Network Characterization and Swelling Behavior of Chemical Hydrogels Based on Acid-Containing Poly(vinyl alcohol)

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ABSTRACT: Poly(vinyl alcohol) (PVA) was modified with phthalic and succinic anhydrides to give vinyl alcohol–vinyl ester copolymers that contain carboxylate groups. These half-esters were then crosslinked by using the poly(ethylene glycol) (PEG) 400 diglycidylether. Low crosslinker/carboxylate ratios were used to obtain low degrees of crosslinking, so the capacity of the resulting hydrogel to absorb water was high. Water absorption was determined gravimetrically as a function of time at room temperature. The equilibrium swelling ratio and compressive modulus were characterized for all the resulting PVA hydrogels and related to the network structure. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 3026–3031, 2003

Key words: poly(vinyl alcohol); hydrogel; crosslinking; diglycidylether; swelling

INTRODUCTION

Poly(vinyl alcohol) (PVA) has well-stablished applications in the textile, biomedical technology, paper, and coating industries.[1] It is of particular interest because of its biocompatibility and the special features of its aqueous solutions.[2]

The chemistry of PVA is largely concerned with ester formation by reaction with acid chlorides or acid anhydrides. When the anhydride is a cycle, a carboxylic group is incorporated into the resulting polymer. PVA derivatives that contain a different number of carboxylic groups are of great interest in several industrial fields.[3] These carboxylic groups also enable three-dimensional networks to be obtained in a further step.

In previous studies, we reported the synthesis of half-esters with pendant monosuccinate or monophthalate groups, which in a second step reacted either with diglycidyl aromatic compounds to provide highly crosslinked materials[4] or with lower amounts of the aliphatic 1,4-butanediol diglycidylether to provide low crosslinked hydrogels.[5]

The most common way of obtaining networks with a high average molecular weight between crosslinks is to use low ratios of a low molecular weight crosslinker. Higher ratios of a longer crosslinker, however, can lead to a similar network structure. Some studies have reported that macromolecules such as telechelic-PVA[6,7] or various acrylic-ended oligomers of ethylene glycol can be used as crosslinking agents.[8]

In the present study, we crosslink carboxylic PVA derivatives with a long aliphatic crosslinker—a poly(ethylene glycol) diglycidyl ether whose molecular weight was about 400—to obtain superabsorbent polymers. We then studied their swelling behavior and mechanical properties, and by applying several equations to the obtained data, we were able to calculate various parameters of the crosslinked structure, including the average molecular weight between crosslinks ($\bar{M}_c$), the mesh size (ξ), the crosslinking density (ρ_x), the effective crosslinking degree (ν_e/V_0), and the polymer–solvent interaction parameter (χ). We studied the swelling behavior of these hydrogels and related it to their structure. We also compared them with hydrogels that were obtained previously[5] using a shorter aliphatic diglycidylether crosslinker.

EXPERIMENTAL

Materials

PVA (Fluka, Germany) 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. Poly(ethylene glycol) (PEG 400) diglycidylether (Aldrich, USA), pyridine (Panreac, Spain), 4-dimethyl-amino-

pyridine (DMAP) (Fluka), benzyltrimethylammonium chloride (BTMA) (Aldrich), tetrahydrofuran (THF) (SDS, France), and dimethylsulfoxide (DMSO) (SDS) were used as received.

Esterification reaction

PVA ($0.05M$ of hydroxyl group) was dissolved by stirring in DMSO (50 mL) at room temperature. Different ratios of carboxylic acid anhydride (OH/acyl group 1/0.5 and 1/0.2) and pyridine (py/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 precipitating with $0.1M$ HCl (two times). Finally, a third precipitation took place in dioxane. The least modified vinyl alcohol–vinyl succinate copolymer was precipitated in diethylether. Despite the fact that diethylether and water are unmixable, after magnetic stirring of the mixture precipitation of the polymers could be accomplished. All polymers were dried under vacuum at room temperature to constant weight. The obtained polymers had a different modification degree: for phthalate derivatives: 33% (PVA-PA33$^-$) and 14% (PVA-PA14$^-$) and for succinate derivatives: 38% (PVA-SA38$^-$) and 15% (PVA-SA15$^-$). These modification degrees were calculated by ^{1}H-NMR and elemental analysis. The comparison of the integrals of succinate or phthalate protons with methyl acetate and main chain methylene protons allowed us to determine the degree of modification that was very close to those calculated by elemental analysis.

Crosslinking with PEG 400 diglycidylether

An amount of 1.6 g (5 mmol) of PVA-PA33$^-$ was dissolved in 8 mL water at 60°C. Slowly added was 0.73 g of PEG 400 diglycidylether (Peggly) in a COO$^-$/glycidyl group ratio of 33/20. The reaction mixture was placed between two glasses of $170 \times 120 \times 3$ mm with spacers of 2 mm in an oven at 60°C for 1 day, obtaining a hydrogel. Small samples ($10 \times 5 \times 2$ mm) of the crosslinked polymers were repeatedly washed with water and dried with phosphorus pentoxide under vacuum at room temperature until their weight stopped changing (about 3 days). The other half-esters—PVA-SA38$^-$ (38/20 COO$^-$/glycidyl group ratio), PVA-PA14$^-$ (14/5 COO$^-$/glycidyl group ratio), and PVA-SA15$^-$ (15/5 COO$^-$/glycidyl group ratio)— were crosslinked in a similar way.

Water absorption measurements

The dynamic water absorption of the samples was measured by a gravimetric procedure. A polymer sample, which had been weighed accurately, was im-

mersed in distilled water at room temperature (25°C) and left until equilibrium was reached. This was after an immersion time of about 24 h. Once the swelling had terminated, the surface was dried with a tissue and the weight gain was measured. The samples were weighed at different time intervals until the hydrated weight was constant. Water absorption was calculated as weight or volume of hydrogel in the equilibrium per weight or volume of dry polymer and expressed as the swelling ratio weight (SRw) or swelling ratio volume (SRv), respectively. The volume was measured with an electronic digital caliper with an accuracy of 10^{-2} mm.

Instrumentation

^{13}C-NMR spectra were obtained by using a Gemini 300 spectrometer with D$_2$O as solvent.

The equilibrium water absorption of all the samples was measured at room temperature by using an electronic microbalance (Mettler AB204) with an accuracy of $\pm 10^{-4}$ g. The reported values of equilibrium water uptakes are averaged over nine measurements and, for each type of sample, water absorption was replicated three times.

Network mechanical properties were measured using by a dynamic mechanical thermal analyzer (DMTA) (TA 2980) with a parallel plate accessory. Cylinder samples of the swollen networks, between 10 and 40 mm of diameter, were slightly compressed to assume small deformations (<5%) at 37°C. Thus, from the slope of the linear part of the plot, the compression–strain modulus can be measured.

RESULTS AND DISCUSSION

To obtain the half-esters, PVA was dissolved in DMSO in the presence of pyridine and esterified with phthalic and succinic carboxylic acid anhydrides in a homogeneous medium, using different amounts of anhydride. By using the ratios specified in the experimental part, phthalic derivative polymers with a modification degree of 33 phthalic units (PVA-PA33$^-$) 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$^-$) and 15 succinic units (PVA-SA15$^-$) per 100 total units were obtained, as has been previously described.[5]

The reaction of half-esters with diglycidylether of PEG 400—of molecular weight 400—led to crosslinked polymers. Diglycidyl compounds reacted with the carboxylate groups in the modified PVA to give a network with different polar groups (PVA-PA$^-$ + Peggly and PVA-SA$^-$ + Peggly; see Scheme I).

The reaction of epoxy compounds with simple alcohols can lead to the expected ethers,[9] but the results
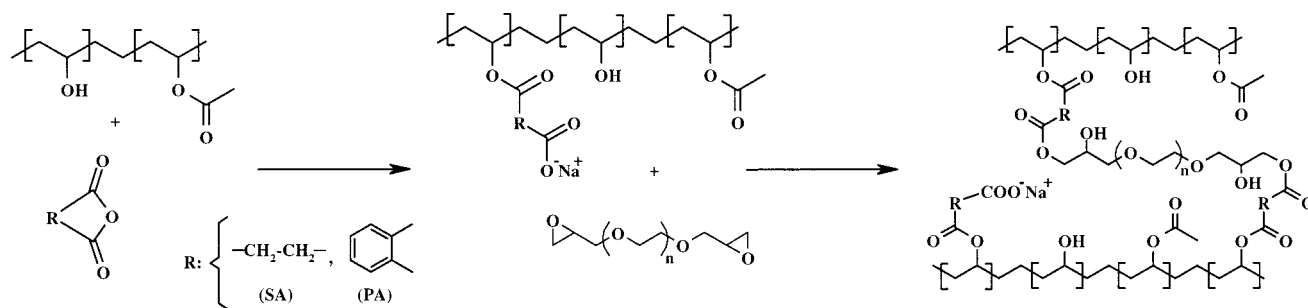
Scheme 1 Synthesis of PVA-PA⁻ + Peggly and PVA-SA⁻ + Peggly.

are not always satisfactory and there are few examples of analogous polymer reactions in the literature. It has recently been reported that PVA can be partially modified with epoxy compounds but the conditions must be drastic (200°C) and the degrees of modification are low (10%).[10] Therefore, in our reaction conditions, the remaining hydroxyl groups of PVA must not be competitive with carboxylic groups.

Reactions were carried out in water at 60°C between two glass slides with a spacer of 2 mm to obtain suitable slabs to carry out the mechanical measurements and swelling study. 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 ^{13}C-NMR spectra. Figure 1 shows, for example, the crosslinked vinyl alcohol–vinyl succinate copolymer PVA-SA15⁻ Fig. 1 (A) and the crosslinked vinyl alcohol-vinyl phthalate copolymer PVA-PA33⁻ Fig. 1(B). Figure 1(A) shows carbonylic carbons at 180 and 175 ppm, which can be assigned to the carboxylate and ester (succinate and acetate), respectively. Between 72 and 60 ppm, there is a complex signal that includes main chain methine, methine, and methylene corresponding to the opening of the oxirane ring, and ethylene glycol methylene. Main chain methylene carbons are present between 45 and 37 ppm and the succinate methylene appears [Fig. 1(A)], at 30 ppm. Around 20 ppm, the methyl carbon of the acetate moiety can also be observed.

The difference between both spectra is due to the aliphatic or aromatics moieties introduced in the first modification with anhydride. Thus, in Figure (B) the aromatic signals at 140–125 ppm corresponding to phthalate can 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 (SRw) and by means volume measurements (SRv) as a function of time by immersing the sample in deionized water. Figure 2 shows the equilibrium swelling

ratios of the different hydrogels. We can see that the absorption does not differ significantly, although their structures must be very different. For PVA-PA33⁻ + Peggly and PVA-SA38⁻ + Peggly, which are more modified and crosslinked than PVA-PA14⁻ + Peggly and PVA-SA15⁻ + Peggly, the absorption is mainly because there are more remaining carboxylate groups. The absorption of the two less modified hydrogels that contain fewer ionic groups is similar because of their lower crosslinking degree.

These results can be related to those obtained when these half-esters were crosslinked with 1,4-butanediol diglycidylether,[5] that is, a shorter diglycidyl compound with a similar aliphatic structure. In general, a longer crosslinker should increase the absorption capacity, whereas a higher crosslinking degree (which in this case is associated with a decrease in the amount of ionic groups) should have the opposite effect. For the less-modified, PVA-PA14⁻ + Peggly and PVA-SA15⁻ + Peggly, where the molar ratio of carboxylate/Peggly used is the same as for the analogous hydrogels crosslinked with the 1,4-butanediol diglycidylether, the absorption capacity was significantly increased (twice as high). For the more modified, PVA-PA33⁻ + Peggly and PVA-SA38⁻ + Peggly, where the molar ratio of carboxylate/Peggly used is twice that used for the analogous crosslinked with the 1,4-butanediol diglycidylether, the absorption capacity is reduced to one-half. The absorption capacity decreases despite the longer crosslinker because the crosslinking degree is higher and there are few remaining carboxylate groups.

Analysis of crosslinked structure

One of the basic parameters that describe the structure of an electrolyte and nonelectrolyte-type hydrogel is the average molecular weight of polymer chains between two consecutive junctions ($\bar{M}_c$). These junctions may be chemical crosslinks, physical entanglements, crystalline regions, or even polymer complexes.[11] Several theories for calculating the molecular weight be-
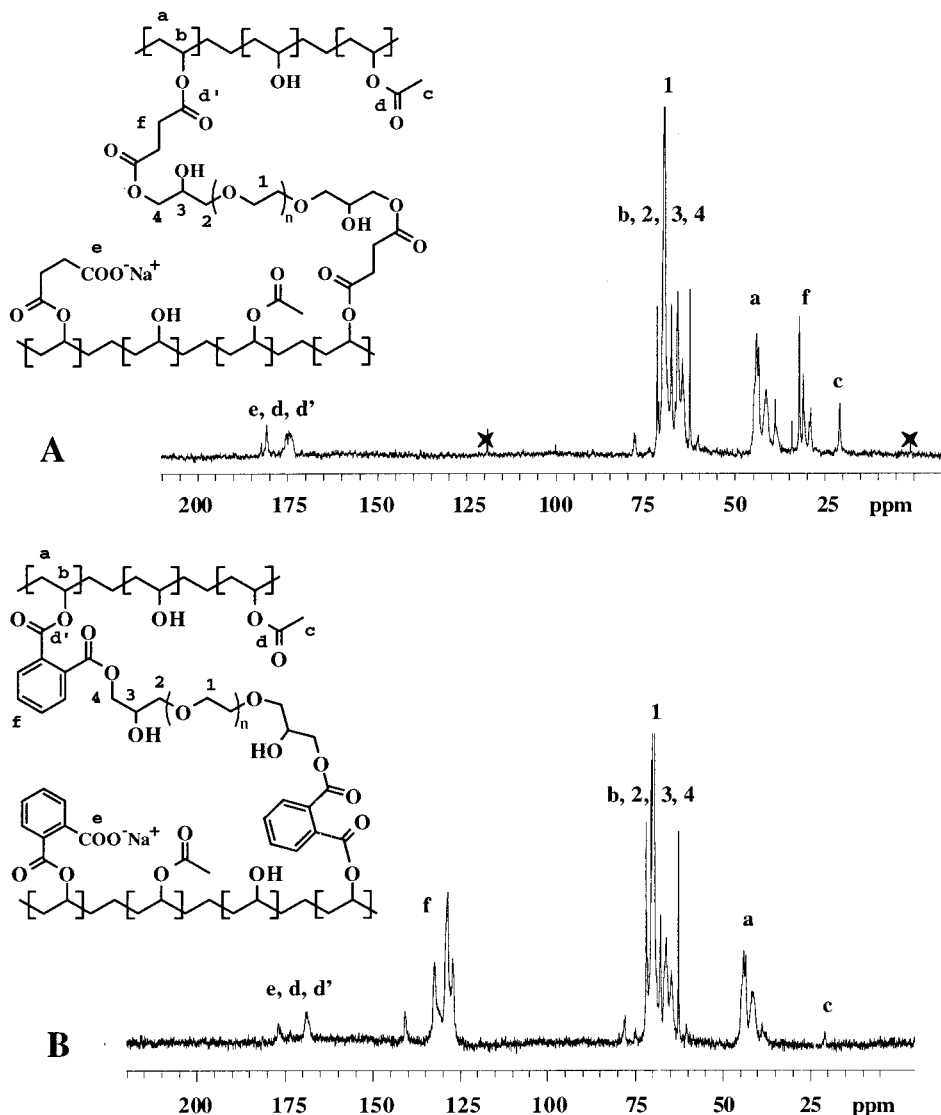
Figure 1 ^{13}C-NMR spectra of PVA-SA15$^-$ + Peggly (A) and PVA-PA33$^-$ + Peggly (B) recorded in D$_2$O.

tween crosslinks in polymer networks have been proposed and we calculated $\bar{M}_c$ from mechanical and swelling data using the equation[7]

$$\bar{M}_c = \frac{\rho_2}{\left(\dfrac{\nu_e}{V_0}\right) + \left(\dfrac{2\rho_2}{\bar{M}_n}\right)} \tag{1}$$

Here, ρ_2 is the density of dry hydrogel and (ν_e/V_0) is the effective crosslinking degree.

This effective network chain concentration (ν_e/V_0) can be calculated from the stress compression–strain modulus for small deformations by using the equation[12]

$$\tau_s = \left(\frac{\nu_e}{V_0}\right) RT \nu_{2m}^{1/3} \nu_{2r}^{2/3} (\alpha - \alpha^{-2}) \tag{2}$$

Here, τ_s is the applied force per unit area of swollen hydrogel, R is the gas constant, T is absolute temper-
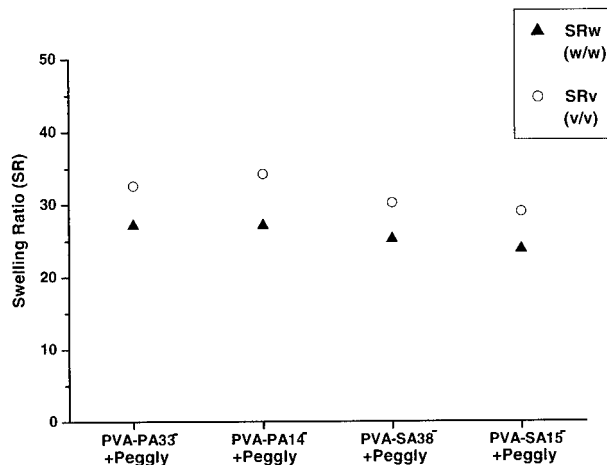

Figure 2 Equilibrium swelling ratio (volume and weight ratio) of PVA-PA$^-$ + Peggly and PVA-SA$^-$ + Peggly hydrogels in deionized water at 20°C.

TABLE I
Swelling Characterization Results: Swelling Ratio Volume (SRv) and Volume Fractions in Relaxed ($\nu_{2,r}$) and Swollen ($\nu_{2,s}$) State

	SRv (v/v)	$\nu_{2,r}$	$\nu_{2,s}$
PVA-PA33$^-$ + Peggly	32.6	0.20	0.031
PVA-PA14$^-$ + Peggly	34.2	0.19	0.029
PVA-SA38$^-$ + Peggly	30.2	0.19	0.033
PVA-SA15$^-$ + Peggly	29.0	0.19	0.034

ature, $\nu_{2m} = V_{pol}(dried)/V_{pol}$ (swollen) is the polymer volume fraction in the swollen state, $\nu_{2r} = V_{pol}$ (dried)/V_{pol}(relaxed) is the polymer volume fraction in the gel in the relaxed state, and α is the deformation ratio ($\alpha = L/L_0 \geq 0.95$).

From the stress compression–strain experiments, the polymer–solvent interaction parameter, χ, can be calculated from eq. (3), where V_1 is the molar volume of solvent and

$$\ln(1 - \nu_{2s}) + \nu_{2s} + \chi\nu_{2s}^2$$
$$+ V_1(\nu_e/V_0)(\nu_{2s}^{1/3}\nu_{2r}^{2/3} - \nu_{2s}/2) = 0 \quad (3)$$

Table I shows the volume fractions in the relaxed and swollen states obtained from absorption data (with an uncertainty of ±5%). Figure 3 plots the stress of the swollen hydrogel against the strain expressed as $(\alpha - 1) * 100$. From the slopes, we can calculate elastic moduli (E), and from a plot of τ_s against $(\alpha - \alpha^{-2})$, which is linear at low deformations, we can also calculate (ν_e/V_0). All these values (with an uncertainty of ±10%) are given in Table II, which also shows the polymer–solvent interaction parameter χ.

We can see that the more crosslinked polymers, PVA-PA33$^-$ +Peggly and PVA-SA38$^-$ + Peggly, show the better mechanical properties; that is, their elastic modulus is higher, which is in agreement with

TABLE II
Mechanical Characterization Results: Young Modulus (E), Effective Crosslinking Degree (ν_e/V_0), Average Molecular Weight Between Crosslinks ($\bar{M}_c$), and PVA-PA$^-$ + Peggly–Water and PVA-SA$^-$ + Peggly–Water Interaction Parameter (χ)

	E (kPa)	$(\nu_e/V_0) \times 10^3$ (mol/L)	$\bar{M}_c$ (g/mol)	χ
PVA-PA33$^-$ + Peggly	55	66	8500	0.406
PVA-PA14$^-$ + Peggly	14	17	9500	0.479
PVA-SA38$^-$ + Peggly	38	45	8900	0.437
PVA-SA15$^-$ + Peggly	13	16	9000	0.490

a greater effective crosslinking degree. However, similar to the absorption capacities, the $\bar{M}_c$ values are similar for the four hydrogels in a parallel way. Thus, we can obtain hydrogels with similar $\bar{M}_c$ either by low crosslinking of the less modified PVA (PVA-SA15$^-$ and PVA-PA14$^-$) or by moderate crosslinking of the more modified PVA (PVA-SA38$^-$ and PVA-PA33$^-$) with higher molecular weights.

The polymer–solvent interaction parameters χ of all the hydrogels are lower than the PVA–water parameter (0.494) reported in the literature,[13] although for the less modified hydrogels, they are close. These calculated values are introduced in the Peppas and Merrill eq. (4) to determine new $\bar{M}_c$ values.[14] From these values, mesh size ζ[15] and crosslinking density ρ_x[16] were calculated using eqs. (5) and (6). All these results are summarized in Table III.

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{\left(\dfrac{\bar{\nu}}{V_1}\right)[\ln(1 - \nu_{2m}) + \nu_{2m} + \chi\nu_{2m}^2]}{\nu_{2r}\left[\left(\dfrac{\nu_{2m}}{\nu_{2r}}\right)^{1/3} - \dfrac{2}{\phi}\left(\dfrac{\nu_{2m}}{\nu_{2r}}\right)\right]} \quad (4)$$

Here, $\bar{M}_n$ is the number-average molecular weight of the polymer before crosslinking, $\bar{\nu}$ is the specific vol-
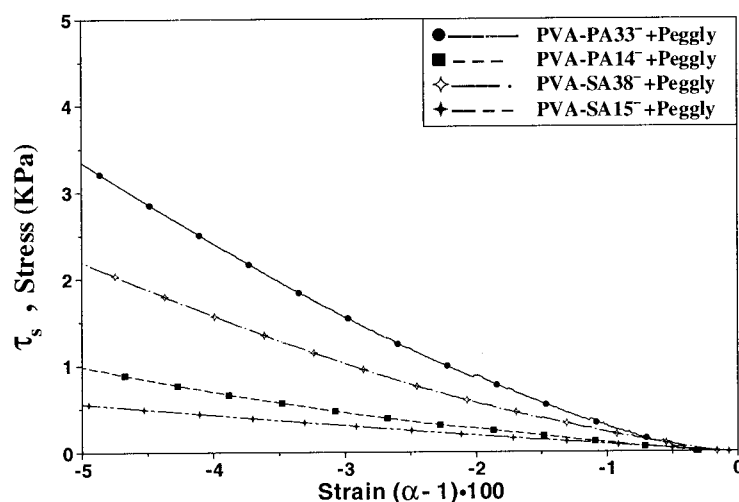
Figure 3 Stress–strain plot, PVA-PA$^-$ + Peggly, and PVA-SA$^-$ + Peggly hydrogels.

TABLE III
Mechanical and Swelling Characterization Results: Average Molecular Weight Between Crosslinks ($\bar{M}_c$)
from Mechanical and Swelling Data, Mesh Size (ξ), and Crosslinking Density (ρ_x)

	$\bar{M}_c$ (g/mol) (mechanical data)	$\bar{M}_c$ (g/mol) (swelling data)	ξ (Å)	$\rho_x \times 10^4$ (mol/mL)
PVA-PA33$^-$ + Peggly	8500	8600	181	1.41
PVA-PA14$^-$ + Peggly	9500	9500	233	1.33
PVA-SA38$^-$ + Peggly	8900	8800	188	1.38
PVA-SA15$^-$ + Peggly	9000	8900	223	1.37

ume of the polymers, and ϕ is the junction functionality = 3;

$$\xi = \nu_{2m}^{-1/3}\left[C_n\left(\frac{2\bar{M}_c}{M_r}\right)\right]^{1/2}l \tag{5}$$

Here, C_n is the Flory characteristic ratio (=8.3) for PVA,[17] M_r is the average of the molecular weights on the repeating units, and l is the carbon–carbon bond length (=1.54 Å),

$$\rho_x = \frac{1}{\nu\bar{M}_c} \tag{6}$$

We can see in Table III that the $\bar{M}_c$ values calculated from the Peppas equation are very close to those obtained from mechanical measurements. This coincidence between both calculation methods, that we have previously reported for other PVA-hydrogels,[18] could be explained because the use of a compression clamp probably does not lead to a disentanglement process which is described as significant for tensile stress testing[19,20] and would lead to higher $\bar{M}_c$ values. The mesh size, that is, the space between crosslinks, is similar for the hydrogels with the same crosslinker content and lower for the more crosslinked hydrogels. However, there are no significant differences in the crosslinking density.

References

1. Toyoshima, K. in Polyvinyl Alcohol: Properties and Applications Finch, C. A., Ed., Wiley: New York, 1973, Chapter 3.
2. Peppas, N. A.; Scott, J. E. J Controlled Release 1992, 18, 95.
3. Maruhashi, M. Polyvinylalcohol Developments; ed., Finch, C. A., Wiley: New York, 1992, chapter 6.
4. Giménez, V. Mantecón, A.; Ronda, J. C.; Cádiz, V. J Appl Polym Sci 1997, 65, 1643.
5. Ruiz, J.; Mantecón, A.; Cádiz, V. J Appl Polym Sci 2001, 81, 1444.
6. Paradossi, G.; Lisi, R.; Paci, M.; Crescendi, V. J Polym Sci, Polym Chem Ed 1996, 34, 3417.
7. Paradossi, G.; Cavalieri, F.; Capitani, D.; Crescenzi, V. J Polym Sci, Polym Phys Ed 1999, 37, 1225.
8. Smith, P. B.; Cutié, S. S.; Henton, D. E.; Powell, C. Kosman, J. J Polym Sci, Polym Chem Ed 1997, 35, 799.
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. Peppas, N. A. J Bioact Compat Polym 1991, 6, 241.
12. Flory, P. J.; Leutner, F. S. J Chem Phys 1943, 11, 521.
13. Peppas, N. A.; Wright, S. L. Macromolecules 1996, 29, 8798.
14. Peppas, N. A.; Merril, E. W. J Polym Sci, Polym Chem Ed 1976, 14, 441.
15. Peppas, N. A., ed. Hydrogels in Medicine and Pharmacy; CRC Press Boca Raton, FL; 1986, Vol. 1, p. 54.
16. Peppas, N. A., Ed. Hydrogels in Medicine and Pharmacy, CRC Press Boca Raton, FL, 1986, Vol. 1, p. 48.
17. Gudeman, L. F.; Peppas, N. A. J Appl Polym Sci 1995, 55, 919.
18. Ruiz, J.; Mantecón, Cádiz, V. Polymer 2001, 42, 6347.
19. Peppas, N. A.; Merrill, E. W. J Appl Polym Sci 1977, 21, 1763.
20. Peppas, N. A.; Benner, R. F., Jr. Biomaterials 1980, 1, 158.