Poly(acrylic acid)–Poly(vinyl alcohol) Copolymers with Superabsorbent Properties

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ABSTRACT: Biodegradable polyacrylates were produced by a series of novel copolymerization and/or crosslinking techniques using poly(vinyl alcohol) (PVA) moieties modified by the incorporation of olefinic structures. PVA was modified by a tosylation and/or detosylation reaction. The functionalized PVA was copolymerized and/or crosslinked with acrylic acid or its partially neutralized form to give crosslinked polyacrylates that could swell in water. Their swelling behavior was determined under load. Degradation studies were performed in α-chymotrypsin, trypsin, and papain solutions. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 817–829, 1998

Key words: poly(vinyl alcohol); poly(acrylic acid); superabsorbent polymers; biodegradation; swelling

INTRODUCTION

Crosslinked polyacrylates are unique materials because of their valuable applications such as diapers, incontinence products, feminine hygiene products, hospital products, thickening agents, and condensation preventing agents.[1] Aqueous solution polymerization processes are used for the polymerization of acrylic acid or acrylates in the presence of an appropriate crosslinking agent to produce water-soluble polyacrylates.

In a continuation of our research in the field of superabsorbent polyacrylate polymers,[2,3] we have directed our attention towards the preparation of superabsorbent polyacrylates crosslinked with PVA-based crosslinking agents.

The present research relates to processes of forming water-absorbing crosslinked polyacrylates, which are water insoluble, absorb a large quantity of an aqueous fluid, and exhibit a relatively good stability. We have studied a process for preparing potentially biodegradable polyacrylates using functionalized PVA as a crosslinking agent. As PVA is known to biodegrade,[4–8] such structures will be biodegradable in principle, leading to low-molecular-weight polyacrylates, depending on the ratio of acrylic acid to functionalized PVA used.

In our work, the functionalization of PVA was achieved by making the use of two different synthetic approaches. In the first approach, a commercially available PVA was subjected to a condensation–elimination reaction (that is, tosylation–detosylation) to obtain a functionalized PVA having randomly distributed double bonds in its backbone. The second synthetic approach used the condensation of PVA with an appropriate moiety to obtain the functionalized PVA having the functional groups (double bonds) pendant to the PVA chain. The ensuing PVA polymers were reacted with partially neutralized acrylic acid to form three dimensional networks that swelled in water.

Incorporation of PVA units provided an additional advantage to the ensuing product. PVA is

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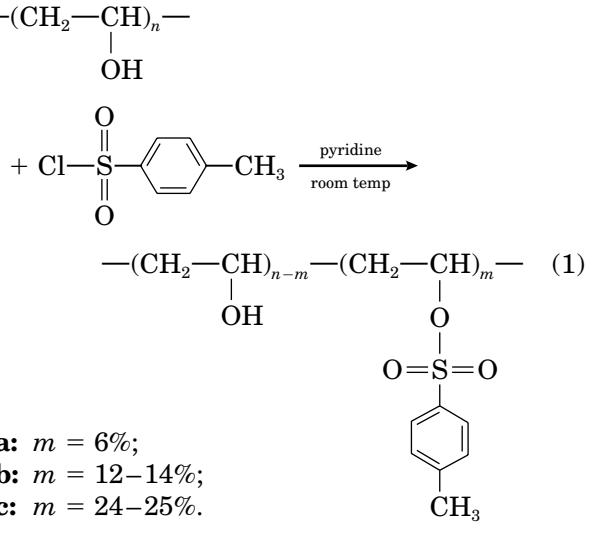
known to crystallize upon heat treatment at temperatures of 50 to 120°C for 5 to 60 min.[9] This crystallization process may lead to a significantly densified structure, which may swell to provide gels of significantly improved mechanical strength. Thus, the modulus and ultimate strength of the final PVA-containing polyacrylates could be expected to be significantly improved.

EXPERIMENTAL

In order to prepare water-insoluble polyacrylates having superabsorbent properties, we used functionalized PVA grades as crosslinking agents.

Partial Tosylation of PVA

The condensation of PVA (Elvanol, E.I. du Pont de Nemours, Wilmington, DE; $\bar{M}_n$ = 52,800; degree of hydrolysis, 99.2%) with *p*-toluene sulphonyl chloride (*p*-TsCl; 1 : 1 molar ratio) in the presence of anhydrous pyridine at room temperature[10] yielded 6% tosylated PVA (**1a**) according to the following reaction.



(1)

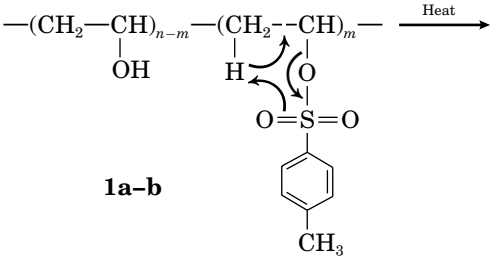
1a: m = 6%;
1b: m = 12–14%;
1c: m = 24–25%.

Similarly, molar ratios of 1 : 1.5 and 1 : 30 of PVA to *p*-toluene sulphonyl chloride resulted in the formation of 12–14% tosylated PVA (**1b**) and 24–25% tosylated PVA (**1c**), respectively, as indicated in Table I.

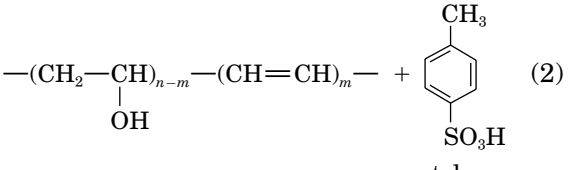
These partially tosylated PVA samples were isolated by filtration and purified by washing them with dilute HCl, aqueous $NaHCO_3$ solution, and distilled water in order to remove pyridine and *p*-toluene sulphonic acid, respectively. The products were characterized by ^1H nuclear magnetic resonance (NMR) spectroscopy. The NMR spectra were recorded in deuterated dimethyl sulfoxide (XL-200 MHz and Gemini 200 MHz instruments). These samples were used for the preparation of the functionalized PVA. Triethylamine could also be used as a reagent instead of pyridine.

Detosylation of Partially Tosylated PVA

The conversion of various arylsulphonate esters to the corresponding olefins using dimethyl sulphoxide, hexamethelene phosphoramide, and diethyl and dimethyl formamide at around 80–100°C has been reported by Nace.[11] Thus, we used this procedure for the conversion of the partially tosylated PVA (**1a–c**) into the corresponding olefins. In order to achieve total elimination (detosylation) of *p*-toluene sulphonic acid unit (*p*-TsOH) from the partially tosylated PVA (**1a–c**), reactions were made under different reaction conditions, such as time, temperature, and solvent, as summarized in Table II. The resulting solid products were wasted with water, dilute HCl, and aqueous $NaHCO_3$ and again with water.



1a–b



(2)

2a : 6%; **2b** 12−14%.

p-toluene sulphonic acid

The following experiments were successful in giving the desired product after total elimination of *p*-TsOH groups:

1. A sample of 6% tosylated PVA (**1a**) gave the desired product (**2a**) upon heating at

Table I Partial Tosylation of PVA[1]

Experiment	Molar Ratios PVA to *p*-TsCl	Temperature (°C)	Time (h)	Tosylation (%)
1	1 : 0.17	23	36	—
2	1 : 1	22.5	48	6 (product **1a**)
3	1 : 1.5	22.5	60	12–14 (product **1b**)
4	1 : 3	23.5	60	24–25 (product **1c**)

[1] PVA is poly(vinyl alcohol) with $\bar{M}_n$ = 52,800.

75°C for a period of 6 h under neat conditions after total detosylation.

2. A sample of 12% tosylated PVA (**1b**) gave the desired product (**2b**) upon heating with or without DMF at 75°C for a period of 6 h after a complete elimination of *p*-TsOH groups. These products were isolated by filtration of aqueous solution and purified by washing with dilute HCl, aqueous $NaHCO_3$, and distilled water. The total elimination of *p*-TsOH groups was confirmed by ^{1}H-NMR spectroscopy. The disappearance of *p*-toluene sulphonyl group protons at δ 7.00–8.00 was indicative of total elimination of *p*-TsOH groups from **1a** and **1b** to give **2a** and **2b,** respectively [Fig. 1(a) and (b)].
3. When 24–25% tosylated PVA (**1c**) was heated with and without DMF at 75 and 70°C for 8 and 6 h, respectively, it was observed that there was no complete elimination of *p*-toluene sulphonyl groups, which was confirmed by ^{1}H-NMR spectroscopy in deuterated DMSO. Since the solubility of detosylated PVA, such as **2a** and **2b,** was found to be very poor in most of the organic solvents, the polymers were heated with deuterated DMSO at 70–80°C for 2–3 h, and these solutions were used to record the ^{1}H-NMR spectrum.

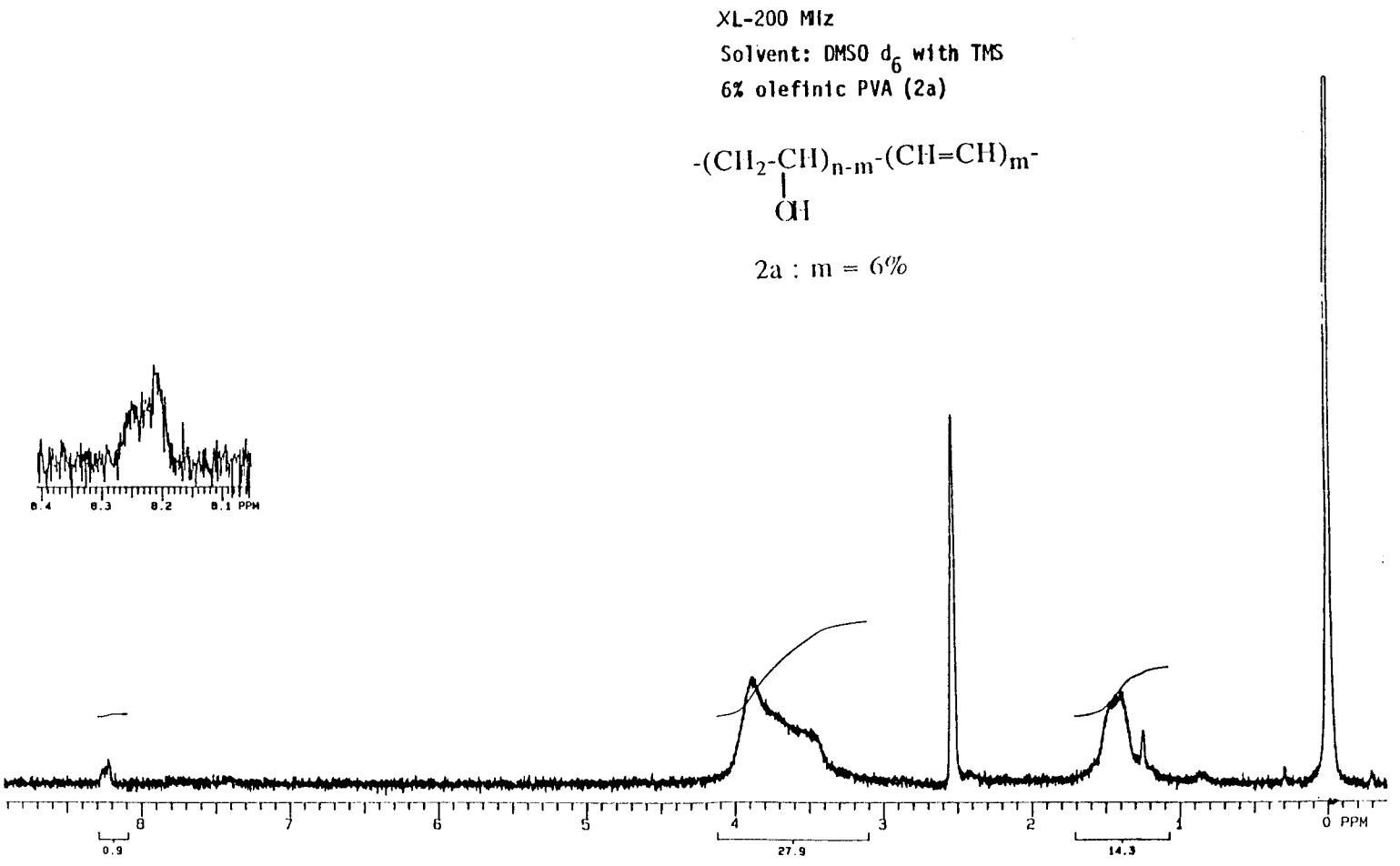
Condensation of PVA with *p*-Styrene Sulphonyl Chloride

p-Styrene sulphonyl chloride was required for the condensation of PVA. It was prepared from the reaction of sodium *p*-styrene sulphonate with phosphorous oxychloride[12] at 80–90°C for a period of 2 h (72% isolated yield; mp, 32°C).

It was isolated by extraction with methylene chloride, followed by drying with anhydrous Na_2SO_4 and evaporation of methylene chloride under reduced pressure. Its structure was established with ^{1}H-NMR spectroscopy. Furthermore,

Table II Detosylation of Tosylated PVA Samples (1a–c)

Experiment	Tosylated PVA	Solvent	Temperature (°C)	Time (h)	Results
11	0.5 g (**1a**)	Neat	70	6	0.39; Partial detosylation
12	0.5 g (**1a**)	Neat	75	6	0.38; Complete detosylation (Product **2a**)
21	2 g (**1b**)	DMSO (5 mL)	80–90	1	Difficult to isolate
22	1 g (**1b**)	Water (3 mL)	Reflux	2	No detosylation
23	1 g (**1b**)	Neat	60–70	2	0.7 g; partial detosylation
24	1 g (**1b**)	Neat	65	6	0.78 g; partial detosylation
25	0.5 g (**1b**)	Neat	65	12	0.36 g; partial detosylation
26	0.5 g (**1b**)	DMF/neat	75	8	0.38 g; total detosylation (Product **2b**)
31	0.5 g (**1c**)	Neat	70	6	0.3 g; partial detosylation
32	0.5 g (**1c**)	DMF (3 mL)	75	8	0.32 g; partial detosylation



(a)

Figure 1 (a) ^{1}H-NMR spectrum of 6% olefinic PVA (**2a**).

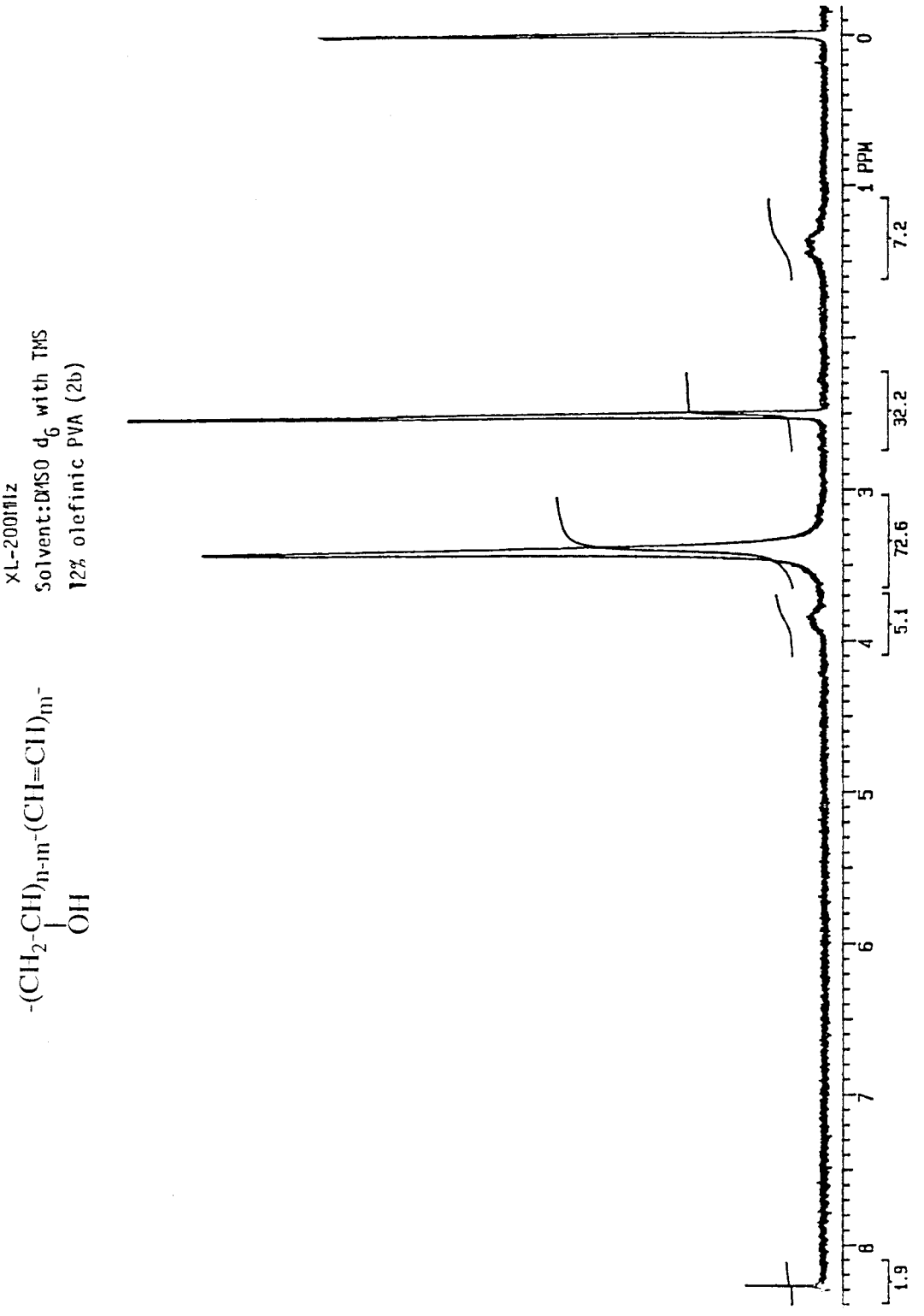
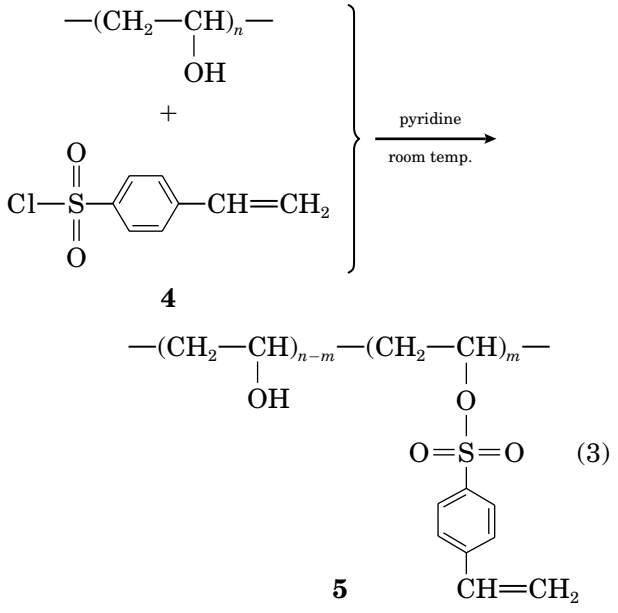


Figure 1 (b) ^{1}H-NMR of 12% olefinic PVA (**2b**).

the condensation of PVA ($\bar{M}_n$ = 52,800) was attempted with 2 equivalents of *p*-styrene sulphonyl chloride (**4**) in anhydrous pyridine at room temperature for 48 h. The product (**5**) was isolated by filtration and purified by washing with dilute HCl, aqueous $NaHCO_3$, acetone, and distilled water. The expected percentage of pendent group introduced was around 10–15%.



Polymerization of Acrylic Acid with Functionalized PVA

Solution polymerization of partially neutralized acrylic acid was performed in the presence of modified PVA as a comonomer and/or crosslinking agent at 37°C for 24 h. The copolymer agents used were **2a** and **2b,** having 6 and 12% double bonds in their backbone, respectively, and styrene-based PVA (**5**).

In a typical reaction for the polymerization of 40% neutralized acrylic acid with modified PVA (**2a**), 7.2 g (0.1 mol) of a freshly distilled acrylic acid was added and neutralized with an aqueous solution of sodium hydroxide (1.56 g of sodium hydroxide in 18 mL of distilled water) at room temperature. A sample of 0.166 g (0.01 mol %) of 6% olefinic PVA (**2a**) was dissolved in 3 mL of distilled water and heated at 70–80°C for 5–6 h. This product was added to the 40% neutralized AA solution along with 0.29 g of 18% solution of ammonium persulphate (0.5 wt % of monomer) as a free radical initiator under continuous nitrogen purge.

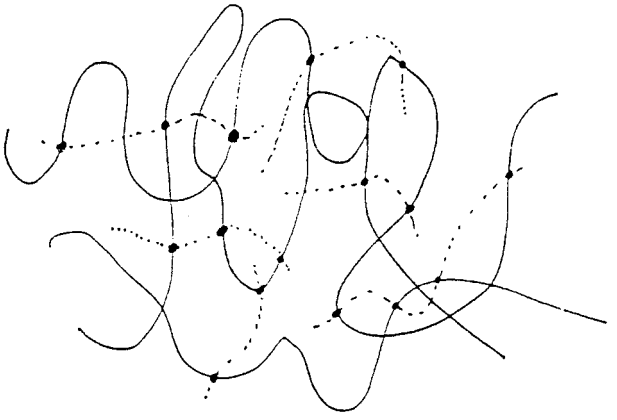


Figure 2 Crosslinked polyacrylate network, with poly(acrylic acid) chains, olefinic PVA chains (- - -), and crosslinking bridges (●).

Polymerization was carried out in polypropylene vials kept at 37°C for 24 h. The resulting polyacrylate, obtained at yields of 90%, was dried at room temperature and atmospheric pressure. By employing this representative procedure, the polymerization of 40 and 60% neutralized acrylic acid was achieved with copolymers such as **2a, 2b,** and **5,** having 3 different ratios of 0.01, 0.005, and 0.0025 mol PVA per mole of AA to obtain the corresponding polyacrylates (Fig. 2 and Table III).

Dynamic Swelling

The short-term swelling of polyacrylate samples prepared by copolymerization of 40 and 60% neutralized AA with 6% olefinic PVA and having crosslinking ratios of 0.01, 0.005, and 0.0025 mol/mol was investigated in a situation simulating superabsorbent applications. Polyacrylate samples were ground into microparticles. Particles of the desired size (30–60 mesh) and 0.1 g were placed in sealed tea bags (40 × 50 mm). These were placed in 60 mL of buffered pH solutions of 5.01, 6.02, 7.01, and 8.00 at 25°C. The samples were removed and weighed in set intervals.

Swelling Under Load

In order to characterize these polyacrylates in a manner that simulated applications in a disposable diaper, the swelling behavior of these polyacrylate samples at 25°C was investigated under load (Fig. 3). First, 0.5 g of 30–60-mesh micropar-

Table III Polymerization of Partially Neutralized AA with Olefinic PVA as a Crosslinker

Experiment	AA (g)	NaOH/H_2O (g/mL)	Neutralization (%)	18% APS (g)	6% Olefinic PVA (mol %)	Yield (g)
41	7.2	1.56/18	40	0.29	0.01 (**2a**) (0.166 g)	8.12
42	7.2	1.56/18	40	0.29	0.005 (**2a**) *(0.6839)*	8.02
43	7.2	1.56/18	40	0.29	0.0025 (**2a**) (0.041 g)	7.98
51	7.2	2.3/18	60	0.29	0.01 (**2a**) (0.166 g)	9.02
52	7.2	2.3/18	60	0.29	0.005 (**2a**) (0.081 g)	9.15
53	7.2	2.3/18	60	0.29	0.0025 (**2a**) (0.041 g)	8.78
61	7.2	1.56/18	40	0.29	0.01 (**2b**) (0.348 g)	8.20
62	7.2	1.56/18	40	0.29	0.005 (**2b**) (0.174 g)	8.11
63	7.2	1.56/18	40	0.29	0.0025 (**2b**) (0.098 g)	7.50
71	7.2	2.3/18	60	0.29	0.01 (**2b**) (0.3489)	9.10
72	7.2	2.3/18	60	0.29	0.005 (**2b**) (0.174 g)	9.30
73	7.2	2.3/18	60	0.29	0.0025 (**2b**) (0.087 g)	9.00
81	7.2	1.56/18	40	0.29	0.01 (**6**) (0.819 g)	8.18
82	7.2	1.56/18	40	0.29	0.005 (**6**) (0.409 g)	8.90
83	7.2	1.56/18	40	0.29	0.0025 (**6**) (0.204 g)	8.95
91	7.2	2.3/18	60	0.29	0.01 (**6**) (0.819 g)	8.95
92	7.2	2.3/18	60	0.29	0.005 (**6**) (0.409 g)	8.95
93	7.2	2.3/18	60	0.29	0.0025 (**6**) (0.204 g)	8.95

ticles were placed on the wire mesh in the bottom of the sample holder.[3] Then, these particles were spread as uniformly as possible. Next, the Teflon cover was placed on the sample layer. The sample holder was then suspended in a beaker and placed under the measuring unit, in such a way that the plunger of the device rested on the sample cover and the measuring dial read zero. A load of weighing 76 g was then added to the measuring device. The Teflon cover weighed 27 g. The beaker was then filled with 250 mL, and the height was recorded at various time intervals. For each sample, the change in height was measured up to 1 h.

Equilibrium Swelling Studies

Equilibrium swelling studies were performed at 37°C using 0.9% saline solution as the swelling agent. The dried polyacrylate samples produced from 40 and 60% neutralized AA at various crosslinking ratios were cut into disks of 0.3-mm thickness using a diamond saw and then weighed to determine the dry sample weight. These disks were then immersed in glass jars containing 50 mL of 0.9% saline solution. The disks were weighed after every 24 h until they reached equilibrium swelling weight.

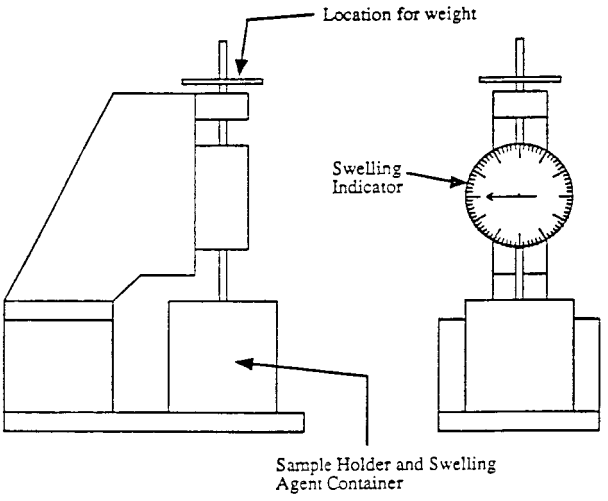


Figure 3 Device for measuring the swelling behavior of polyacrylate microparticles under load.

Degradation Studies

The degradation of crosslinked polyacrylate samples was investigated by determining their swelling behavior in various enzyme solutions at 37°C. The polymers tested were prepared by copolymerization of 40 and 60% neutralized AA with 6 or 12% olefinic PVA or styrene-based modified PVA as crosslinking agents and had crosslinking ratios of 0.0025 mol/mol. These samples were cut into disks of 0.3-mm thickness using a diamond blade, low-speed saw and weighed to determine the dry weight. The disks were swollen in 60 mL of 0.9% saline solution at room temperature for 1 h. After 1 h, the disks were weighed and placed in aqueous enzyme solutions at 37°C. The enzyme solutions (1 mg/mL of deionized water) were α-chymotrypsin, trypsin, and papain solution. During the degradation experiments, the disks were weighed every 24 h until maximum degradation (that is, loss of weight). The enzyme solutions were changed every 24 h for the first 72 h. Degradation of these samples was investigated by determining their swelling behavior and loss of weight in various enzyme solutions.

RESULTS AND DISCUSSION

Dynamic Swelling Studies

The crosslinked PAA samples prepared above and containing PVA as a potentially biodegradable component were highly swollen polymeric networks of the general crosslinked structure shown in Figure 2. As indicated before,[1,2] such materials, in order to be successfully applied for superabsorbent applications, must exhibit swelling capacities or equilibrium swelling ratios of at least 30 (in saline or equivalent solutions). As it is well known, this corresponds to a swelling ratio of at least 40 in deionized water; as increased ionic strength decreases the swelling ratio.

Figure 4 shows typical swelling data of PAA networks crosslinked with styrene-based modified PVA. The swelling process was complete in 45 to 60 min, and the equilibrium swelling ratio attained is 38 to 48, depending on the nominal crosslinking ratio used during the preparation. Indeed, the swelling increases as the crosslinking ratio decreased from $X = 0.01$ to 0.0025. The dynamic swelling uptake of these samples was Fickian in nature. Similar studies at a higher pH of the swelling medium were performed at values of 7.01 and 8.01, indicating a significant expansion of the network due to the ionization of the PAA structure (Figs. 5 and 6). These studies indicate that the swelling ratio values can increase up to 60, but that the crosslinking ratio is not an important parameter to the swelling process.

Figure 7 shows the effect of the pH of the solution on the dynamic swelling ratio of the PAA microparticles. All 4 studies were for nominal crosslinking ratio of 0.01. Clearly, those samples swollen at the highest pH exhibited a high dy-

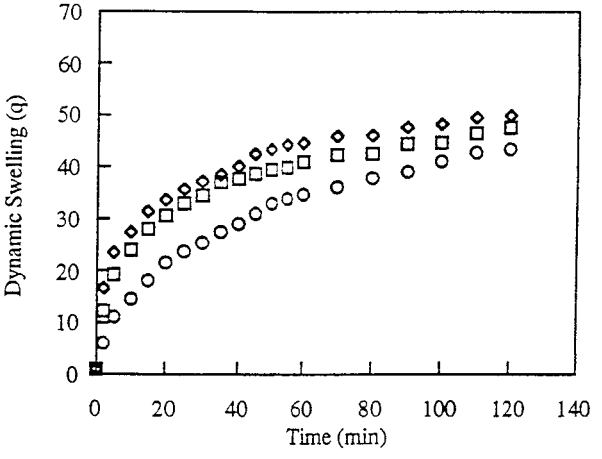


Figure 4 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in pH 5.01 for samples prepared from copolymerization of 40% neutralized AA with styrene-based modified PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

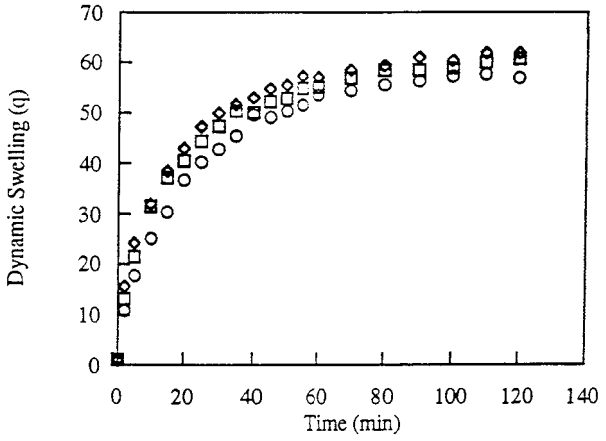


Figure 5 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in pH 7.01 for samples prepared from copolymerization of 40% neutralized AA with styrene-based modified PVA as a crosslinking agent. Nominal crosslinking ratios: *X* equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

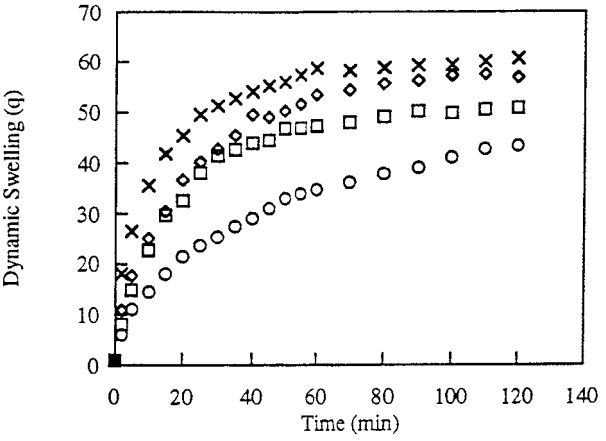


Figure 7 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in different pH solutions for samples prepared from copolymerization of 40% neutralized AA with styrene-based modified PVA as a crosslinking agent (0.01 mol/mol). PH solutions: (○) 5.01, (□) 6.02, (◇) 7.01, and (×) 8.01.

namic swelling, approaching a value of 60 after 2 h. All curves were fitted to Fickian diffusion equations. Thus, the transport from the dry to the swollen state was not relaxation-controlled, confirming what we had previously indicated in another publication.[2] An additional parameter of importance was the degree of neutralization of the acrylic acid used in preparation of the PAA microparticles. Figure 8 shows that the dynamic swelling in such particles is a function of the pH of the solution but that all the swelling curves are much closer than in the case of the 40%-neutralized PAA samples (Fig. 7).

In addition, the nature of the PVA crosslinks makes a big difference in the overall swelling behavior. For example, Figure 9 presents the dynamic swelling data of PAA microparticles copolymerized with 6% olefinic PVA as a crosslinking

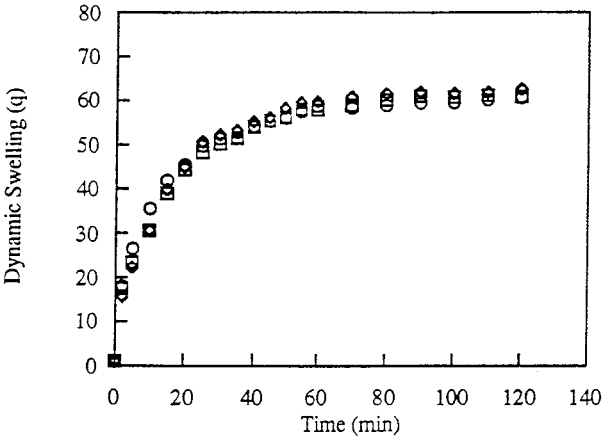


Figure 6 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in pH 8.01 for samples prepared from copolymerization of 40% neutralized AA with styrene-based modified PVA as a crosslinking agent. Nominal crosslinking ratios: *X* equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

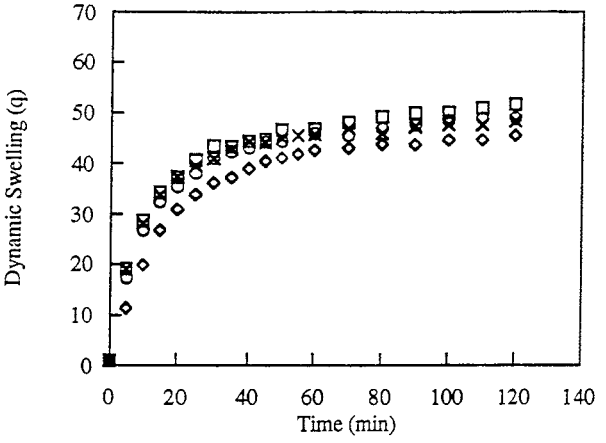


Figure 8 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in different pH solutions for samples prepared from copolymerization of 60% neutralized AA with styrene-based modified PVA as a crosslinking agent (0.01 mol/mol). PH solutions: (○) 5.01, (□) 6.02, (◇) 7.01, and (×) 8.00.

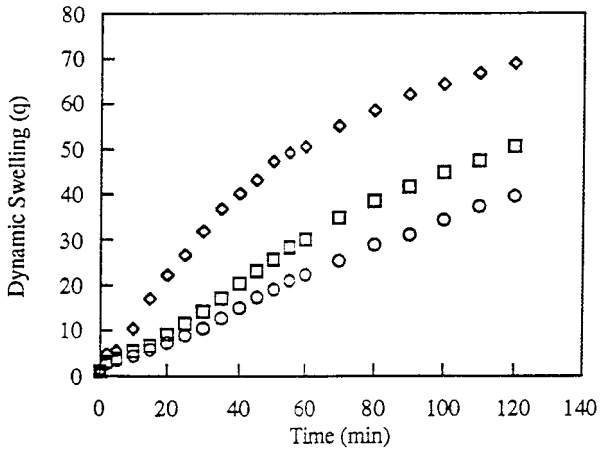


Figure 9 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in pH 5.01 solution for samples prepared from copolymerization of 60% neutralized AA with 6% olefinic PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

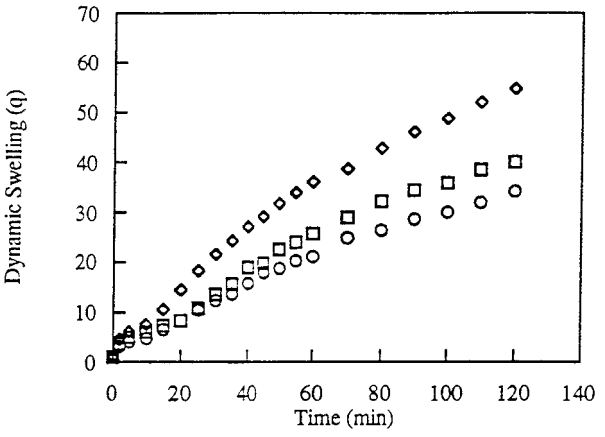


Figure 10 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in pH 8.01 solution for samples prepared from copolymerization of 60% neutralized AA with 6% olefinic PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

agent. Three distinct swelling curves are shown for nominal crosslinking ratios of 0.01, 0.005, and 0.0025. These particular curves indicate that although high swelling ratios are obtained after two h, approaching in the case of the last sample a value of 60, the dynamic behavior, especially in the first 40 min, is almost linear, that is, characteristic of a non-Fickian transport of water in the particles. The reason for this swelling abnormality is the fact that the 6% olefinic PVA imparts a hydrophobic nature to the overall structure. Comparison of the swelling data of the same PAA samples at pH 8.01 (Fig. 10) to the data of Figure 9 indicates that the linear portion of the swelling behavior from 0 to 40 min prevails, even when the PAA structure is highly ionized.

The linear swelling behavior at the beginning of the swelling process is not a very desirable characteristic for superabsorbent materials[1,2] as it may impart unnecessary stresses. To avoid this, we studied PAA microparticles produced from 40 and 60% neutralized AA and containing 12% olefinic PVA as a crosslinking agent. The results of the swelling behavior are shown in Figures 11 and 12. These figures indicate that Fickian swelling behavior was again attained in these PAA microparticles and that the equilibrium swelling value approached 44 in the most loosely crosslinked and highly swollen samples. As expected, the dynamic swelling ratio was highest for the gels with the lowest crosslinking ratio.

Dynamic Swelling Behavior Under Load

The dynamic swelling behavior of the previous PAA samples was determined under load using the equipment described in Figure 3. In a typical experiment, the height (thickness) of the swollen gel was measured as a function of time.

The height was translated into a volume change using the following equation:

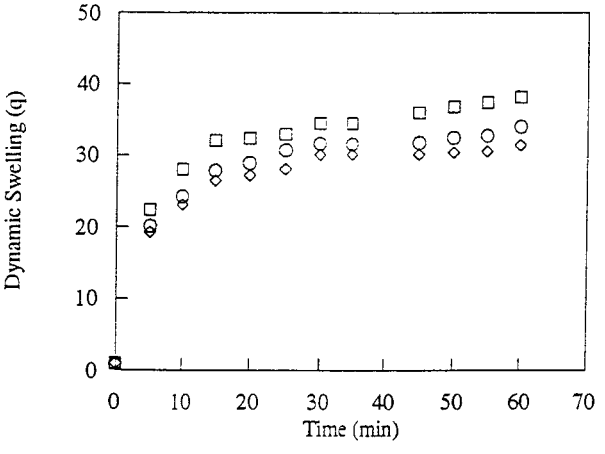


Figure 11 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in saline solution for samples prepared from copolymerization of 40% neutralized AA with 12% olefinic PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.0025, and (◇) 0.0025.

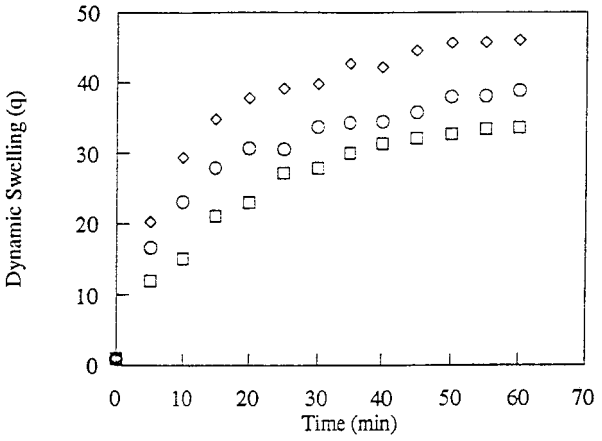


Figure 12 Dynamic swelling ratio (g swollen PAA/g dry PAA) of polyacrylate microparticles in pH 8 solution for samples prepared from copolymerization of 60% neutralized AA with 12% olefinic PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.0025, and (◇) 0.0025.

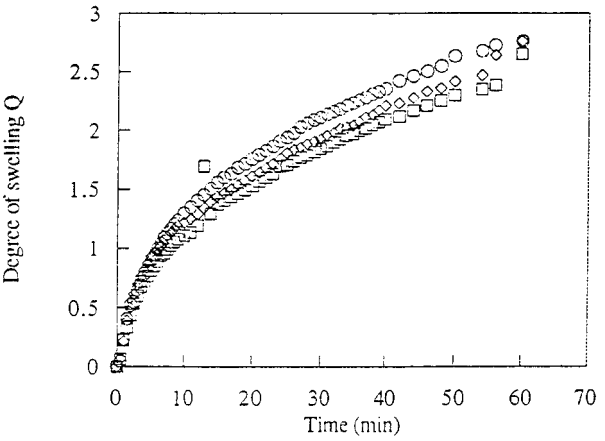


Figure 13 Degree of swelling (vol swollen PAA/vol dry PAA) of polyacrylate microparticles in saline at 25°C under a load of 103 g for samples prepared from copolymerization of 40% neutralized acrylic acid with styrene-based modified PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

$$V_s = h_s \frac{\pi D^2}{4} \tag{4}$$

where V_s is the volume of swollen gel, h_s is the height of swollen gel, and D is the diameter of the sample (4.45 cm).

The volume of dry polymer, V_d, was calculated from the following equation

$$V_d = \frac{W_d}{\rho} \tag{5}$$

where W_d is the weight of dry polymer sample, and ρ is the density of polymer (1.276 g/cm^3).

From the above data, the volume degree of swelling, Q was determined using the following equation.

$$Q = \frac{V_s}{V_d} \tag{6}$$

Figures 13 to 15 show the dynamic swelling behavior of PAA microparticles under a load of 103 g. Clearly, the degree of swelling was significantly lower than in the free swelling experiments. For example, PAA microparticles from 40% neutralized acrylic acid and crosslinked with styrene-based, modified PVA exhibited equilibrium swelling values of about 2.8 after approximately 1 h (as compared to values of 40 for the free swelling samples). Such values corresponded to an equilibrium polymer volume fraction of about 35% versus a value of 2.5% for the free swelling samples. The equilibrium value was even lower for samples prepared from 6% olefinic PVA (Fig. 14). In all samples, the dynamic swelling behavior was Fickian. Per-

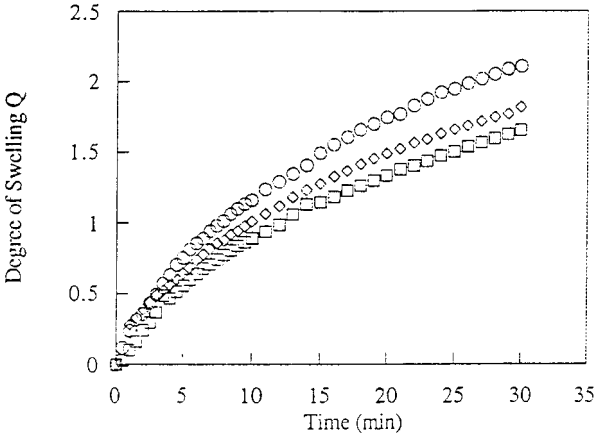


Figure 14 Degree of swelling (vol swollen PAA/vol dry PAA) of polyacrylate microparticles in saline at 25°C under a load of 103 g for samples prepared from copolymerization of 40% neutralized acrylic acid with 6% olefinic PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

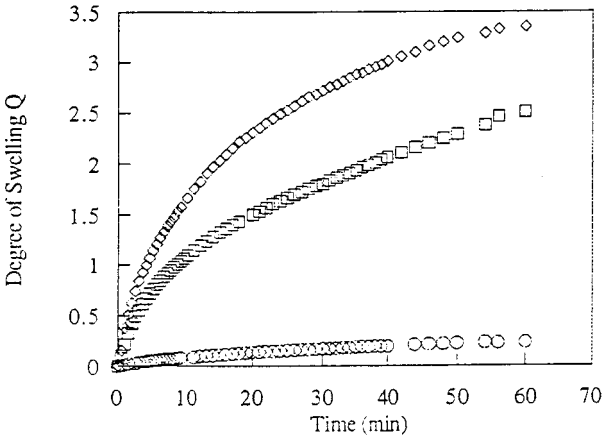


Figure 15 Degree of swelling (vol swollen PAA/vol dry PAA) of polyacrylate microparticles in saline at 25°C under a load of 103 g for samples prepared from copolymerization of 60% neutralized acrylic acid with 6% olefinic PVA as a crosslinking agent. Nominal crosslinking ratios: X equals (○) 0.01, (□) 0.005, and (◇) 0.0025.

haps the most striking difference in swelling behavior was observed with PAA microparticles produced from 60% neutralized acrylic acid and crosslinked both 6% olefinic PVA. As shown in Figure 15, small changes in the nominal crosslinking ratio led to drastic differences in the swelling ratio. Of course, analysis of the load-dependent conditions can be done, as discussed by Bell and Peppas.[3]

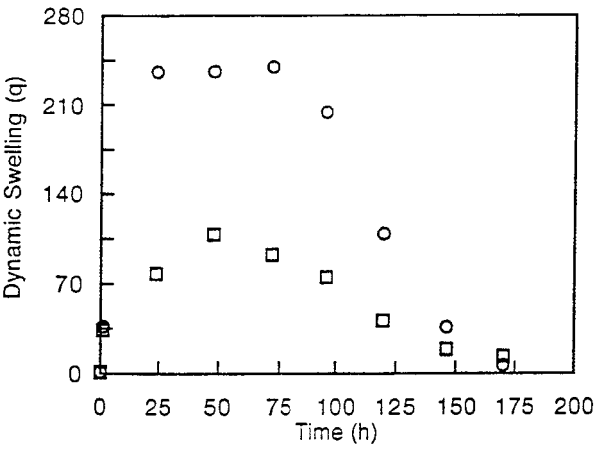


Figure 17 Dynamic swelling ratio of polyacrylate networks in α-chymotrypsin solution (1 mg/mL) at 37°C for samples prepared from copolymerization of AA with styrene-based modified PVA (X = 0.0025 mol/mol). Samples prepared from (○) 40 and (□) 60% neutralized AA.

Swelling During Degradation Studies

To investigate the possible biodegradation characteristics of the PVA links between PAA chains, we examined the swelling behavior of PAA networks in α-chymotrypsin and papain solutions. Figures 16 and 17 show the swelling behavior in α-chymotrypsin solutions for 2 different types of PAA microparticles. In both cases, degradation began anywhere from 25 to 75 min after contact

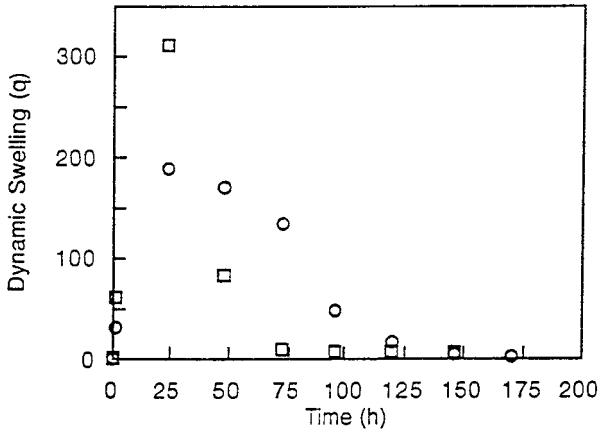


Figure 16 Dynamic swelling ratio of polyacrylate networks in α-chymotrypsin solution (1 mg/mL) at 37°C for samples prepared from copolymerization of AA with 6% olefinic PVA (X = 0.0025 mol/mol). Samples prepared from (○) 40 and (□) 60% neutralized AA.

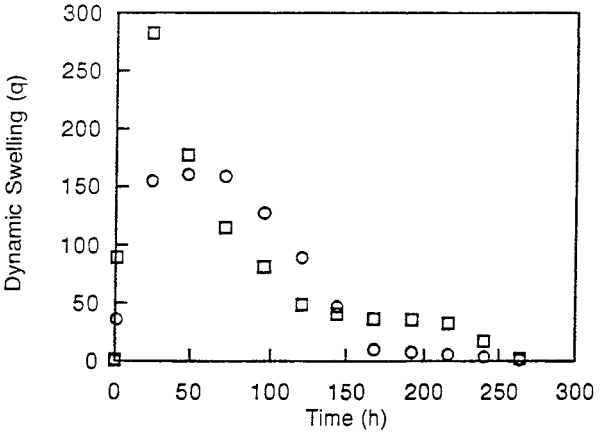


Figure 18 Dynamic swelling ratio of polyacrylate networks in papain solution (1 mg/mL) at 37°C for samples prepared from copolymerization of AA with 6% olefinic PVA (X = 0.0025 mol/mol). Samples prepared from (○) 40 and (□) 60% neutralized AA.

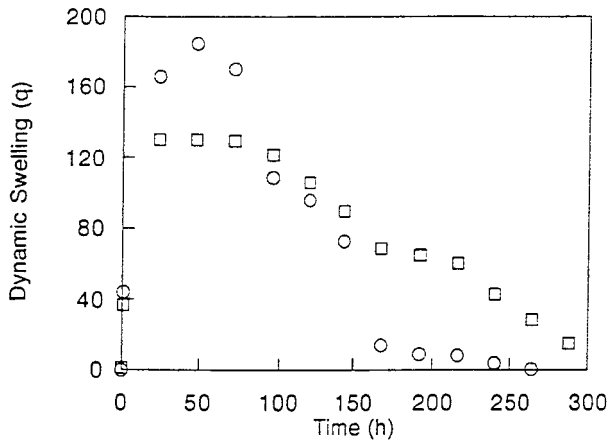


Figure 19 Dynamic swelling ratio of polyacrylate networks in papain solution (1 mg/mL) at 37°C for samples prepared from copolymerization of AA with styrene-based modified PVA ($X = 0.0025$ mol/mol). Samples prepared from (○) 40 and (□) 60% neutralized AA.

with the enzyme solution, and the dynamic swelling ratio changed from values of 250 to values of 2, indicating a significant loss of the three-dimensional structure of the network. The same behavior was observed in papain solutions (Figs. 18 and 19), although there the dynamic swelling ratio and the associated degradation process were functions of the degree of neutralization of the initial AA used. These results clearly indicate that PVA can be considered a desirable moiety for the development of biodegradable superabsorbent materials.

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