Effect of Porosigen and Hydrophobic Monomer on the Fast Swelling–Deswelling Behaviors for the Porous Thermoreversible Copolymeric Hydrogels

Wen-Fu Lee, Yu-Chen Yeh

Department of Chemical Engineering, Tatung University, Taipei, Taiwan, Republic of China

ABSTRACT: A series of porous thermoreversible copolymeric hydrogels were prepared from *N*-isopropylacrylamide (NIPAAm) and hydrophobic monomers such as 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) and *n*-butyl methacrylate (BMA) and $CaCO_3$ or poly(ethylene glycol) 8000 (PEG8000) as porosigen by emulsion polymerization. The effect of hydrophobic monomers and porosigens on the fundamental properties, such as equilibrium swelling ratio, swelling kinetics, gel strength, crosslinked densities, etc., and fast swelling–deswelling behavior for the present copolymeric hydrogels were investigated. Results showed that the deswelling rates for the gels porosigened by $CaCO_3$ were more rapid than those gels foamed by PEG8000. Results also showed that the swelling rates for the gel foamed by $CaCO_3$ were higher than those for the gel foamed by PEG8000. At the same time, results also showed that the gels with OFPMA foamed by $CaCO_3$ exhibit a faster swelling–deswelling behavior than those gels with BMA. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3152–3160, 2006

Key words: NIPAAm; perfluoroalkyl methacrylate; hydrogel; swelling–deswelling behavior

INTRODUCTION

Environmentally sensitive hydrogels have the ability to make response to change in their external environment. They can exhibit marked changes in their swelling behavior, network structure, permeability, or mechanical strength in response to change in the pH, ionic strength, temperature, electrical, or magnetic fields, etc.[1–5] Because of their nature, the materials can be used in a wide variety of applications, such as separation membranes, biosensors, artificial muscles, chemical valves, and drug delivery devices.[6–11] Thermosensitive hydrogels are attractive materials because of the ability of the hydrogels to swell or deswell as a result of changing temperature of the surrounding solution, and have been studied for their applications, such as on–off drug release regulations, biosensor, and intelligent cell culture dishes.[12]

Drug molecules loaded in a dried hydrogel are slowly released because of the slow diffusion of water through the glassy matrix of the dried hydrogels. Because of the aforementioned description, absorption of water into hydrogels by capillary wetting was explored to overcome the slow swelling. Formation of pores in hydrogels was one of the methods that make dried hydrogels swell rapidly by effective capillary action. Furthermore, the pores had to interconnect to provide capillary channels. That is, open channels had to be formed. Dried hydrogels with open channel structure swelled rapidly by capillary action instead of diffusion of water through the glassy matrix, and this allows extremely fast swelling of the hydrogels. Slow swelling of dried hydrogels was useful for many applications, but fast swelling was also important in some applications.[13,14] For instance, Park and coworkers reported that dried poly(vinyl pyrrolidone) (PVP) hydrogels were emptied from the stomach in less than an hour. Fully swollen PVP hydrogels were retained in canine stomach for more than 24 h and up to 60 h.[15,16] That is, fast swelling was necessary for PVP hydrogels to retain in stomach for a long time. Porous hydrogels can be prepared by a variety of methods, such as the porosigen method, phase separation technique, and gas blowing technique. In the porosigen method, porous hydrogels may be prepared by adding dispersed water-soluble porosigens, such as PEG,[17] sodium chloride,[18,19] and micronized sucrose,[20] which can be removed by washing with water. Park and coworkers also used the gas-blowing technique to prepare a series of superporous hydrogels based on *N*-Isopropylacrylamide (NIPAAm)/acrylamide and poly(acrylic acid) gels.[21–23] The NIPAAm/ OFPMA (2,2,3,3,4,4,5,5-octafluoropentyl methacrylate)

TABLE I
Feed Compositions, Yields, and Equilibrium Swelling Ratios for the Present Copolymeric
Hydrogels Porosigened by PEG8000 and CaCO$_3$

Sample codes	NIPAAm (mol %)	OFPMA (mol %)	BMA (mol %)	Yield (%)		Swelling ratio (g/g)	
				PEG8000	CaCO$_3$	PEG8000	CaCO$_3$
N	100	0	–	98	95.5	7.67	7.0
F1	99	1	–	98	95.6	7.49	6.95
F3	97	3	–	97	94.2	7.41	6.89
F5	95	5	–	97	95.5	7.33	6.80
F7	93	7	–	98	95.4	7.30	6.75
B1	99	–	1	98.2	97.2	7.21	6.84
B3	97	–	3	98.6	97.3	7.09	6.82
B5	95	–	5	97	97.5	7.01	6.75
B7	93	–	7	97.5	98.8	6.99	6.69

and NIPAAm/BMA (*n*-butyl methacrylate) copolymeric hydrogels were reported in our previous study.[24] Those gels showed that NIPAAm/hydrophobic monomers copolymeric hydrogels had better gel strengths than poly(NIPAAm) gel. Hydrophobic moiety could improve deswelling rate of the gels. However, strong hydrophobicity made gels form thicker and denser skin layer at surface under high temperature, and so the hydrogels could not reswell at a short time period. To improve this problem in these gel systems, introducing porous structure into these gels was designed. Hence, a series of porous gels were prepared by adding PEG8000 and CaCO$_3$ as porosigen in this article. The effect of hydrophobic monomer and porosigen on the fast swelling–deswelling behavior for these thermoreversible porous gels was investigated.

EXPERIMENTAL

Materials

N-Isopropylacrylamide (NIPAAm) (Wako Pure Chemical Industries, Osaka, Japan) was recrystallized in *n*-hexane before use. Perfluoroalkyl methacrylate, 2,2,3,3,4,4,5,5-octafluoropentyl methacrylate (OFPMA) (Aldrich Chemical, St. Louis, MO) and butyl methacrylate (BMA) (Fluka Chemical, Buchs, Switzerland) were used as received. *N,N'*-methylenebisacrylamide (NMBA) (Sigma Chemical, St. Louis, MO) as a crosslinker, ammonium persulfate (APS) (Wako Pure Chemical Industries, Osaka, Japan) as an initiator, sodium lauryl sulfate (SLS) (Nippon Shiyaku Industries, Osaka, Japan) as emulsifier, and *N,N,N',N'*-tetramethylethylene diamine (TEMED) (Fluka Chemical, Buchs, Switzerland) as an accelerator were used as received. Calcium carbonate (CaCO$_3$) (Shimakyu's Pure Chemicals, Osaka, Japan) and poly(ethylene glycol) 8000 (PEG 8000) (Fluka Chemical, Buchs, Switzerland) as porosigens were used as received. All solvents and other chemicals were of analytical grade.

Preparation of copolymeric hydrogels

NIPAAm and hydrophobic monomer (OFPMA or BMA) with various molar ratios were dissolved in 10 mL of deionized water. To these solutions, 3 mol % NMBA, 0.2 mol % APS, 2 mol % SLS, and 0.1 g porosigen were added and well mixed. Finally, 0.2 mol % TEMED was added and the monomer solution was immediately injected into the space between glass plates. Polymerization was carried out at 25°C for 1 day. After the gelation was completed, the gel membrane was cut into disks, 8 mm in diameter. If CaCO$_3$ was used as porosigen, the gels were immersed into 1*N* HCl solution for 1 day to remove CaCO$_3$. Then the gels were immersed in an excess amount of deionized water for 3 days. If PEG8000 was used as porosigen, the gels were directly immersed in an excess amount of deionized water for 3 days. Swollen gels were dried at 40°C for 2 days, and these samples were further dried in a vacuum oven (room temperature) for 1 day. The feed compositions, yields, and equilibrium-swelling ratios of the porous copolymeric hydrogels are shown in Table I.

Measurement of swelling kinetic

The swelling kinetics of the gels was measured at 25°C after wiping off water on the surface with filter paper. The swelling ratios of the gels were recorded at the course of swelling at each regular time interval.

$$SR = (W_w - W_d)/W_d \qquad (1)$$

where W_w is the weight of the wet gel at different times and W_d is the weight of the dry gel.

To obtain diffusion coefficient (*D*) of the hydrogels, the initial swelling data ($W_t/W_\infty \leq 0.8$) were fitted to the following equation[25]:

$$\frac{W_t}{W_\infty} = \frac{4}{\sqrt{\pi}}\left(\frac{Dt}{L^2}\right)^{1/2} \qquad (2)$$

where W_t is the weight of the gel at regular time intervals and W_∞ is the weight of the fully swollen gels. L is the thickness of the dried hydrogel. The diffusion coefficient D can be calculated from the slope $4(D/\pi)^{1/2}$ of the plot of W_t/W_∞ against $(t/L^2)^{1/2}$ from eq. (2).

Besides, to obtain more quantitative understanding of the sorption kinetic for the hydrogels, the initial swelling data ($W_t/W_\infty \leq 0.6$) were fitted to the following equation[26,27]:

$$W_t/W_\infty = kt^n \tag{3}$$

where k is a characteristic constant of the gel and n is a characteristic exponent of the transport mode of the penetrate. n and k were calculated from the slopes and intercepts of the plot of $\log(W_t/W_\infty)$ against $\log(t)$.

Measurement of deswelling kinetics

The kinetic of deswelling behavior of the hydrogels is measured at 45°C. Before the measurement of deswelling kinetics, the hydrogel reached swollen equilibrium in distilled water at 25°C in advance. After wiping off water on the surface with filter paper, the weight change of the gel was recorded during the course of deswelling at regular time intervals.

The deswelling ratio (DSR)(%) is defined as follows:

$$\text{DSR (\%)} = (\text{SR}/\text{SR}_{\text{eq}})100\% \tag{4}$$

where SR_{eq} is the swelling ratio at equilibrium of the gel.

Physical properties of the copolymeric gels

The dried gels were immersed in 10 mL of deionized water at 25°C for 2 days to reach equilibrium. The diameter and thickness of the gels were recorded. The mechanical strength of the copolymeric gels was measured by uniaxial compression experiment with universal tester (LLOYD LRX). The shear modulus was calculated by the following equation[28,29]:

$$\tau = F/A = G(\lambda - \lambda^{-2}) \tag{5}$$

where τ is compression stress, F is compression load, A is crosssectional area of the swollen gels, and λ is the compression strain (L/L_0), where L is the thickness of the wet gel after compression, L_0 is the thickness of the dried gels. At low strain, a plot of shear stress versus $-(\lambda-\lambda^{-2})$ would yield a straight line whose slope is shear modulus (G). The effective crosslinking density (ρ_x) can then be calculated from shear modulus and polymer volume fraction (V_2) as follows[28,29]:

$$\rho_x = GV_2^{-1/3}/(RT) \tag{6}$$

where R is the gas constant and T is the absolute temperature.

Fast swelling–deswelling behavior of the copolymeric hydrogels

Preweighed dried gels were immersed in deionized water at 25°C to reach equilibrium. The gels were transferred into 10 mL of deionized water at 45°C at each fixed time interval (5 min), then the gels were immediately transferred into deionized water at 25°C. The above steps were repeated for 2 h and the weights of the gels were measured to calculate the swelling ratio for each time interval.

SEM morphologies

Samples were equilibrated in deionized water for 1 day, and then the swollen gels were frozen-dried for 2 days. The gels were immersed in liquid nitrogen and fractured. The fractured specimens were examined for morphological details by using scanning electron microscopy (SEM) (JEOL JXA6700) with an acceleration voltage of 15 kV. The specimens were coated with a gold metal layer to provide proper surface conduction.

RESULTS AND DISCUSSION

Effect of hydrophobic monomer content and porosigen on swelling behaviors

The influence of the hydrophobic monomer content and pore-foaming agent on the swelling ratio of the copolymeric hydrogels is shown in Table I. The results in Table I indicated that the equilibrium-swelling ratios for the copolymeric gels decreased with an increase of the hydrophobic monomer content. The results also explicitly demonstrated that the higher the content of hydrophobic monomer in the gels, the more the hydrophobicity of the gels, and the less the swelling ratio of the gels. Similar results were observed from our previous studies.[24,30] In addition, the results also showed that the swelling ratios for F-series gels were higher than those for B-series gels. But, this result is contrary to the previous study, which showed the swelling ratios for F-series gels slightly lower than those for B-series gels.[24] This contrary result can be attributed to the pore-effect of the porous gels. The results also indicated that the swelling ratios for the gels foamed by PEG8000 were higher than those gels foamed by $CaCO_3$.
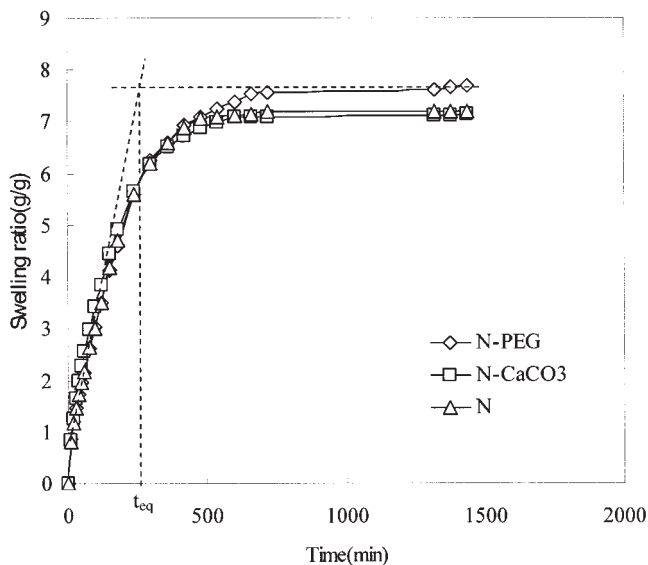
Figure 1 Swelling ratios as a function of time for the poly-(NIPAAm) hydrogels with different porosigens (0.1 g) at 25°C.

Figure 3 Swelling ratios as a function of time for the B3 copolymeric hydrogels with different porosigen (0.1 g) at 25°C.

Investigation of water diffusion in xerogels

The typical profiles of the swelling ratios as a function of time for N, F3, and B3 gel porosigened with PEG8000 and CaCO$_3$ are shown in Figures 1–3, respectively. From these figures, the swelling parameters such as n, k, and D can be calculated from eqs. (2) and (3). The swelling exponents, n, for the copolymeric hydrogels shown in Table II are less than 0.5. These results imply that the transport mechanism belongs to Fickian diffusion according to the classification of the relative rates of diffusion and polymer relaxation pro-
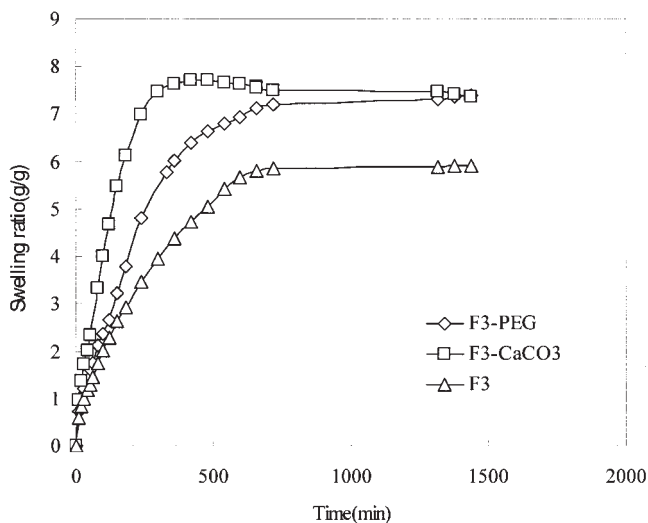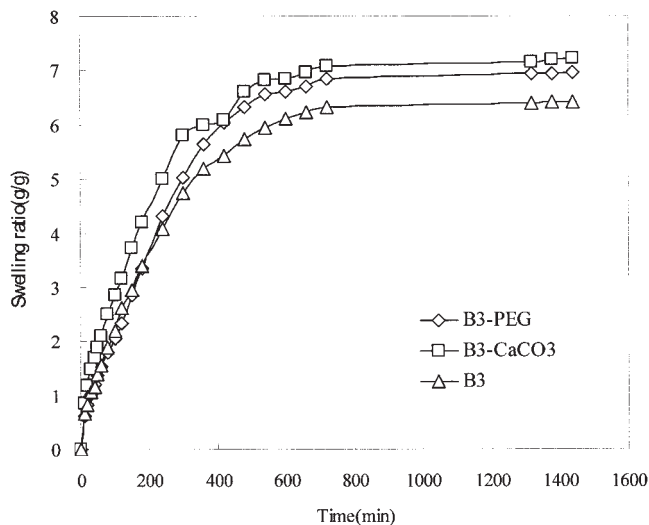
posed by Alfrey et al.[31] In addition, the results also showed that the gels porosigened by CaCO$_3$ had larger D than those porosigened by PEG8000. The initial swelling rates and the times required to approach equilibrium swelling ratio for the N, F3, and B3 gels porosigened by CaCO$_3$ and PEG8000 are shown in Table III. The results showed that the initial swelling rate at initial period (60 min) decreased when the hydrophobic monomer was incorporated into N gel. But, CaCO$_3$ significantly improved the initial swelling rates for F3 and B3 gels porosigened. The results also indicated that the gels porosigened by CaCO$_3$ could reach swelling equilibrium faster than those porosigened by PEG8000, especially for F3 gel. This can be attributed that bigger and interconnected pores in the gels porosigened by CaCO$_3$ were formed. Interconnected pores could effectively create capillarity channels, so the water absorption rate could be improved. Comparing the effect of these two porosigens, the gels porosigened by CaCO$_3$ had faster absorption rate than those porosigened by PEG8000.

Effect of organic/inorganic porosigen on deswelling behaviors

The typical profiles of the deswelling ratios as a function of time for N, F3, and B3 gel porosigened with PEG8000 and CaCO$_3$ are shown in Figures 4–6, respectively. The results showed that the equilibrium deswelling ratios are 14.7, 19.3, and 25.3% for N, F3, and B3 gels, respectively. This result indicated that when the hydrophobic monomer was incorporated into the NIPAAm gel, the skin layer of the copolymeric gel became denser and resulted in more water residing in the inside gel. But after adding porosigen,

Figure 2 Swelling ratios as a function of time for the F3 copolymeric hydrogels with different porosigens (0.1 g) at 25°C.

TABLE II
Initial Diffusion Coefficient of Water (D), Kinetic Exponent (n), and Characteristic Constant (k) of Water Penetrated Through Copolymeric Gels Porosigened by PEG8000 (0.1 g) and $CaCO_3$ (0.1 g)

Sample code	n		K (10^2)		D (10^8, cm^2/s)	
	PEG8000	$CaCO_3$	PEG8000	$CaCO_3$	PEG8000	$CaCO_3$
N	0.35	0.39	2.0	1.74	7.16	11.8
F1	0.38	0.42	1.8	1.27	7.27	9.16
F3	0.35	0.44	2.0	1.27	6.38	14.5
F5	0.35	0.45	2.0	1.24	6.59	11.9
F7	0.35	0.41	2.0	1.67	6.25	10.9
B1	0.37	0.36	1.96	2.12	6.88	8.94
B3	0.35	0.34	2.45	2.31	6.24	8.99
B5	0.34	0.34	2.67	2.43	7.10	8.20
B7	0.33	0.34	2.58	2.76	6.60	9.80

the deswelling ratio decreased 6.1, 7.2, and 18.4% for N, F3, and B3 gels porosigened with PEG8000; and 2.7, 9.0, and 12.5% for N, F3, and B3 gel porosigened with $CaCO_3$. The result obviously indicated that the water inside the gel could be easily drained out of the gels, especially for B3 gel. However, the porosigen effect for N gel was not significant, especially for $CaCO_3$. In addition, the initial deswelling rate (IDR) significantly increased with incorporating the porosigen into the gel, such as for N gel, the IDR increased from 1.18 to 2.8 (%/min) and 2.7 (%/min) for PEG8000 and $CaCO_3$; for F3 gel, the IDR increased from 0.9 to 1.57 (%/min) and 2.10 (%/min) for PEG8000 and $CaCO_3$; for B3, the IDR increased from 0.94 (%/min) to 1.37 (%/min) and 1.43 (%/min) for PEG8000 and $CaCO_3$. In contrast, the time required for approaching the start of the equilibrium-deswelling ratio (t_{eq}), is defined in Figure 4 (shown in Table IV). The t_{eq}s were shortened from 60, 65, and 61 min to 31, 38, and 45 min for N, F3, and B3 gels porosigened with $CaCO_3$, respectively. Hence, adding $CaCO_3$ in the gels can approach the deswelling equilibrium for F3 and B3 gel faster.

Effect of organic/inorganic porosigen on mechanical properties

The effect of organic/inorganic porosigen on mechanical properties was shown in Table V. The results

TABLE III
Initial Swelling Rates and Times Required to Approach Equilibrium Swelling Ratio for the Gels Porosigened by PEG8000 and $CaCO_3$

Sample codes	Initial swelling rates (10^2, g/min)			Time (min)[a]	
		PEG8000	$CaCO_3$	PEG800	$CaCO_3$
N	3.63	3.57	3.79	480	660	540
F3	2.42	2.90	3.88	900	660	300
B3	2.62	2.57	3.51	780	660	660

[a] The time required approaching equilibrium swelling ratio for the gels porosigened by PEG8000 and $CaCO_3$ that is defined in Figure 1.

showed that the shear moduli (G) and effective crosslinking densities (ρ_x) increased with an increase of the hydrophobic monomer content in the gels. The G and ρ_x values ranged from 338 to 1175 (g/cm^2) and 2.59 to 8.47 $\times$ 10^{-5} (mol/cm^3) for the gels without adding porosigen as well as those values from 262 to 435 (g/cm^2) and 1.72 to 3.33 $\times$ 10^{-5} (mol/cm^3) for the gels with adding porosigen, respectively. From these data, we find that the shear modulus and effective crosslinking density were much lower for the gels foamed by porosigen than those gels without adding porosigen. This maybe attributed that there is much pore in the gels, which led the dense structure of the gel to be destroyed. In addition, the G and ρ_x values for F-series gels porosigened by PEG8000 were smaller than those gels porosigened by $CaCO_3$, but, for B-
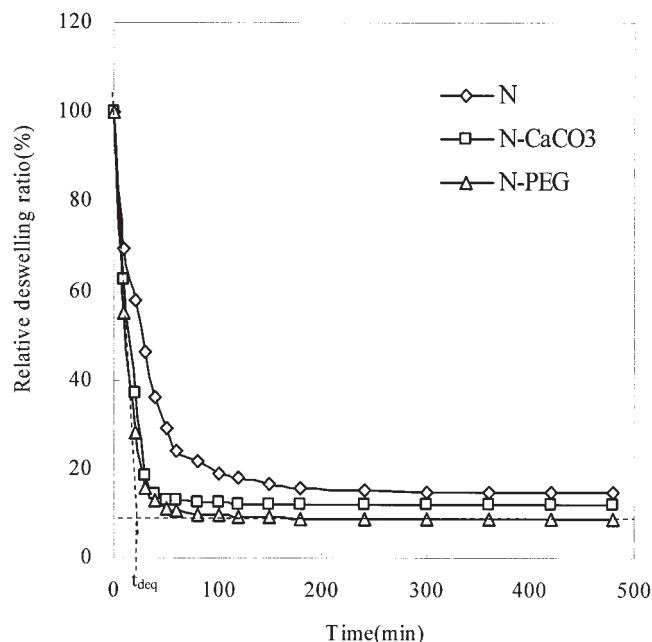
Figure 4 Swelling ratios as a function of time for the poly-(NIPAAm) hydrogels with different porosigens (0.1 g) at 45°C.
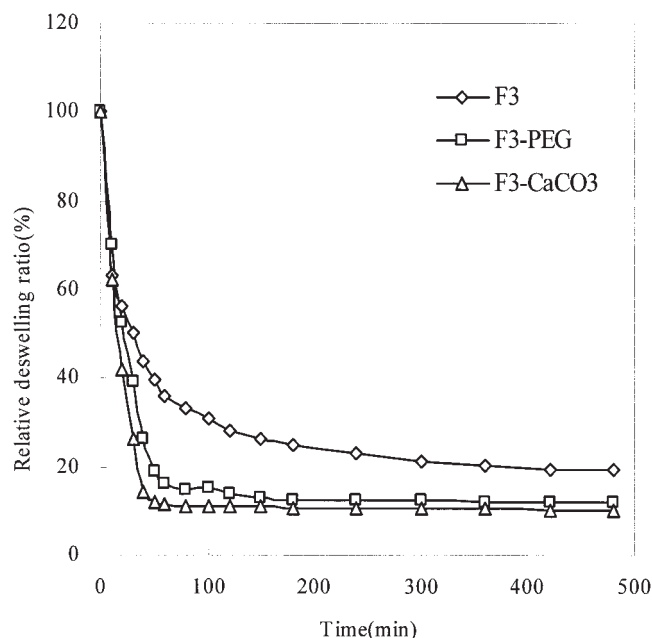
Figure 5 Swelling ratios as a function of time for the F3 copolymeric hydrogels with different porosigens (0.1 g) at 45°C.

series gels, a contrary result was obtained. This may be due to PEG8000 having higher molecular weight and longer chain length. Hence, it may produce much more "open channel". And, more open channels would make the strength of the gels weaker. Besides, PEG8000 is soluble in monomer solution homoge-
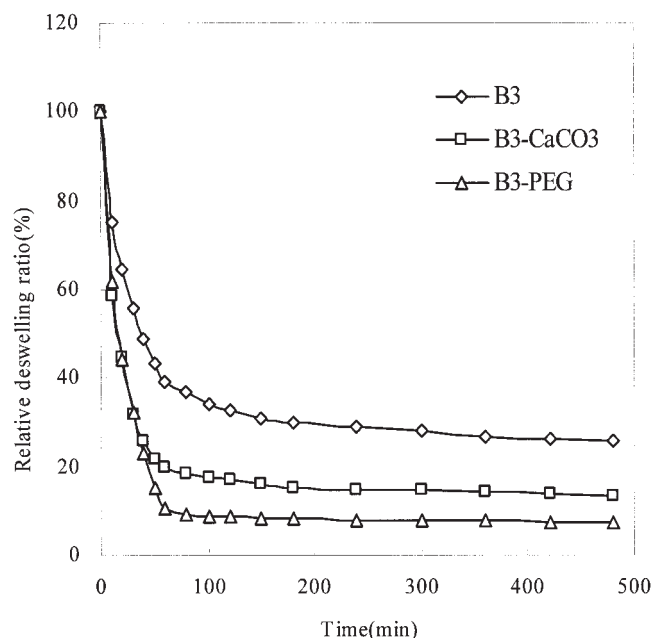

Figure 6 Swelling ratios as a function of time for the B3 copolymeric hydrogels with different porosigens (0.1 g) at 45°C.

TABLE IV
Effect of Porosigen on the Deswelling Behavior for N, F3, and B3 Gels

				PEG8000			CaCO₃		
	DSR (%)	IDR (%/min)	t_{eq}^a (min)	ΔDSR (%)	IDR (%/min)	t_{eq}^a (min)	ΔDSR (%)	IDR (%)	t_{eq}^a (min)
N	14.7	1.18	60	6.1	2.8	29	2.72	2.70	31
F3	19.3	0.90	65	7.2	1.57	48	9.0	2.10	38
B3	25.7	0.94	61	18.5	1.37	55	12.5	1.43	45

DSR, equilibrium deswelling ratio (%); IDR, initial deswelling rate (%/min).

ΔDSR is defined as the difference of DSR between the deswelling ratios of the gels having or no porosigens, i.e. $\Delta DSR = DSR - DSR_{PEG\ or\ CaCO3}$.

[a] The time required to approach the start of the equilibrium deswelling ratio that is defined in Figure 4.

neously, and these properties can make PEG8000 produce more open channels than CaCO₃.

Effect of porosigens on fast swelling–deswelling behavior

The effect of organic or inorganic porosigen on fast swelling–deswelling behavior for the gels, N, F3, and B3, were preformed during 25 and 45°C at each fixed time interval (5 min). The results in Figures 7–9 showed that the gels foaming with porosigens reached to swelling–deswelling equilibrium more rapidly and much more water could be drained out of the gels, especially for N and F3 gels. This is because more pore channels were formed in the gels. Hence, when the temperature became higher (45°C), much more water stored in the gels could drain out of the gels through pore channel. In addition, the time required approaching the fast swelling–deswelling equilibrium (defined in Fig. 7) were listed in Table VI. From Table VI, the time required to approach the fast swelling–deswelling equilibrium for N gel porosigened by CaCO₃ was shortened from 100 to 50 min. But for F3 and B3 gels, the times were only, shortened from 50 to 45 and from

TABLE V
Effect of Porosigen on the Gel Strengths and Crosslinking Densities of Copolymeric Hydrogels Porosigened by PEG8000 (0.1 g) and CaCO₃ (0.1 g)

Sample codes	G (g/cm²)			ρ_x (10⁵, mol/cm³)		
		PEG8000	CaCO₃		PEG8000	CaCO₃
N	338[a]	300	262	2.59[a]	2.10	1.72
F1	424[a]	290	274	3.21[a]	2.10	1.90
F3	853[a]	290	312	6.47[a]	2.13	2.20
F5	1006[a]	297	318	7.44[a]	2.17	2.27
F7	1175[a]	305	429	8.47[a]	2.17	2.89
B1	499[a]	304	315	3.79[a]	2.33	2.42
B3	541[a]	349	333	4.02[a]	2.67	2.55
B5	659[a]	417	340	4.85[a]	3.19	2.61
B7	956[a]	435	390	6.92[a]	3.33	2.86

[a] The gel was formed without adding porosigen.

Figure 7 Fast swelling–deswelling behaviors of poly-(NIPAAm) hydrogels with different porosigens between 25 and 45°C.

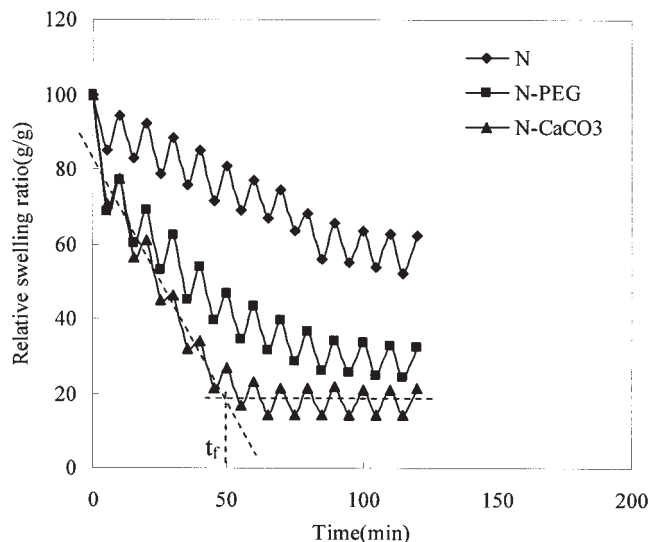**Figure 9** Fast swelling–deswelling behaviors of B3 gels with different porosigens between 25 and 45°C.

40 to 35 min, respectively. Hence, the porosigen effect was not obvious in those gels. Compared to two different kinds of porosigen, there was no significant difference. They both could improve deswelling rate, but the response time was still not short enough and the amplitude of the fast deswelling–swelling were not satisfactory.

Morphologies

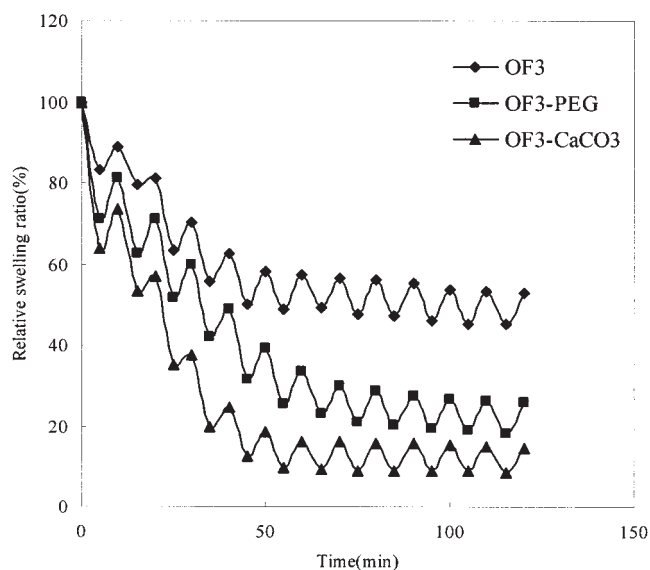SEM microphotographs of the copolymeric hydrogels were shown in Figure 10. From these microphoto-

graphs, we could find that after adding porosigen, the gels had more open channels and the pore size for gels porosigened by PEG8000 increased in the order B3 > F3 > N, but those for gels porosigened by $CaCO_3$ had nearly uniform size. This is because $CaCO_3$ particles were homogeneously dispersed in the monomer solution; the pores size of the gels would be homogeneous. In addition, the pore size for the gels without adding porosigen had irregular size morphologies. These morphologies explicitly indicted that adding porosigen can control the pore size of the gel. The pore volume and pore size of the gels were also affected by the content of the porosigen.

CONCLUSIONS

Porous NIPAAm/OFPMA, NIPAAm/BMA copolymeric hydrogels were prepared from adding organic (PEG8000) or inorganic ($CaCO_3$) porosigen and leached them out to form porous structure. The gels porosigened by porosigen could enhance swelling, deswelling behaviors and fast swelling–deswelling behavior. The results indicated that the gels porosigened by $CaCO_3$ could reach swelling equilibrium faster than those porosigened by PEG8000, especially for F3 gel. The IDR significantly increased with the

Figure 8 Fast swelling–deswelling behaviors of F3 gels with different porosigens between 25 and 45°C.

TABLE VI
Time Required for Approaching the Fast Swelling–Deswelling Equilibrium (min)

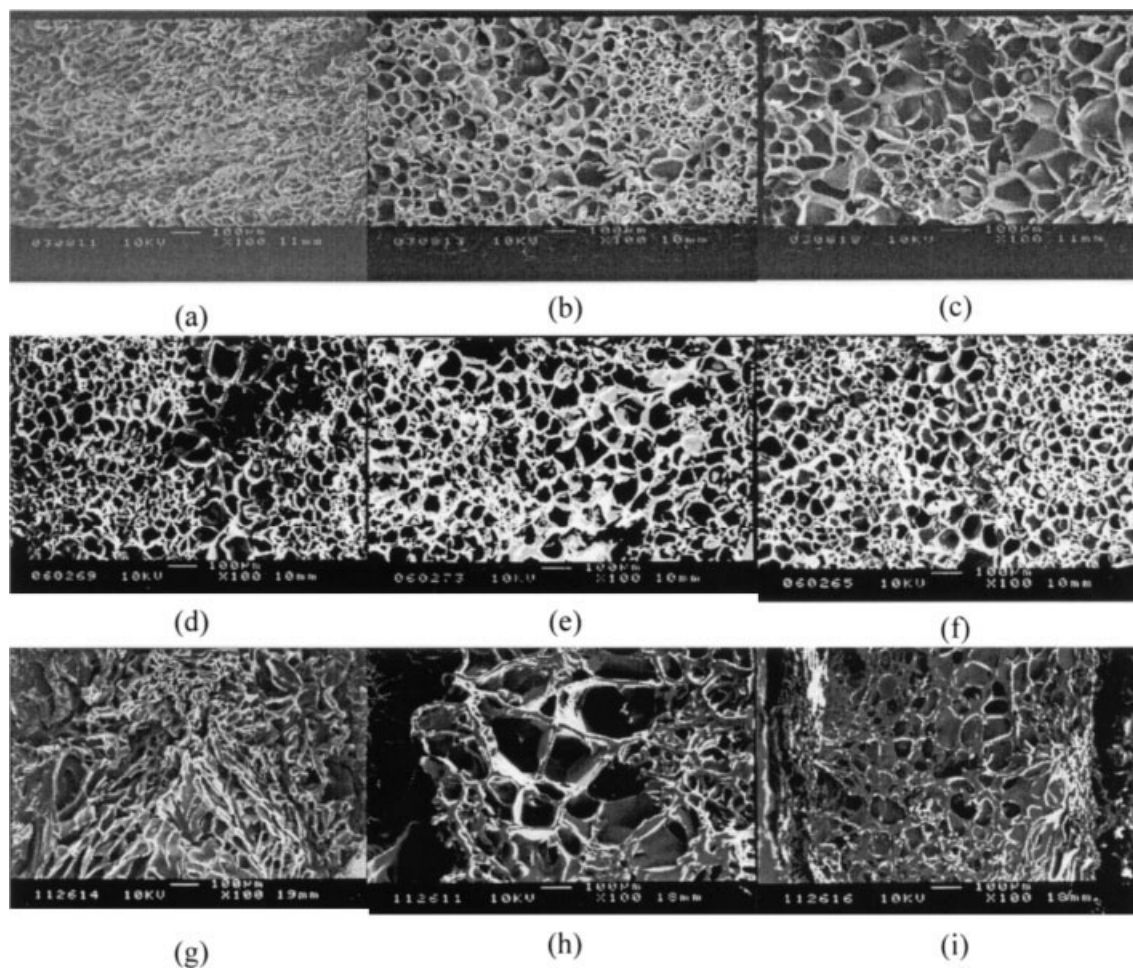| Time	N	F3	B3
–	100	50	40
PEG 8000	80	60	40
$CaCO_3$	50	45	35

Figure 10 The crosssectional SEM microphotographs for the NIPAAm copolymeric hydrogels. (a) NIPAAm–PEG; (b) F3–PEG; (c) B3–PEG; (d) NIPAAm–CaCO3; (e) F3–CaCO3; (f) B3–CaCO3; (g) NIPAAm; (h) F3; and (i) B3 ($\times$100).

incorporation of the porosigen into the gel, and adding $CaCO_3$ makes the gels approach the deswelling equilibrium faster. The gels foaming with porosigens reached to swelling–deswelling equilibrium more rapidly and much more water could be drained out of the gels. From mechanical properties, we find that the shear moduli and effective crosslinking densities were much lower for the gels foamed by porosigen than those gels without adding porosigen. The SEM microphotographs showed that the gels porosigened by PEG8000 had many homogeneous pores, but not the gels porosigened by $CaCO_3$. The results showed that the porous effect actually could enhance the deswelling behavior of the present copolymeric gels, but the response time and the amplitude of the fast deswelling–swelling were not satisfactory. In the future study, we shall further investigate how to increase the amplitude of the fast deswelling–swelling.

References

1. Kodzwa, M. G.; Staben, M. E.; Rethwisch, D. G. J Membr Sci 1999, 158, 85.
2. Zrinyi, M.; Szabo, D.; Kilian, H. G. Polym Gels Networks 1998, 6, 441.
3. Hsu, C. S.; Block, L. H. Pharm Res 1996, 13, 1865.
4. Goldbart, R.; Kost, J. Pharm Res 1999, 16, 1483.
5. Miyazaki, T.; Asami, N.; Uragami, T. Nature 1999, 399, 765.
6. Miyazaki, T.; Asami, N.; Uragami, T. Macromolecules 1999, 32, 2082.
7. Peppas, N. A. J Bioact Compat Polym 1991, 6, 241.
8. Khare, A. R.; Peppas, N. A. Biomaterials 1995, 16, 559.
9. Brannon-Peppas, L.; Peppas, N. A. Chem Eng Sci 1991, 46, 715.
10. Yu, E.; Kramarenko, A.; Khoklov, A. R. Macromolecules 1997, 30, 3383.
11. Cornejo-Bravo, J. M.; Siegel, R. A. Biomaterials 1996, 17, 1187.
12. Kikuchi, A.; Okano, T. in Biorelated Polymers and Gels; Okano, T., Ed.; Academic Press: Boston, MA, 1998; p 1.
13. Chen, J.; Park, H.; Park, K. J Biomed Mater Res 1999, 44, 53.
14. Yang, S. C.; Fu, Y. R.; Hoon, S.; Park, J. K.; Park, K. J Pharm Pharmacol 2004, 56, 49.
15. Shalaby, W.; Blevins, W. E.; Park, K. Biomaterials 1992, 13, 289.
16. Shalaby, W.; Blevins, W. E.; Park, K. J Controlled Release 1992, 19, 131.
17. Badiger, M. V.; McNeill, M. E.; Graham, N. B. Biomaterials 1993, 14, 1059.
18. Kon, M.; de Visser, A. C. Plast Reconstr Surg 1981, 67, 288.
19. Chen, J.; Park, K. J Controlled Release 2000, 65, 73.
20. Oxley, H. R.; Corkhill, P. H.; Fitton, J. H.; Tighe, B. J. Biomaterials 1993, 14, 1065.

21. Chen, J.; Park, K. J Macromol Sci Pure Appl Chem 1999, 36, 917.
22. Geminhart, R. A.; Park, H.; Park, K. Polym Adv Technol 2000, 11, 617.
23. Geminhart, R. A.; Park, H.; Park, K. J Biomed Mater Res 2001, 55, 54.
24. Lee, W. F.; Yeh, Y. C. Eur Polym J 2005, 41, 2488.
25. Kabra, B. G.; Gehrke, S. H.; Hwang, S. T. J Appl Polym Sci 1991, 42, 2409.
26. Franson, N. M.; Peppas, N. A. J Appl Polym Sci 1983, 28, 1299.
27. Korsmeyer, R. W.; Merrwal, E. W.; Peppas, N. A. J Polym Sci Polym Phys Ed 1986, 24, 409.
28. Peppas, N. A.; Barr-Howell, B. D. Hydrogels in Medicine and Pharmacy, Vol. 1; CRC: Boca Raton, FL, 1986; p 27.
29. Treloar, L. R. G. The Physics of Rubber Elasticity; Clarendon: Oxford, 1975.
30. Lee, W. F.; Hung, G. C. J Appl Polym Sci 1997, 64, 1477.
31. Alfrey, T.; Gurnee, E. F.; Lloyd, W. G. J Polym Sci Part C: Polym Symp 1966, 12, 249.