ionic or nonionic water-soluble polymers such as polyacrylic acid (PAA), poly(4-vinyl pyridine) (PVPy), and poly(vinyl pyrrolidone) (PVP). The polymers used for blending were also selected, not only because they are pH responsive but also because they are expected to behave mechanically in a different manner. PVAA shows ductile behavior when dry, whereas PAA, PVP, and PVPy are expected to exhibit a brittle type of fractures. The interest in PVAA is primarily centered on its mechanical properties derived from its degree of crystallinity, although some other interesting features draw the attention of investigators. First, PVAA has been suggested as a biomaterial because of its controllable water content, low friction coefficient, high permeability, and tensile strength.[10] Second, PVAA offers the possibility of being crosslinked with a variety of methods including chemical reaction, freezing/thawing, and electron beam radiation.[11–13] In spite of these advantages, PVAA has been blended with a number of additives to improve equilibrium water content (EWC) and mechanical performance.[14–16] However, in these studies little is mentioned concerning PVAA's dynamic mechanical behavior and its temperature dependency. Dynamic mechanical properties in tension were pursued in the course of this study, not only because any reinforcing effect can be easily detected but also because truly uniaxial tension is found in biological systems.

EXPERIMENTAL

Materials

PVAA (M_n = 125,000 and 87–89% hydrolyzed), PVP (M_n = 44,000), glutaraldehyde (50% aqueous solution), and lactic acid were obtained from BDH Chemicals (Toronto, Canada) and used without further purification. PAA (M_n = 1,250,000) was obtained from Aldrich Chemicals (Milwaukee, WI). PVPy (M_n = 50,000) was obtained from Polysciences (Warrington, PA). Buffers of pH 2 (citrate), pH 4 (phthalate), and pH 7 (phosphate) were purchased from BDH Chemicals. The pH 9 buffer (borate) was supplied by Merck (West Point, PA).

Blends and Hydrogel Preparation

PVAA aqueous solutions (1% w/w) were mixed with either PAA, PVP, or PVPy dissolved in water at the same concentration as PVAA and then crosslinked with glutaraldehyde (5% w/w) using lactic acid as catalyst. Poly(4-vinyl pyridine) does not dissolve in distilled water and hence was dissolved under acidic conditions with lactic acid. The chemical crosslinking reaction was carried out at 60°C for 1 h. Films were cast on polystyrene petri dishes and peeled after drying. The degree of crosslinking was further increased by thermal treatment of the blends at 120 and 150°C, as previously reported.[17] Hydrogels were obtained after immersing the corresponding film in water. Control hydrogels were prepared in the same manner using polyvinyl alcohol–vinyl acetate.

Swelling Kinetics Studies

Discs (diameter, 20 mm; thickness, 0.1 mm) were used for studying the swelling kinetics in different media. All samples were preswollen in distilled water to ensure minimal interference from any extractables on their swelling kinetics. Buffer solutions of pH 2, 4, 7, and 9 were used to evaluate the relationship between their equilibrium water content (EWC) and the pH of the swelling medium at a constant temperature of 37°C. Distilled water was used as control. The EWC was calculated using the following expression:

$$\frac{W_g - W_d}{W_g} \times 100 \qquad (1)$$

where W_g is the mass of the swollen gel and W_d is the mass of the dried gel. The reported values of EWC are an average of at least three repetitions.

Water-Binding Studies

The state of water in hydrogels swollen at different pH values was studied using a Perkin–Elmer DSC-7 differential scanning calorimeter (DSC; Perkin Elmer Cetus Instruments, Norwalk, CT). Temperature scans from 20 to $-50°C$ (cooling cycle) and from -50 to $20°C$ (heating cycle) were carried out at a heating rate of $2.5°C/min$ on a 10-mg sample. From the total area of the peak obtained during the heating cycle (ΔH_{fg}), the amount of freezable water was quantified . The nonfreezable water was the difference between the EWC and the freezable water, as described in eq. (3):

$$W_{tf} = \frac{\Delta H_{fg}}{\Delta H_{fw}} \qquad (2)$$

$$W_{nf} = \text{EWC} - W_{tf} \qquad (3)$$

where W_{tf} is the freezable water and W_{nf} is the nonfreezable water. Calibration of the DSC for subambient temperature was performed using cyclopentane and water. The heat of fusion of water (ΔH_{fw}) was taken as 328.45 J/g, which is close to the reported values of 331 J/g.[18]

Scanning Electron Microscopy of Blends and Hydrogels

Three different techniques were used to assess the structure of PAA–PVAA, PVP–PVAA, and PVPy–PVAA blends and their corresponding hydrogels. Blends obtained after casting (nonthermally treated) were gold coated and observed under an accelerating voltage of 10 keV in a Hitachi S450 microscope (Hitachi, Tokyo, Japan). Their corresponding hydrogels, swollen in distilled water for 24 h, were dehydrated by critical point drying (CPD). Mixtures of water and ethanol followed by mixtures of ethanol/amyl acetate and CO_2 were used for the dehydration procedure. Uncoated samples were placed on aluminum stubs with a carbon adhesive and observed in a JEOL-6300F (JEOL, Peabody, MA) with an accelerating voltage of 1 keV.

Hydrogels were also observed after removing the water by freeze-drying. In these experiments, strips of 20×3 mm were placed on carbon adhesive (xylene-based) and then placed in an oven for 20 min at $60°C$ to harden the adhesive. After attaining room temperature, a drop of water was placed in the center of the strip by means of a syringe. After the water was absorbed, the superficial water was removed with filter paper. The hydrogel was then frozen to $-117°C$ by immersion in liquid nitrogen and placed on a Phillips 501B microscope with a cryo-stage (EMSCOPE SP2000). Frost was removed from the surface of the gel by heating the cryo-stage to $-70°C$. The specimen was removed from the microscope and placed on a cryo-work chamber, where it was gold coated. For SEM observations, the cryo-stage was kept at $-117°C$ and the micrographs were taken at an accelerating voltage of 15 keV. After this initial observation, the sample was freeze-dried overnight and observed again in the microscope at $25°C$.

Dynamic Mechanical Properties of Hydrogels

Dynamic mechanical properties of hydrogels were studied by using a Perkin–Elmer DMA-7 in the tension mode. These properties were obtained with a low-volume water bath fitted to the analyzer. Blends of PAA, PVP, and PVPy with PVAA were swollen in distilled water between tension grips and then securely fixed. A 100-mN total force was applied to either PAA- or PVP-containing hydrogels, whereas 70 mN was applied to PVPy hydrogels. A maximum of 2% deformation was achieved after applying the combined dynamic and static loads. The storage modulus of hydrogels was measured after 15 min at $20°C$ at 1 Hz. To determine the temperature dependency of the modulus, the temperature of the bath was increased from 20 to $60°C$ at a heating rate of $3°C/min$. At least five samples were tested for each formulation. To assess changes in the degree of swelling with temperature, hydrogels were swollen in distilled water at 20, 37, and $60°C$.

RESULTS AND DISCUSSION

Swelling Behavior

Anionic hydrogels were obtained by blending PVAA and PAA, as can be inferred from the effect of pH on their swelling in Figure 1. Hydrogels with high water content were obtained by swell-
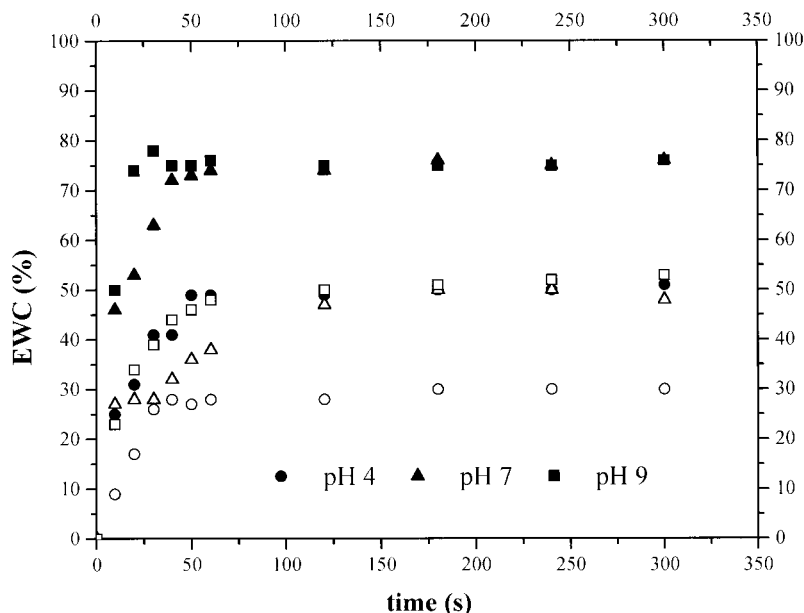
Figure 1 Effect of the pH on equilibrium water content of PAA–PVAA hydrogels. Filled markers correspond to samples thermally treated at 120°C and unfilled markers correspond to samples thermally treated at 150°C. Samples were conditioned at 37°C.

ing under alkaline conditions (pH 9), whereas low water content gels were observed at pH 4. Poly-acrylic acid is in its coiled configuration at this pH, whereas at pH 7, the pendant carboxylate side chains experience repulsion by neighboring anions and expand to minimize charge concentration. At pH 9, the ionization of these groups approached a maximum and the change in swelling was minimal. The presence of poly(4-vinyl pyridine) in blends with polyvinyl alcohol–vinyl acetate rendered cationic hydrogels under acid conditions, as depicted in Figure 2. A high water uptake was found at low pH where protonation of the pyridine ring occurred. The PVP–PVAA hydrogel blends are nonionic in nature and variations in water uptake, as observed in Figure 3, can be explained by considering the different types of buffers used and by the presence of PVAA. Hydrogels prepared just with PVAA and thermally treated at 120°C exhibited EWC values of 52.6 ± 0.8 at pH 9, whereas at pH 4 they exhibited EWC values of 45.1 ± 1.8. Therefore, we conclude that at pH 9 a complex is formed between borate and PVAA, thus leading to the unusually high degree of swelling. The same unusual swelling was observed for PVPy–PVAA hydrogels at pH 9.

The effect of increasing the temperature during thermal treatment of the blends was the reduction in EWC and the increase in crosslinking density, whose magnitude of change was depen-

dent on the composition of blend. PAA-containing hydrogels rendered more highly crosslinked hydrogels by anhydride formation.[19] PVP-containing gels were not altered by thermal treatments, possibly because of the presence of a bulky pyrrolidone ring. Although this behavior may be expected for PVPy-containing hydrogels, attributed to a similar size of the pendant group, increasing thermal treatments reduced their water content. We believe that the underlying cause rests on changes in PVAA only (resulting from a phase separation) during heating and on the more hydrophobic nature of PVPy.

The use of distilled water as the swelling medium led to a reduction in the water uptake of the PAA–PVA hydrogels. This can be explained by the increasing hydrophilicity of the network attributable to the binding of sodium ions. In addition, it has been reported that for PVA hydrogels, the presence of increasing amounts of electrolytes (NaCl) enhances the swelling ability over swelling in pure solvent.[20] However, in PVP–PVAA and PVPy–PVAA hydrogels the presence of buffer salts did not have any apparent effect on their swelling when compared to that of a buffer of pH 7.

Swelling Kinetics

The unusual fast rate of swelling observed in these hydrogels (Figs. 1–3) can be explained by
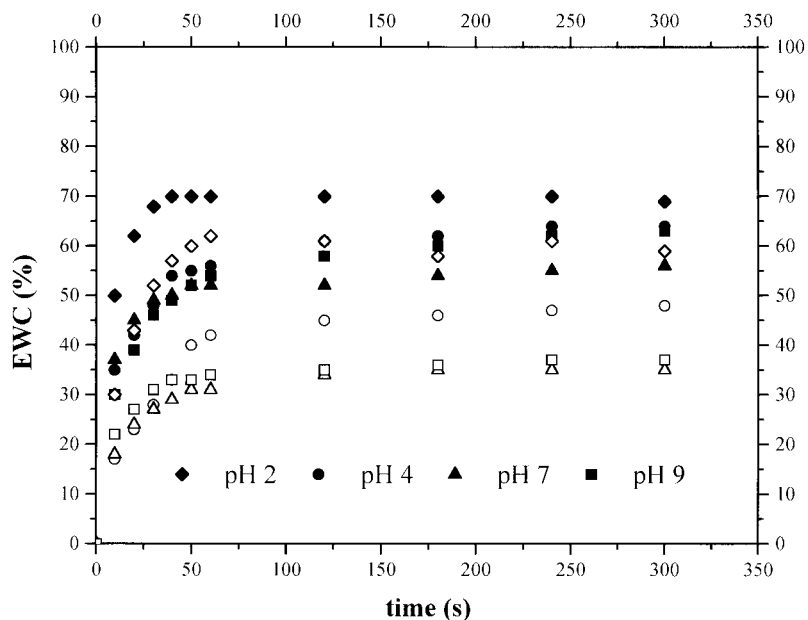
Figure 2 Effect of the pH on equilibrium water content of PVPy–PVAA hydrogels. Filled markers correspond to samples thermally treated at 120°C and unfilled markers correspond to samples thermally treated at 150°C. Samples were conditioned at 37°C.

two factors. On one hand, the thickness of the samples used allows a rapid swelling. On the other hand, the hydrophilicity of the network, given either by the pH of the swelling medium or

by the nature of the polymer, resulted in a rapid swelling. Bearing in mind these factors, an attempt was made to follow their swelling kinetics. For highly swollen hydrogels, like those obtained
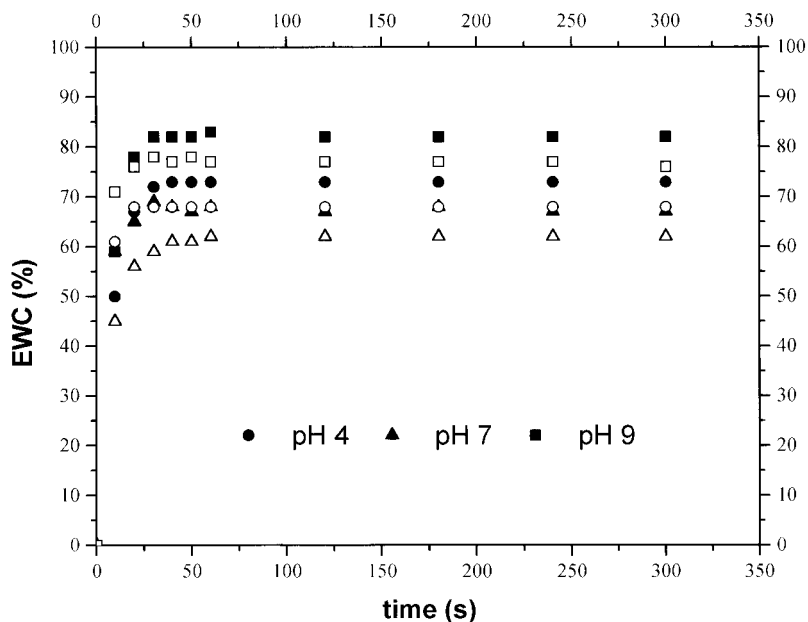

Figure 3 Effect of the pH on equilibrium water content of PVP–PVAA hydrogels. Filled markers correspond to samples thermally treated at 120°C and unfilled markers correspond to samples thermally treated at 150°C. Samples were conditioned at 37°C.
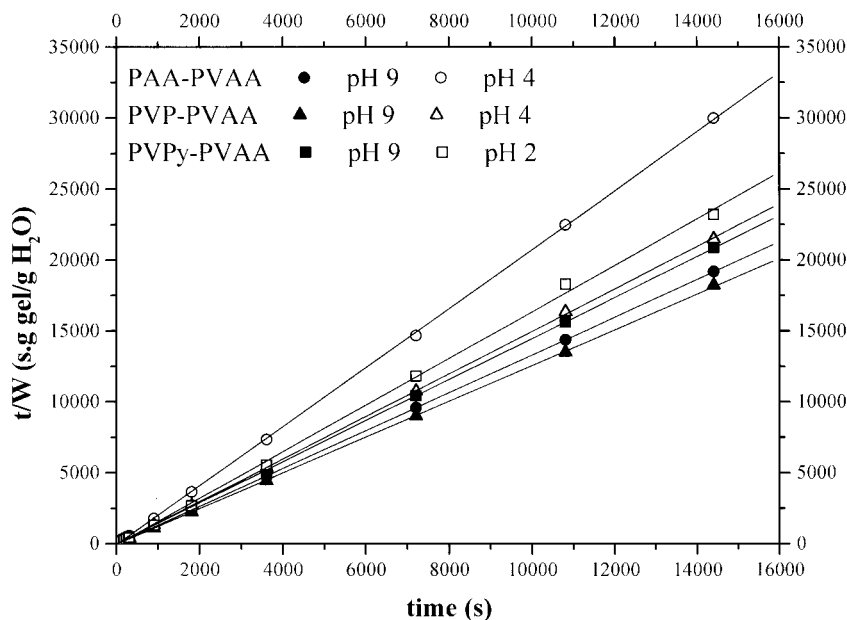
Figure 4 Second-order swelling kinetics in PVAA-based hydrogels. Samples were thermally treated at 120°C.

here, first-order swelling kinetics do not apply and therefore we used eq. (4), suggested by Schott[21] to fit the experimental data:

$$\frac{t}{W} = A + Bt \qquad (4)$$

In this equation, W is the solvent uptake at time t and A and B are constants. All the hydrogels in this study, whether swollen in different media or at different temperatures, showed a linear relationship between the reciprocal of the average rate of swelling and time with good correlation coefficients ($r > 0.99$), as seen in Figure 4. This clearly indicates that second-order kinetics apply to these hydrogels.

Diffusion Behavior

The diffusion behavior of PVAA based hydrogels was obtained from the swelling experiments by the relationship

$$\frac{M_t}{M_\infty} = kt^n \qquad (5)$$

where M_t and M_∞ are weight of water at time t and at an infinite time, respectively; t is the time; n is a constant related to the type of diffusion; and k is a constant associated with a structural pa-

rameter. From Table I, it can be observed that an anomalous behavior occurred in most of the hydrogels as $0 < n < 1$. This type of non-Fickian behavior has been related to a coupling mechanism between the relaxation of the polymer and the diffusion of the solvent. Although a Fickian behavior ($n = 0.5$) was observed in some cases, it is difficult to establish a relationship between pH and degree of crosslinking (i.e., thermal treatment) and it is concluded that these hydrogels are non-Fickian in character.

Water-Binding Behavior

DSC and NMR are the most common techniques used to study water in hydrogels.[22,23] In the present study we used DSC because of practical considerations such as use of small quantities of sample and ease of the technique. We observed that hydrogels prepared by polymer blending exhibited a single peak during crystallization but multiple peaks during melting, as observed in a typical thermogram in Figure 5. The difference between the crystallization and melting temperatures (ΔT_p), however, exhibited little variation in spite of the differences in chemical composition and swelling media. The effect of pH of the swelling medium on the heat of crystallization and fusion of PVAA-based hydrogels is reported in Table II. Hydrogels with high EWC exhibited a corresponding higher heat of fusion. High heats of

Table I   Diffusion Behavior of Hydrogels Based on PVAA

Hydrogels	Solution	Thermal Treatment at 120°C				Thermal Treatment at 150°C			
		EWC (%)	n	No. of Experimental Points	r^a	EWC (%)	n	No. of Experimental Points	r^a
PAA–PVAA	pH 4	48.8 ± 2.6	0.634	6	0.959	29.7 ± 1.7	0.778	6	0.963
	pH 7	73.9 ± 2.3	0.706	6	0.972	46.9 ± 4.9	0.287	5	0.954
	pH 9	74.1 ± 1.3	0.584	4	0.915	52.7 ± 3.1	0.621	7	0.995
	Water	51.7 ± 10.1	0.36	5	0.954	27.1 ± 3.4	0.672	6	0.964
PVP–PVAA	pH 4	69.3 ± 1.4	0.587	4	0.972	65.4 ± 1.0	0.249	4	0.907
	pH 7	68.1 ± 1.6	0.25	4	0.946	60.0 ± 2.7	0.355	4	0.975
	pH 9	81.0 ± 0.9	0.869	4	0.958	74.2 ± 1.0	0.196	4	0.951
	Water	71.3 ± 1.5	0.348	4	0.946	67.5 ± 3.1	0.645	4	0.964
PVPy–PVAA	pH 2	62.8 ± 0.3	0.455	6	0.962	57.6 ± 2.8	0.754	6	0.996
	pH 4	62.9 ± 2.5	0.47	6	0.99	54.4 ± 1.1	0.704	6	0.974
	pH 7	57.5 ± 0.2	0.331	6	0.984	35.8 ± 3.0	0.426	6	0.989
	pH 9	69.9 ± 0.2	0.538	6	0.998	45.4 ± 1.3	0.342	6	0.972
	Water	57.7 ± 2.6	0.459	6	0.977	37.0 ± 2.4	0.486	6	0.976

^{a} r = correlation coefficient.

fusion were also related to a large amount of freezable water and the reduction in the nonfreezable component, as reported in Table III.

In all hydrogels studied, the heat of fusion was higher than the heat of crystallization; however, PVP-containing hydrogels exhibited crystallization upon heating, suggesting that not all the water crystallized, even at the slow cooling rate used (2.5°/min). These findings are surprising, given that PAA–PVAA hydrogels with slightly lower EWC than that of PVP–PVAA did not exhibit this behavior. To minimize crystallization during melting we conducted isothermal crystallization of PVP–PVAA hydrogels at −15°C for up to 8 h. Unfortunately, this experiment did not lead to a reduction in crystallization upon heat-
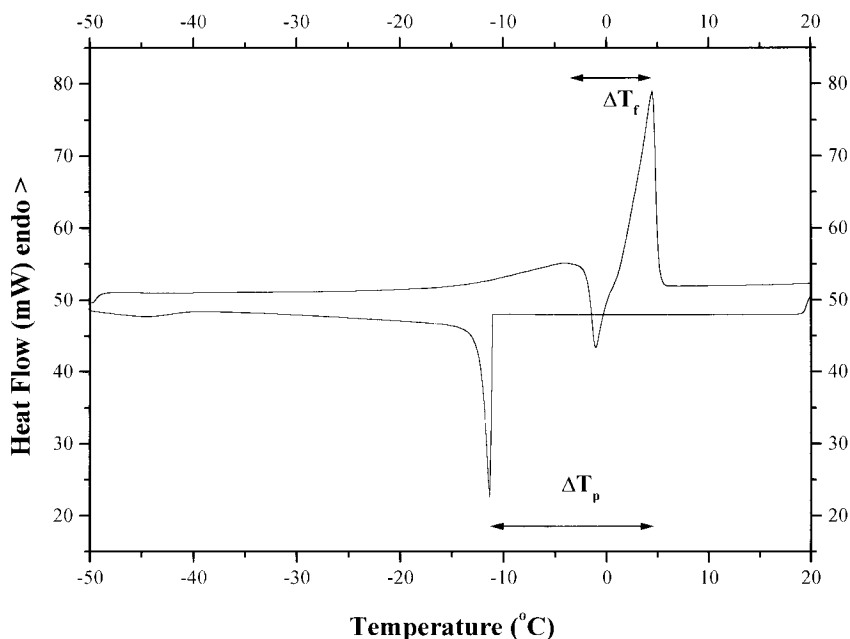

Figure 5   Typical melting and crystallization curves of PVPy–PVAA hydrogels.

Table II Heat of Crystallization and Heat of Fusion of PVAA Hydrogels Swollen in Different Media[a]

Hydrogel	Solution	$\Delta H_c{}^a$ (J/g)	$\Delta H_{fg}{}^b$ (J/g)	$\Delta T_p{}^c$ (°C)	$\Delta T_f{}^d$ (°C)
PAA–PVAA	Buffer pH 4	-75.0 ± 6.1	90.6 ± 7.6	16.4 ± 0.6	—
	Buffer pH 7	-105.8 ± 8.9	128.3 ± 10.6	16.6 ± 0.4	—
	Buffer pH 9	-98.2 ± 7.2	110.4 ± 18.1	15.2 ± 1.1	—
	Distilled Water	-79.6 ± 3.6	92.5 ± 7.0	14.8 ± 1.5	—
PVP–PVAA	Buffer pH 4	-128.8 ± 4.9	144.6 ± 6.2	14.2 ± 1.3	8.0
	Buffer pH 7	-103.2 ± 9.8	116.6 ± 12.3	15.4 ± 1.7	9.0
	Buffer pH 9	-162.0 ± 18.5	184.6 ± 12.9	16.1 ± 1.0	8.3
	Distilled Water	-133.0 ± 1.5	148.2 ± 4.6	15.9 ± 0.5	8.26
PVPy–PVAA	Buffer pH 2	-132.8 ± 2.7	146.2 ± 3.7	15.4 ± 1.2	5.7
	Buffer pH 4	-88.6 ± 8.0	104.2 ± 9.4	15.3 ± 0.3	9.4
	Buffer pH 7	-81.6 ± 9.7	93.7 ± 10.7	17.0 ± 1.2	7.2
	Buffer pH 9	-72.2 ± 23.5	118.7 ± 9.5	15.6 ± 1.1	9.2
	Distilled Water	-107.2 ± 23.3	118.3 ± 24.9	14.6 ± 0.7	5.1

[a] Blends thermally treated at 120°C.
[b] ΔH_c = heat of crystallization.
[c] ΔH_{fg} = heat of fusion.
[d] ΔT_p = temperature difference between crystallization and melting.
[e] ΔT_f = temperature difference between melting peaks.

ing, although an increase in the melting area (ΔH_{fg}) was observed. PVPy-containing hydrogels exhibited an increased number of melting peaks as the pH of buffer was lowered. This observation suggests that as the pyridine ring becomes more protonated, the water is able to organize itself in a greater variety of ways than at pH 9.

Hydrogels containing poly(vinyl pyrrolidone) had the highest water contents, suggesting that this polymer blend was more hydrophilic than either polyacrylic acid or poly(4-vinyl pyridine) at their maximum degree of ionization. Accordingly, it could be expected that PVP–PVAA gels should contain less nonfreezable water, although this was found not to be the case. The phenomenon of nonfreezable water has been attributed to the prevention of nucleation of water by the polymer below its $T_g{}^{24}$ and has been observed on physi-

Table III Effect of Swelling Media on the Amount of Freezable and Nonfreezable Water in PVAA-Based Hydrogels

| Hydrogel	Solution	Thermal Treatment at 120°C		Thermal Treatment at 150°C	
		W_{tf} (%)	W_{nf} (%)	W_{tf} (%)	W_{nf} (%)
PAA–PVAA	Buffer pH 4	27.5	21.5	NA[a]	NA
	Buffer pH 7	39.3	34.3	NA	NA
	Buffer pH 9	33.7	40.3	NA	NA
	Distilled Water	28.1	23.9	NA	NA
PVP–PVAA	Buffer pH 4	44.0	25.0	39.0	27.0
	Buffer pH 7	35.5	32.5	25.8	34.2
	Buffer pH 9	56.2	24.8	46.8	27.2
	Distilled Water	45.1	25.9	34.9	41.3
PVPy–PVAA	Buffer pH 2	44.5	17.5	46.1	9.9
	Buffer pH 4	31.7	31.3	21.4	32.6
	Buffer pH 7	28.5	28.5	5.7	30.3
	Buffer pH 9	36.1	32.9	12.0	33.0
	Distilled Water	36.0	21.0	7.3	33.0

[a] NA, not available.
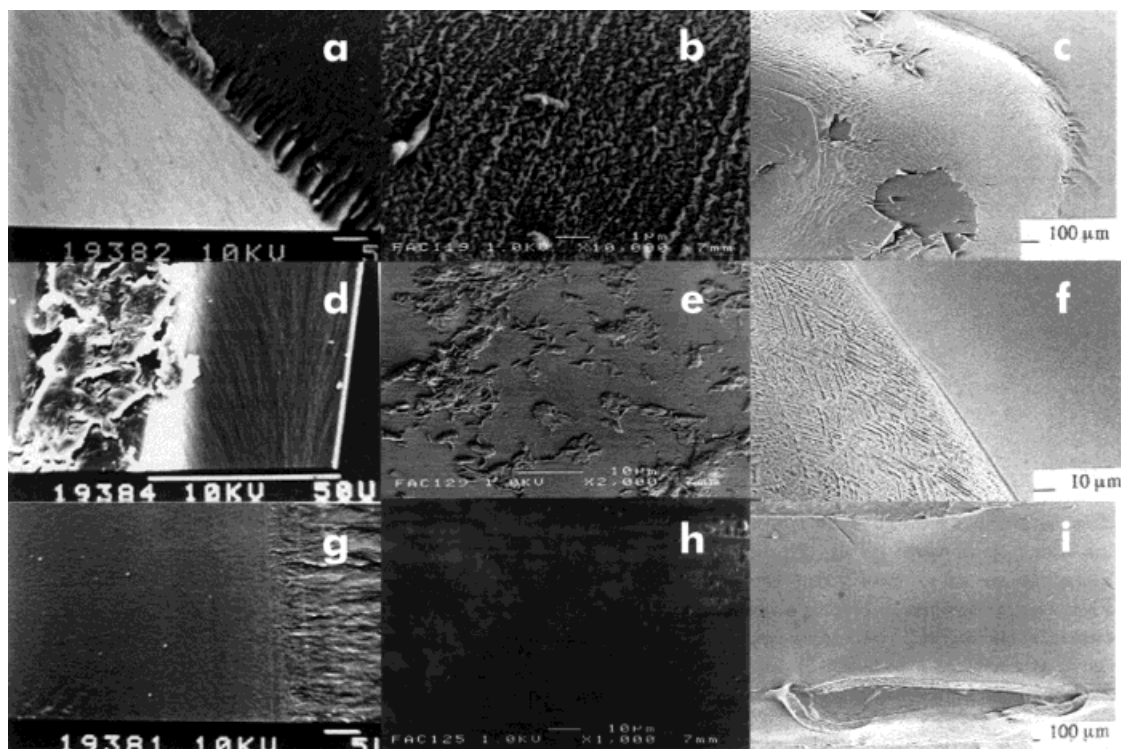
Figure 6 SEM micrographs of PVAA-based hydrogels. PAA–PVAA hydrogels air-dried (a), CPD-dried (b), and freeze-dried (c). PVP–PVAA hydrogels air-dried (d), CPD-dried (e), and freeze-dried (f). PVPy–PVAA hydrogels air-dried (g), CPD-dried (h), and freeze-dried (i).

cally crosslinked hydrogels of methylmethacrylate-*N*-vinylpyrrolidone, where an increase in nonfreezing water was associated with increasing amounts of the hydrophobic content.[25] We believe that in PVP–PVAA hydrogels interactions between the hydroxyl groups of PVAA and water predominates over water-to-water interactions, thus increasing the amount of nonfreezable water.

Microstructure of PVAA-Based Hydrogels

Microstructures of blends and the corresponding hydrogels obtained after drying with different techniques are shown in Figure 6(a)–(i). Air-dried blends exhibited smooth surfaces with no evident phase separation [Fig. 6(a), (d), and (g)]. Only PVP–PVAA blends exhibited a fibrillar pattern along the edge.

Simple evaporation of liquid from a specimen can result in a surface tension large enough to distort the actual surface and because of this, CPD has been suggested as a good alternative for studying hydrated specimens. Drying the hydrogels by CPD revealed some structural features

not found in air-dried blends. The smoothness of the PAA–PVAA blend was modified by the presence of deposits on the surface [Fig. 6(b)]. Furthermore, a striated surface was developed in these hydrogels. These patterns may be explained by the folding of the gel after drying, where regions of high stress may have developed that lead to chain aligment. PVP–PVAA hydrogels exhibited large amounts of debris on the surface but the fibrillar pattern previously observed was not modified [Fig. 6(e)]. PVPy–PVAA hydrogels exhibited deposits only on the surface, as seen on Figure 6(h). We believe that thermal treatment is an important factor regarding the presence of debris on the surface because thermally crosslinked hydrogels exhibited a lesser amount of deposits. The composition of these deposits is not known, although we believe that they are mixtures of the polymers used because PVAA was not fully extracted in water and also because of the solubility of the PAA, PVP, and PVPy in the solvents used during the drying procedure.

Sublimation of the ice formed in a frozen sample is believed to expose the underlying, true sur-

Table IV Dynamic Mechanical Properties of PVAA-Based Hydrogels at 120°C (1 Hz)

Hydrogel	Thermal Treatment (°C)	EWC (%)	$E^{*\,a}$ (MPa)	$E'^{\,b}$ (MPa)	$E''^{\,c}$ (MPa)	Tan δ
PVAA	120	42.8 ± 2.2	10.0 ± 0.9	9.9 ± 0.9	1.7 ± 0.2	0.17 ± 0.03
	150	40.8 ± 1.5	12.4 ± 1.1	12.2 ± 1.3	1.8 ± 0.4	0.14 ± 0.02
PAA–PVAA	120	51.7 ± 10.1	8.4 ± 2.3	7.9 ± 1.9	2.2 ± 2.0	0.25 ± 0.04
	150	27.1 ± 3.4	13.0 ± 2.5	12.9 ± 2.6	1.6 ± 0.3	0.18 ± 0.05
PVP–PVAA	120	71.3 ± 1.5	2.0 ± 0.2	2.0 ± 0.2	0.4 ± 0.05	0.17 ± 0.03
	150	67.5 ± 3.1	3.4 ± 0.4	3.4 ± 0.4	0.4 ± 0.1	0.13 ± 0.02
PVPy–PVAA	120	57.7 ± 2.6	1.6 ± 0.04	1.5 ± 0.03	0.5 ± 0.07	0.35 ± 0.04
	150	37.0 ± 2.4	3.4 ± 0.4	3.3 ± 0.4	0.8 ± 0.08	0.22 ± 0.03

[a] E^* = complex modulus.
[b] E' = storage modulus.
[c] E'' = loss modulus.

face features in gels and because of that, freeze-drying was attempted in all hydrogels. The frozen surface of PAA–PVAA did not reveal any significant features, either in the dry zone or in the area containing water, although some deformed pores were visible on the intermediate zone. The freeze-dried hydrogel showed a collapsed structure resulting from loss of water. In general, the surface was rough (banded pattern) with developing cracks in the intermediate zone [Fig. 6(c)]. PVPy–PVAA frozen hydrogels exhibited a featureless surface in the dry area and no intermediate zone was developed [Fig. 6(i)]. After ice sublimation, the swollen structure collapsed and a rugged pattern was developed. PVP–PVAA frozen hydrogels exhibited a more interesting topography. Although a smooth surface was present in both dry and hydrated areas, the intermediate zone developed oriented polymer strands and some porosity. After freeze-drying, a highly oriented fibrillar structure was formed and zones of high porosity were found [Fig. 6(f)]. This structure is possible, given the low modulus (0.6 MPa) and low strength (0.23 MPa) but high strain to deformation (46%) exhibited by PVP–PVAA hydrogels.[17]

Dynamic Mechanical Properties

Composition and thermal treatment of blends were the main factors that affected their dynamic mechanical properties. PVAA hydrogels exhibited the highest storage modulus when glutaraldehyde was used as crosslinking agent. PAA–PVAA hydrogels exhibited the second highest value of modulus followed by PVP–PVAA and PVPy–PVAA gels. On the other hand, hydrogels sub-

jected to a less rigorous thermal treatment (i.e., at 120°C) showed lower modulus than that of the corresponding hydrogels treated at 150°C. The dynamic mechanical behavior of PVAA-based hydrogels at 20°C is summarized in Table IV.

The effect of temperature on storage modulus is presented in Figure 7(a) and (b). From this figure it can be seen that, with the exception of PVPy–PVAA, no significant change in modulus was observed from 20 to 60°C. Previous studies on the miscibility of PVAA-based blends revealed a single glass-transition temperature for PAA–PVAA (T_g = 124.5°C) and PVP–PVAA (T_g = 127.0°C).[17] These findings and the SEM observations are in agreement with the previously reported miscibility of PVAA with either PAA or PVP.[26,27] Although a single phase is suggested for these blends, microheterogeneities and surface segregation of one of the polymers were previously detected by DSC and X-ray photoelectron spectroscopy.[28,29] The PVPy–PVAA system also exhibited a single T_g (100.0°C) but a phase separation in solution is possible because this was the only system that exhibited modulus variation with temperature. The changes in mechanical properties were not related to changes in the degree of swelling, given that temperature has no effect on the EWC (only affected the rate of swelling) and given the small deformation imposed.

The values of storage modulus and EWC in all hydrogels were different from those of the pure polymer base, PVAA, implying that the addition of a second polymer changed either the water content (EWC) or the storage modulus. This can be clearly seen in Table V, in which the equilib-
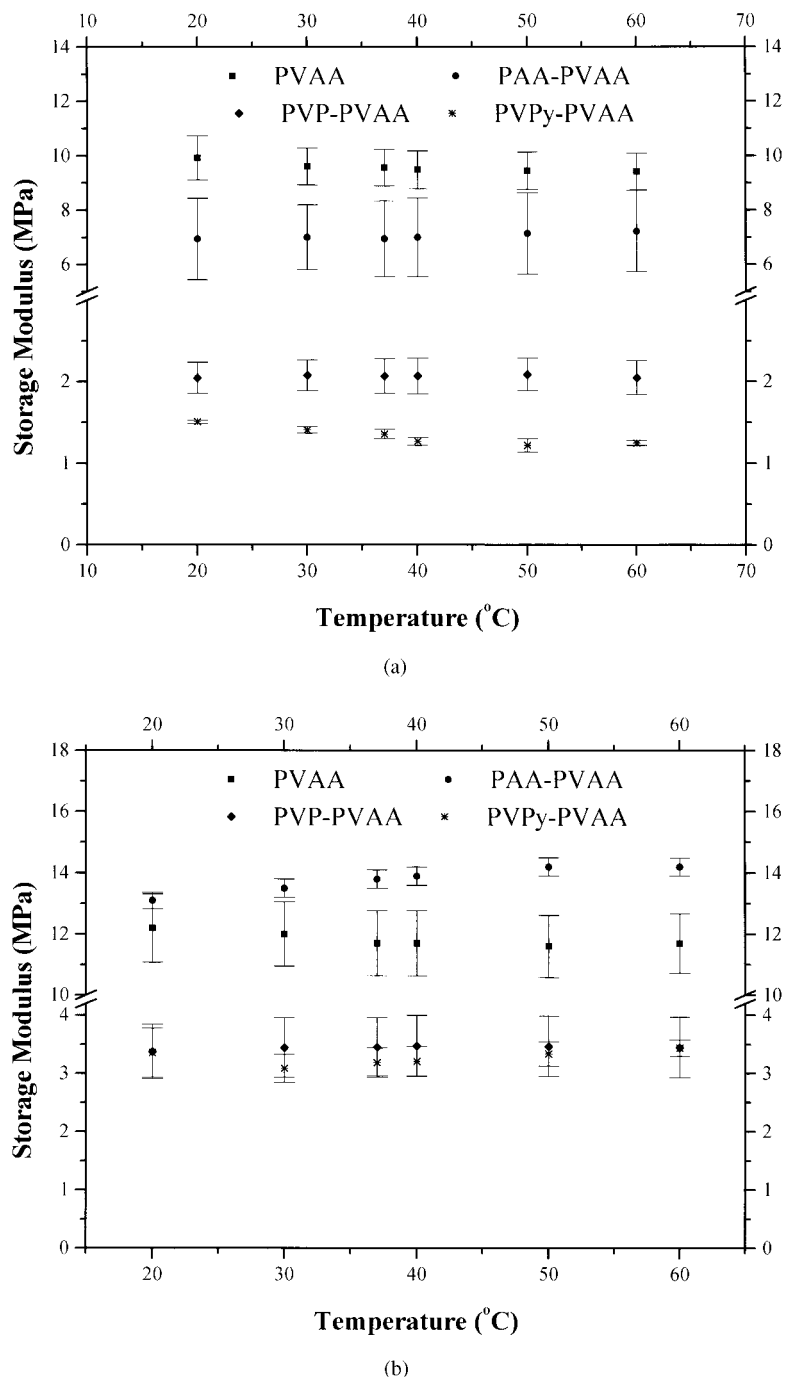
Figure 7 Effect of temperature on the storage modulus of PVAA hydrogels. Samples were thermally treated at (a) 120°C and (b) 150°C.

rium water content (EWC) or storage modulus (SM) of the hydrogel is divided by the EWC or SM of the pure polymer gel (EWC_r and SM_r). From that table, it can be seen that values of EWC_r greater than 1 were obtained at mild thermal treatments for all systems, implying an improvement with respect to the pure polymer, whereas values less than 1 were obtained at severe thermal treatments, indicating a deleterious effect of the second polymer in the hydrogel. With regard to SM_r it was observed that only for PAA–PVAA hydrogels with a high degree of crosslinking was there a beneficial effect of the addition of a second polymer. These observations suggest that a com-

Table V   Reduced Equilibrium Water Content (EWC$_r$) and Reduced Storage Modulus (SM$_r$) for Various Hydrogels at 37°C in Distilled Water

	EWC$_r$		SM$_r$	
Hydrogel	120°C	150°C	120°C	150°C
PAA–PVAA	1.2	0.6	0.8	1.1
PVP–PVAA	1.7	1.6	0.2	0.3
PVPy–PVAA	1.3	0.9	0.1	0.3

promise between water improvement and mechanical behavior should be established in the selection of these hydrogels for a given application.

CONCLUSIONS

By blending water-soluble polymers of ionic and nonionic character, a range of pH-sensitive hydrogels were prepared. Anionic hydrogels (i.e., hydrogels with the ability to swell under alkaline conditions) were obtained by blending PVAA with PAA. On the other hand, cationic hydrogels (hydrogels with enhanced swelling capacity in acidic media) were obtained by blending PVAA and PVPy. High water uptake was also observed in nonionic hydrogels made of PVAA and PVP ascribed to the higher hydrophilicity of the latter polymer. In general, the rate of water absorption was slow at severe thermal treatments on the blend (i.e., thermal treatments at 150°C), at low temperatures of swelling such as 20°C, and either under acid conditions for PAA or alkaline conditions for PVPy. Associated with a high water uptake there was an increasing amount of freezable water, implying that most of the water is free within the network, thus allowing an easier diffusion of small molecules. This feature could be exploited in the controlled release of various products of biological importance.

The microstructure of these hydrogels was highly dependent on the dehydrating technique, as revealed by SEM. From all the systems studied, PVP–PVAA was most significantly affected by the drying technique, exhibiting flat smooth surfaces by air-drying and CPD but also a highly oriented and porous structure by freeze-drying. By using a dynamic mechanical analyzer, hydrogels with a range of mechanical properties were obtained. Polyvinyl alcohol–vinyl acetate-based hydrogels exhibited good mechanical properties at low water contents and high degrees of crosslinking. This improvement in mechanical behavior, however, was temperature dependent for PVPy–PVAA hydrogels because increasing the temperature from 20 to 60°C implied a reduction in the storage modulus.

REFERENCES

1. Peppas, N. A.; Khare, A. R. Adv Drug Deliv Rev 1993, 11, 1.
2. Shalaby, W., Ed. Polymers of Biological and Biomedical Significance; ACS Symposium Series 540; American Chemical Society: Washington, DC, 1994; p. 251.
3. Harland, R. S.; Prud'homme, R. K., Eds. Polyelectrolyte Gels: Properties, Preparation and Applications; ACS Symposium Series 480; American Chemical Society: Washington, DC, 1992; p. 285.
4. Baker, J. P.; Blanch, H. W.; Praunitz, J. M. Polymer 1995, 36, 1061.
5. Park, T. G.; Hoffman, A. S. J Appl Polym Sci 1992, 46, 659.
6. Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. Adv Drug Deliv Rev 1993, 11, 85.
7. Brazel, C. S.; Peppas, N. A. Macromolecules 1995, 28, 8016.
8. Feijin, J.; Feil, H.; Van der Gaag, F. J.; Bae, Y. H.; Kim, S. W. in Proceedings of the 11th European Conference in Biomaterials, Pisa, Italy, 1994; p. 256.
9. Ogata, N.; Kim, S. W.; Feijen, J.; Okano, T., Eds. Advanced Biomaterials in Biomedical Engineering and Drug Delivery Systems; Springer-Verlag: Tokyo, 1996; p. 62.
10. Peppas, N. A. Soc Plast Eng Tech Papers NATEC 1977, 62.
11. Vázquez–Torres, H.; Cauich–Rodríguez, J. V.; Cruz–Ramos, C. A. J Appl Polym Sci 1993, 50, 777.
12. Nambu, M. Eur. Pat. 0058497 b1, 1985.
13. Peppas, N. A.; Merrill, E. W. J Polym Sci Part A Polym Chem 1976, 14, 441.
14. Nagura, M.; Nishimura, H.; Ohkoshi, Y. Jpn J Polym Sci Tech 1991, 48, 517.
15. Nagura, M.; Takagi, N.; Koyano, T.; Ohkoshi, Y.; Minoura, N. Polym J 1994, 26, 675.
16. Yonose, M.; Baba, K.; Kishimoto, H. Polym J 1992, 24, 395.
17. Cauich–Rodríguez, J. V. Ph.D. Thesis, Queen Mary and Westfield College, 1997.
18. Acree, W. E. Handbook of Chemistry and Physics; CRC Press: Boca Raton, FL, 1992; p. 5.

19. Einsenberg, A.; Yokoyama, T. J Polym Sci 1969, 17, 1717.
20. Urushikazi, F.; Yamaguchi, H.; Nakamura, K.; Numajui, S.; Sugibayashi, K.; Morimoto, K. Int J Pharm 1990, 58, 135.
21. Schott, H. J Macromol Sci Phys Ed 1992, B31, 1.
22. Sung, Y. K.; Gregonis, D. E.; John, M. S.; Andrade, J. D. J Appl Polym Sci 1981, 26, 3719.
23. Quinn, F. X.; Kampff, E.; Smyth, G.; McBrierty, V. J. Macromolecules 1988, 21, 3191.
24. Roorda, W. E.; Bouwstra, J. A.; de Vries, M. A.; Junginger, H. E. Biomaterials 1988, 9, 494.
25. Liu, Y.; Huglin, M. B. Polym Int 1995, 37, 63.
26. Herrera–Kao, W.; Aguilar–Vega, M. Polym Bull 1999, 42, 449.
27. Vijayalakshmi Rao, R.; Iatha, P. J Mater Sci Lett 1999, 18, 457.
28. Navarro Cassu, S.; Felisberti, M. I. Polymer 1997, 38, 3907.
29. Li, L.; Chan, Ch.-M.; Weng, L. T. Polymer 1998, 39, 2355.