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### Macroporous Poly(Acrylamide) Hydrogels: Swelling and Shrinking Behaviors

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## Macroporous Poly(Acrylamide) Hydrogels: Swelling and Shrinking Behaviors

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*Macroporous poly(acrylamide) hydrogels have been synthesized by using poly(ethylene glycol) (PEG) with three different molecular weights as the pore-forming agent. Scanning electron microscope graphs reveal that the macroporous network structure of the hydrogels can be adjusted by applying different molecular weights of PEG during the polymerization reaction. The swelling ratios of the PEG-modified hydrogels were much higher than those for the same type of hydrogel prepared via conventional method. However, the swelling/deswelling ratios of the PEG-modified hydrogels were affected slightly by the change in the amount of the PEG. Scanning electron microscopy experiments, together with swelling ratio studies, reveal that the PEG-modified hydrogels are characterized by an open structure with more pores and higher swelling ratio, but lower mechanical strength, compared the conventional hydrogel. PAAm has potential applications in controlled release of macromolecular active agents.*

**Keywords** poly(acrylamide), macroporous, swelling

### Introduction

Responsive hydrogels change their structures and physical properties in response to their surrounding environment, including the pH, temperature, solvent quality, electric or magnetic field, etc. (1–4). Depending on the design of the hydrogel matrices, the volume change may occur continuously over a range of stimulus values, or, intermittently at a critical stimulus level. Because of these characteristics, they can be widely applied in biomaterials such as controlled drug-release and delivery systems, on-off switching materials, artificial muscles, biosensors, separation and adsorptive materials (5–10).

When a swollen poly(acrylamide) [PAAm] hydrogel in water is immersed in a non-solvent (e.g. dioxane), deswelling immediately starts at the gel surface. Then, the gel forms a dense polymer skin layer at the surface. This retards the permeability of water

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or a solute through the gel. To promote the applications of hydrogels in drug-release or fast-response materials, such as artificial muscles, reducing the formation of a dense skin layer is important. Many researchers have shown that incorporating a hydrophilic monomer such as acrylic acid or prepared a comb-type grafted hydrogel can reduce the dense skin layer (11). In addition, using hydrogels with porous structures to increase the surface area can also achieve rapid swelling and deswelling (12, 13).

In this study, we prepared poly(acrylamide) (PAAm) hydrogels with a macroporous network structure by using poly(ethylene glycol) (PEG) with three different molecular weight as the pore forming agent during the polymerization reaction. The PEG-modified PAAm hydrogels were characterized by swelling ratio, swelling/deswelling kinetics and scanning electron microscopy (SEM). The PEG-modified PAAm hydrogels may have potential applications in the controlled release of macromolecular active agents such as proteins and peptides, since the macroporous structure may be able to provide enough space for the loading and releasing of macromolecular active agents.

## Experimental

### Materials

Acrylamide (AAm), *N,N*-methylenebisacrylamide (MBAAm), ammonium persulfate (APS), *N,N,N',N'*-tetramethylethylenediamine (TEMED) and poly(ethylene glycol)s with molecular weights of 4000, 6000 and 10,000 g/mol (defined as PEG-4000, PEG-6000 and PEG-10,000, respectively) and dioxane were purchased from Aldrich Chemical Co. The chemicals were used as received. All aqueous solutions were prepared using deionized water.

### Hydrogel Synthesis

The conventional and PEG-modified PAAm hydrogels were prepared by free-radical crosslinking polymerization of AAm in aqueous solutions. APS (0.056 M) and TEMED (0.32 M) were used as the redox initiator system. The AAm (1.0 g) APS (1.0 mL) and MBAAm (0.12 g) were dissolved in distilled water (3.5 mL). Then, PEG (4.8–20.0 wt%) was dissolved in the monomer solution. The solution was purged with nitrogen gas for 10 min. After the addition of TEMED (0.5 mL), the solution was placed in poly(vinyl chloride) straws of 4 mm diameters and about 20 cm long. The poly(vinyl chloride) straws were sealed and immersed in a thermostated water bath at 20°C, and the polymerization was conducted for 1 day. Here, PEGs with three different molecular weights are employed as the pore-forming agent, which does not react with other chemicals during polymerization. Upon completion of the reaction, the hydrogels were cut into specimens of approximately 10 mm in length and immersed in large excess of water at room temperature for at least 72 h. The water was changed every several hours to wash out the pore forming agent and the unreacted materials. The samples were then dried at room temperature under vacuum to constant weight.

### Scanning Electron Microscopy

The morphology of the dried hydrogels was studied with SEM (JEOL JSM-6360 LV SEM instrument). Before SEM examination, specimens of the hydrogels were fixed on aluminum stubs and coated with gold for 40 s.

**Measurement of the Swelling Ratio**

For the swelling dynamic studies, the dried samples were placed in distilled water at 22°C and removed from water at regular time intervals. After the water on the surfaces of the hydrogels was wiped off with moistened filter paper, the weights of the hydrogels were recorded. The swelling ratio was defined as follows:

$$SR = \frac{m_t - m_d}{m_d} \quad (1)$$

where  $m_d$  and  $m_t$  are the masses of the dry and swollen hydrogels at time  $t$ , respectively.

**Measurements of Equilibrium Swelling Ratio and Pulsatile Kinetics**

For the swelling measurements in water-dioxane mixtures, the dried samples were immersed in water-dioxane mixtures at various compositions. The hydrogel were kept at room temperature for ten days to reach equilibrium. The hydrogels were removed from the solution and blotted with wet filter paper for the removal of excess solvent on the hydrogel surface; they were then weighed. The average values of three measurements were taken for each hydrogel, and the equilibrium swelling ratio was calculated as follows:

$$ESR = \frac{m_s - m_d}{m_d} \quad (2)$$

where  $m_s$  is the mass of the swollen hydrogel.

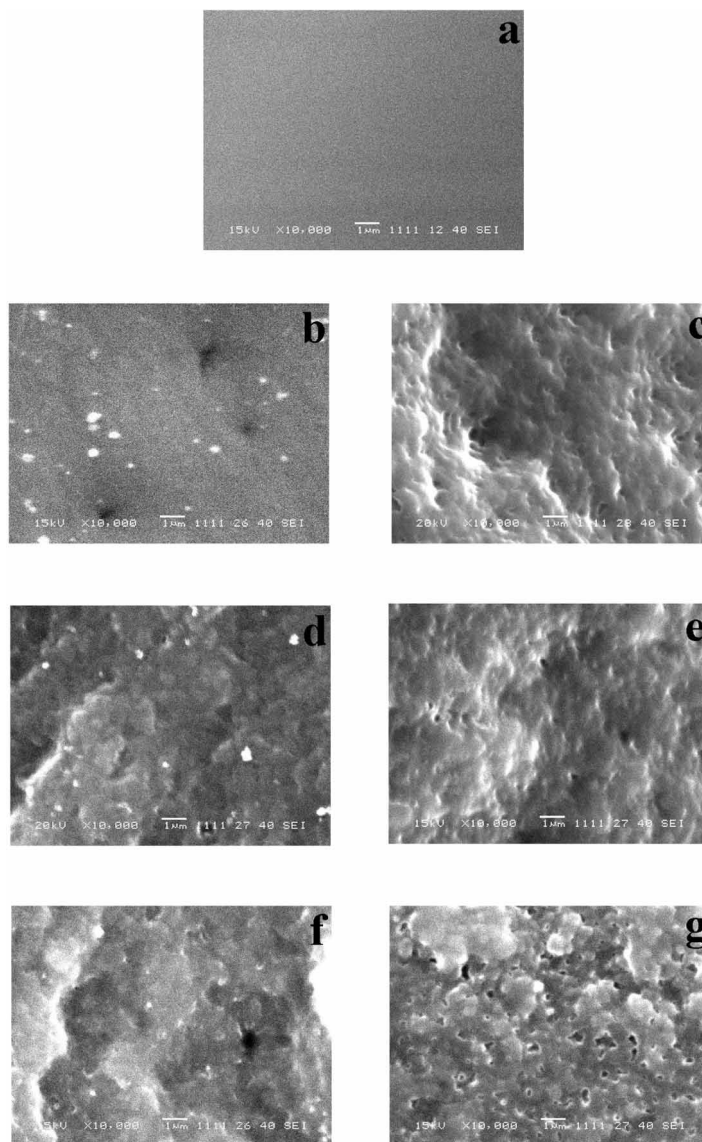
The pulsatile swelling behavior was observed in water and in dioxane. The hydrogels were first immersed in distilled water and kept at 22°C for ten days to reach equilibrium. The equilibrated hydrogels were then quickly transferred into dioxane. During the pulsatile swelling process, the weight change of the hydrogels was measured at 5 min intervals and the solvent was switched every 85 min. Normalized swelling ratio (NSR) was calculated from the following formula:

$$NSR = \frac{m_e - m_t}{m_e - m_d} \quad (3)$$

where  $m_e$  is the mass of the swollen hydrogels at equilibrium.

**Results and Discussion****SEM Micrographs of PAAm Hydrogels**

Figure 1 shows the SEM photos of the surface structure of the conventional and PEG-modified hydrogels. In comparison to these micrographs, it can be noticed that compared to the conventional hydrogel, the PEG-modified hydrogels show more porous network structures, thus displaying a faster swelling/deswelling responsive rate. There are two possible reasons. First, the hydration and thus exclusion volume of PEG may provide spatial hindrance during the polymerization and crosslinking process. Thus, a more porous structure is formed with the PEG-modified hydrogels. Second, due to the presence of PEG, phase separation of formed PAAm chains occurs during the polymerization, leading to macroporous and heterogeneous structures. On the other hand, the average diameter of PEG molecules in aqueous media increases with an increase in

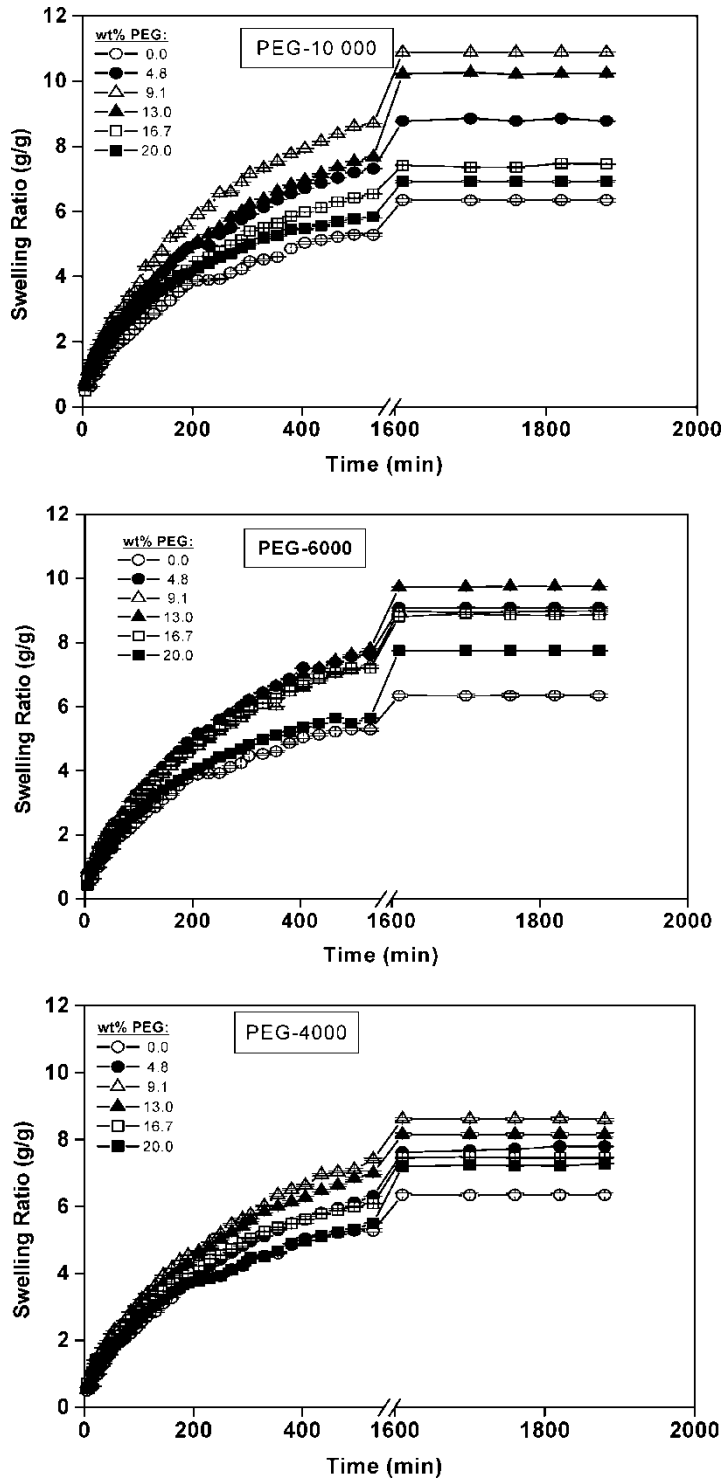


**Figure 1.** SEM micrographs of the conventional and PEG-modified PAAm hydrogels. (a) the conventional PAAm hydrogel, (b) 4.8 wt% PEG-4000-modified PAAm, (c) 20.0 wt% PEG-4000-modified PAAm, (d) 4.8 wt% PEG-6000-modified PAAm, (e) 20.0 wt% PEG-6000-modified PAAm, (f) 4.8 wt% PEG-10 000-modified PAAm, (g) 20.0 wt% PEG-modified PAAm.

PEG molecular weight; the higher the molecular weight of PEG applied during the polymerization, larger the pores within the resultant gel.

### **Swelling Kinetics**

The water adsorption of the conventional and PEG-modified hydrogels was determined gravimetrically as a function of time. Figure 2 shows the swelling ratio-time curves for



**Figure 2.** Swelling kinetics of the conventional and PEG-modified PAAm hydrogels in water. The content and molecular weight of PEG are indicated as the insert.

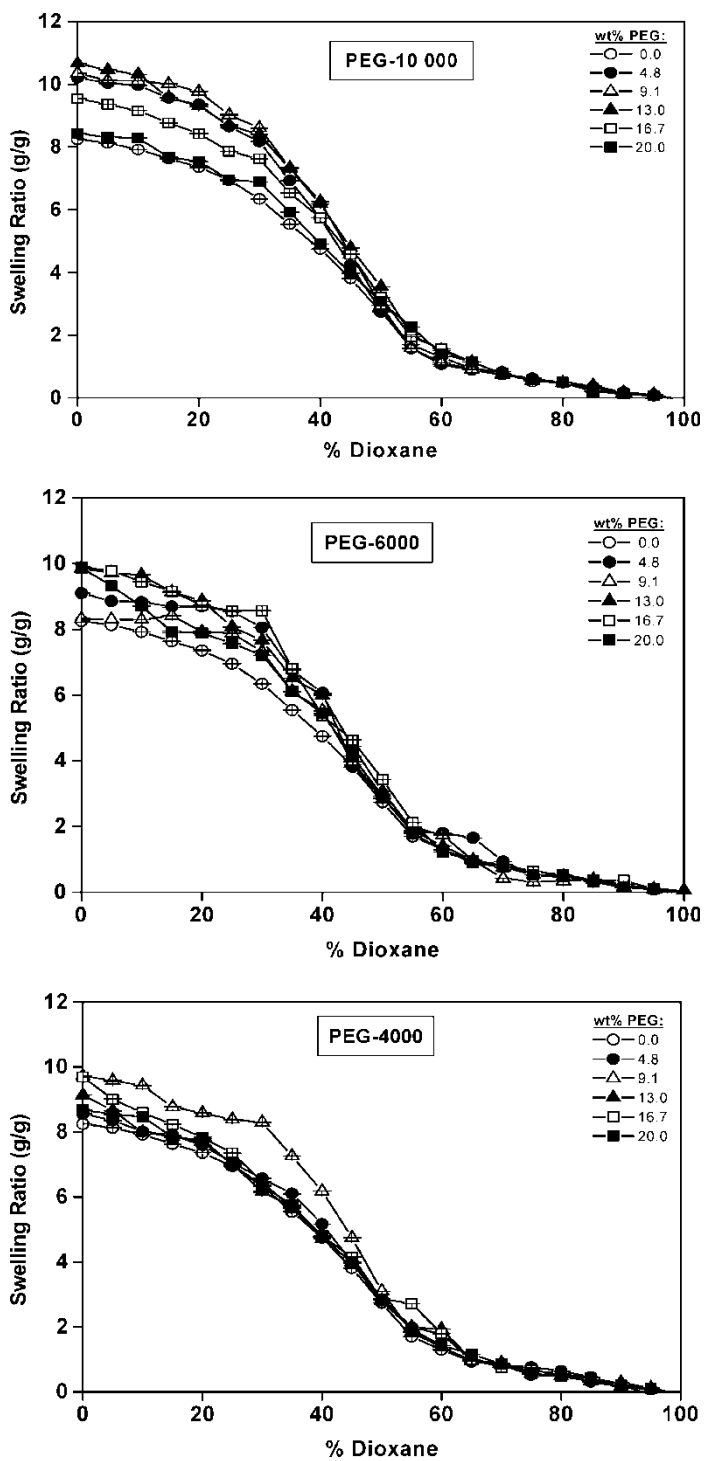
the conventional and PEG-modified hydrogels depending on the content and molecular weight of PEG. As shown in Figure 2, all the PEG-modified hydrogels absorb water more quickly than the conventional hydrogel because their macroporous structures make transfer of water molecules easier between the hydrogel matrix and the external aqueous phase. Figure 2 also implies that the PEG-modified hydrogels have superior swelling behavior. However, the swelling ratio is not improved accordingly by applying an increased PEG content. On the other hand, the hydrogels modified by PEG-4000 and PEG-6000 contain some lower swelling rates than that modified by PEG-10 000. The increase in the porosity affects their swelling ratios. Thus, the PEG-10 000 modified hydrogels lead to the highest swelling rate among the PEG-modified hydrogels because of their highly porous structure.

### ***Equilibrium Swelling Ratio in Dioxane and Water Solvent Mixtures***

Equilibrium swelling ratios of the conventional and PEG-modified hydrogels are shown in Figure 3 as a function of dioxane concentration in the external dioxane-water mixtures. The content and molecular weight of PEG used in the hydrogel preparation are also indicated in the figures. As shown in Figure 3, the hydrogels have high swelling ratios in pure water. This behavior indicates that attractive interactions between polymer chain and water molecule dominate over the attraction between the polymer chains. When dioxane and water are mixed, the two solvents have an attractive interaction resulting in an increase in the free energy for polymer-polymer contact. The increase in the affinity among polymer segments could induce the collapse of the polymer network. As the dioxane concentration increases, the swelling ratios of all the hydrogels decrease and undergo a discontinuous phase transition at about 35–60% (v/v) dioxane concentration. Particularly at a concentration below the phase transition concentration, the equilibrium swelling ratio of the conventional hydrogels is lower than those of the PEG-modified hydrogels. This phenomenon may be due to the fact that the porous network structure makes water easier to diffuse in or out of the matrix. Among the PEG-modified hydrogels, irrespective of the amount of the PEG, the PEG-10 000 modified hydrogels have the largest swelling ratio, while the PEG-4000 modified hydrogels yield the smallest one. This may be explainable by various porous structures that PEGs create. There was no obvious effect of the solvent composition on the swelling ratio of all the hydrogels at a composition above their phase-transition composition. This suggests that, regardless of the type of the hydrogels, all the hydrogels would collapse into similar collapsed structure at a composition above their phase-transition solvent composition.

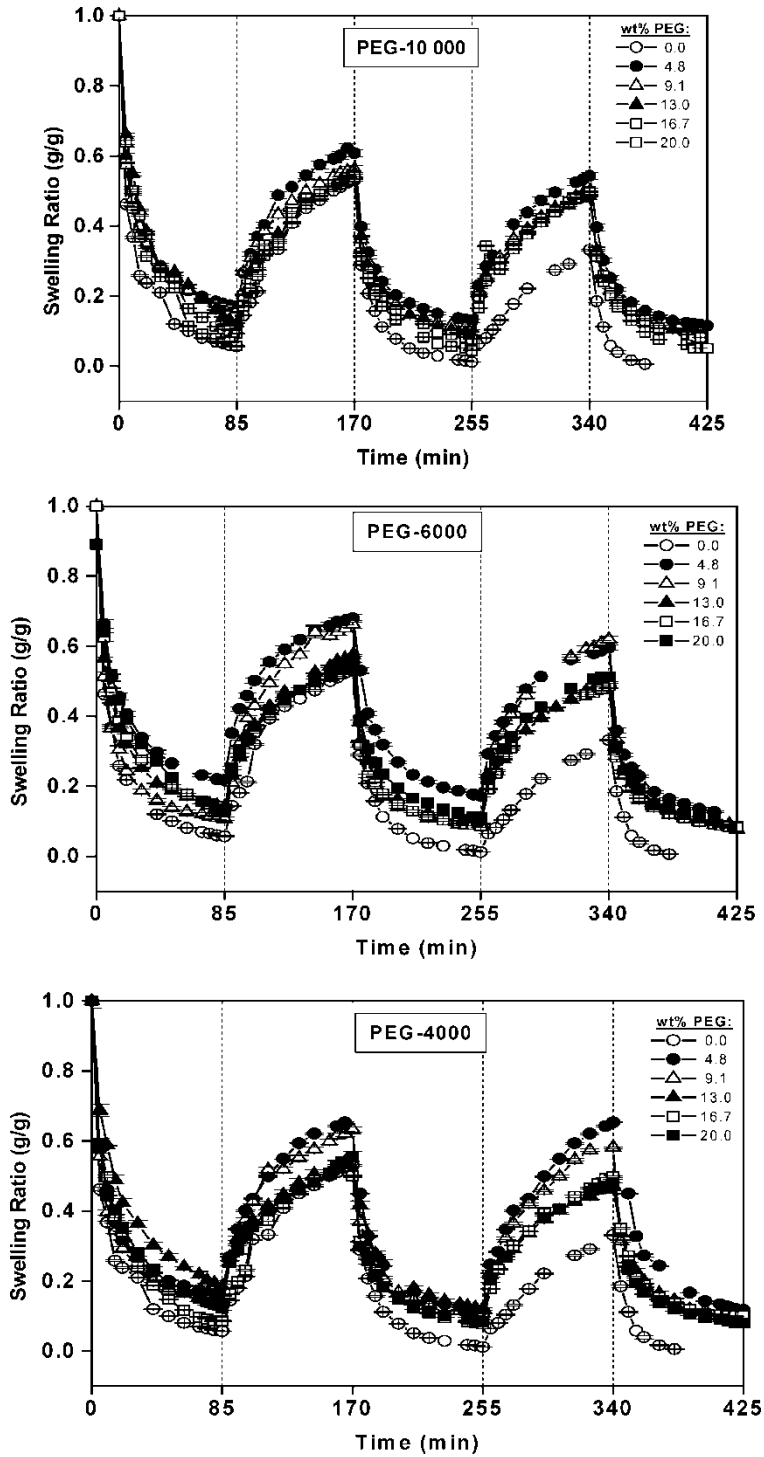
### ***Pulsatile Swelling Behavior***

The pulsatile swelling behavior of the conventional and PEG-modified hydrogels at 22°C in water and in dioxane was investigated to confirm swelling process reproducibility (Figure 4). The hydrogels underwent a number of swelling-deswelling cycles without exhibiting any deformation in their shapes. When the completely swollen hydrogel was placed in dioxane, the deswelling process started with the formation of weak hydrogen bonds between dioxane and the network chains. This facilitated the movement of individual water and dioxane molecules through the network and resulted in the observed rapid deswelling of the hydrogels in dioxane. On the other hand, the inspection of Figure 4 showed a clear decrease in the swelling ratios with each cycle. Especially, some



**Figure 3.** Variation in the equilibrium swelling ratio of the conventional and PEG-modified PAAm hydrogels in water-dioxane mixtures. The content and molecular weight of PEG are indicated as the insert.





**Figure 4.** Pulsatile swelling behavior of the conventional and PEG-modified PAAm hydrogels in response to solvent changes between water and dioxane. The content and molecular weight of PEG are indicated as the insert.

irreversible steps are included in the hydrogel prepared via conventional method. This may be explained by various heterogeneous structures, such as a polymer rich and a solvent rich phase, which was created during the post-treatment of the conventional hydrogel with a nonsolvent (dioxane). The diffusion rate is controlled by collective diffusion coefficient and hydrogel morphology. When a conventional hydrogel is immersed into the non-solvent, the hydrogel may start the phase transition and shrink in the utmost surface region, resulting in a thick and dense skin layer at the beginning of the shrinking process. The resultant dense skin layer acts as a barrier for further solvent permeation and prevents the freed solvent diffusion out from the hydrogel matrix. In contrast to the conventional hydrogel, however, the PEG-modified hydrogels have more solvent transfer because of their macroporous structures. This is, in the case of the porous hydrogels, makes it possible for solvent molecules to rapidly transfer through the macropores into the innermost matrix, even though phase separation had occurred on the surface in non-solvent, and this resulted in a rapid deswelling. However, the normalized swelling ratio of the PEG-modified hydrogels was affected very little by the change in the amount and molecular weight of the pore-forming agent.

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