

A Semi-Interpenetrating Network for Temperature-Sensitive Polymer System

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Abstract : A semi-interpenetrating network (IPN) was prepared for a temperature-sensitive polymer system composed of sodium alginate and poly(*N,N*-dimethylaminoethyl methacrylate (DMAEMA)-co-ethyl acrylamide (EAAm)). The role of sodium alginate is to provide crosslinked network and that of poly(DMAEMA-co-EAAm) is to provide temperature responsiveness to the polymer system. Semi-IPN gel shows temperature-induced swelling transition at the same temperature of the lower critical solution temperature of poly(DMAEMA-co-EAAm) and its swelling kinetics is manipulated by the control of crosslinking density.

Introduction

Much interest has been focused on polymer systems that show a phase transition in response to external stimuli such as temperature, pH, and ionic strength because of their scientific or technological importance.¹⁻⁴ Especially, thermosensitive polymer systems have been intensively studied since Heskins and Guillet reported the solution properties of poly(*N*-isopropylacrylamide) (NIPAAm).⁵ Hoffman *et al.*,^{6,7} and Kim *et al.*^{8,9} have studied aqueous swelling and drug release from poly NIPAAm gels in response to temperature change.

In our previous study, the temperature-induced phase transition of aqueous solution of poly(*N,N*-dimethylaminoethyl methacrylate (DMAEMA)-co-ethylacrylamide (EAAm)) was reported as a function of chemical composition.¹ Although poly DMAEMA and polyEAAm were reported to exhibit the lower critical solution temperature (LCST) at 50 and 80 °C, respectively, a LCST shift from 50

to 4 °C was observed with the copolymers of DMAEMA and EAAm. This is due to the formation of hydrogen bonding between DMAEMA and EAAm residues with a hydrophobic contribution to the LCST. Later, we reported the temperature dependence of equilibrium swelling of poly (DMAEMA-co-EAAm) gel.² The transition temperature between shrunken and swollen states was shifted to the higher temperature with the increase of EAAm content. This is contrary to the LCST change of poly (DMAEMA-co-EAAm) aqueous solution as a function of chemical composition. With the formation of gel network, EAAm, which contributed hydrophobically to the LCST via hydrogen bond, contributed hydrophilically to the transition temperature between shrunken and swollen state of gel network.²

In this study, a semi-interpenetrating network (IPN) was prepared and its temperature-sensitive swelling behavior was observed. The first network consists of sodium alginate (SA) which provides a crosslinked network. The other is poly(DMAEMA-co-EAAm) which imparts temperature-sensitivity

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into the polymer network. The difference in the temperature-sensitive swelling behavior between poly (DMAEMA-co-EAAM) gel and semi-IPN composed of SA and poly (DMAEMA-co-EAAM) was examined. And the swelling kinetics of semi-IPN was observed to increase the response dynamics by manipulating the crosslinking density of semi-IPN.

Experimental

Materials. *N,N*-dimethylaminoethyl methacrylate (DMAEMA) monomer, *N,N*-azobis(isobutyronitrile) (AIBN), and calcium chloride were purchased from Aldrich. Sodium alginate (SA) and sodium acetate were purchased from Sigma Chemical Co. DMAEMA monomer was distilled before use. Other reagents were used as received.

Synthesis. EAAM was synthesized in our laboratory as described previously.¹⁰ Copolymers of DMAEMA and EAAM were prepared by free radical polymerization as follows: 7.8 g of distilled monomers (mixtures of DMAEMA and EAAM) and 0.02 g of AIBN as an initiator were dissolved in 100 mL of water/ethanol binary solvent mixture (5/5 by volume). The ampoule containing the solution was sealed by a conventional method and immersed in a water bath held at 75 °C for 15 h. After polymerization, all polymers were dialyzed against distilled-deionized water at 4 °C and freeze-dried.

Preparation of Semi-IPN Gel. Semi-IPN gels composed of SA and poly(DMAEMA-co-EAAM) were prepared as follows: The known amounts of 2 wt% SA aqueous solution and 10 wt% poly(DMAEMA-co-EAAM) aqueous solution were mixed thoroughly using a homogenizer (Janke & Kunkel GmbH). The prepared solution was cast on a known area of a glass plate and dried in a vacuum oven. After drying, the non-crosslinked polymer was removed from the glass plate and immersed in 5 wt% calcium chloride solution. Because SA formed a gel in the presence of divalent ion, the gel network was formed from the surface with the penetration of calcium chloride into the noncrosslinked polymer. The non-crosslinked polymer was completely converted to the crosslinked one (semi-IPN gel) within 30 min. The semi-IPN gel was immersed in distilled-

deionized water for 3 h to remove unreacted calcium chloride.

It is well known that the crosslinked SA (calcium alginate) disintegrates into SA in EDTA (ethylenediaminetetraacetic acid) or alkaline solution (decoupling).¹¹ To control the crosslinking density, semi-IPN gel (0.5 g of dried semi-IPN gel) was treated with 100 mL of 10 wt% sodium acetate aqueous solution. If EDTA or a strong base such as NaOH was used as a decoupling agent, complete disintegration occurred within 1 min. It was hard to control the swelling or crosslinking density of the semi-IPN gel consistently using the strong base because the experimental error caused by the variation of decoupling time was significant. Therefore, a weak base of sodium acetate was selected as a decoupling agent for slow decoupling to consistently control the swelling or the crosslinking density of the semi-IPN gel.

Swelling Measurements. After immersion in water at a desired temperature, the semi-IPN gel was removed from the water and tapped with a filter paper to remove excess water on gel surface. The gel was repeatedly weighed and reimmersed in water at a fixed temperature until the hydrated weight reached a constant value. After equilibration at one temperature, the gel was reequilibrated at a higher temperature. The swelling, defined as the weight of water uptake per unit weight of dried gel, was calculated by measuring the weight of swollen gel until weight changes were within 1% of the previous measurement.

Results and Discussion

Prior to observing the temperature-sensitive swelling behavior of semi-IPN gels, temperature-

Table I. Feed Composition for Copolymers in the Study

Code	DMAEMA		EAAM		$M_w/10^{5a}$
	g	mol%	g	mol%	
Poly DMAEMA	7.8	100	-	-	3.5
Copolymer I	6.6	80	1.2	20	5.2
Copolymer II	5.3	60	2.5	40	4.3
Copolymer III	4.6	50	3.2	50	3.2

^a Measured by laser scattering.

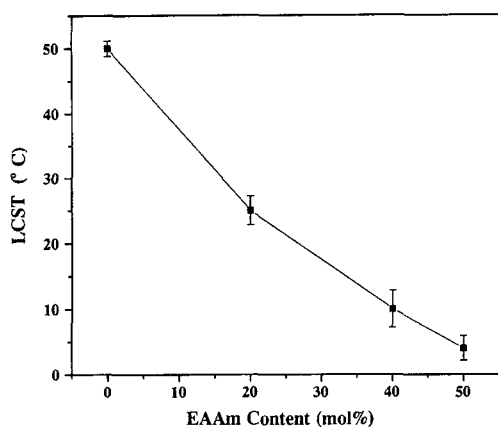


Figure 1. The LCST of poly(DMAEMA-co-EAAm) in water as a function of EAAm content. (adapted from ref. 1)

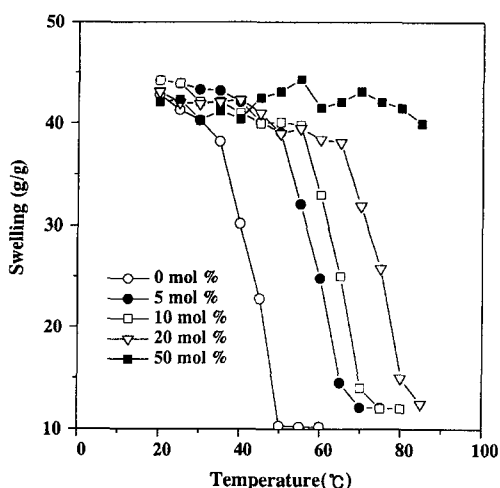


Figure 2. The temperature dependence of equilibrium swelling of poly(DMAEMA-co-EAAm) gel as a function of EAAm content. (adapted from ref. 2)

induced phase transitions of poly(DMAEMA-co-EAAm) and its gel were summarized as presented previously.^{1,2} When the temperature of a poly DMAEMA aqueous solution was raised above 50 °C, the polymer precipitated from the solution. This is due to hydrophobic interaction between *N,N*-dimethylamino groups above LCST. With the incorporation of EAAm in the copolymer, LCST was shifted to a lower temperature as shown in Figure 1. In general, the LCST of copolymer should be increased with the incorporation of hydrophilic comonomer.¹² However, in the

case of poly(DMAEMA-co-EAAm), the LCST was shifted to the lower temperature with the incorporation of hydrophilic EAAm. This is due to the hydrogen bond formation between ethylamide group in EAAm and *N,N*-dimethylamino group in DMAEMA which protects *N,N*-dimethylamino groups from exposure to water resulting in a significant hydrophobic contribution to the LCST.¹ The temperature dependence of equilibrium swelling of poly(DMAEMA-co-EAAm) gel is shown in Figure 2.² The transition temperatures between the shrunken and swollen state were shifted to the higher temperatures with the increase in EAAm content in the poly(DMAEMA-co-EAAm) gel. This is contrary to the LCST change of poly(DMAEMA-co-EAAm) aqueous solution as a function of chemical composition. With the formation of gel network, EAAm, which contributed hydrophobically to the LCST via hydrogen bond, contributed hydrophilically to the transition temperature between shrunken and swollen state of gel network. This study shows that the hydrogen bonds between ethylamide and *N,N*-dimethylamino groups are disrupted and the hydrophobic contribution to LCST via hydrogen bond is restricted in the case of poly(DMAEMA-co-EAAm) gel and non-hydrogen-bonded EAAm contributes hydrophilically to the transition temperature between shrunken and swollen state of gel network.

Therefore, it is valuable to observe the temperature-induced swelling transition of the polymer gel composed of SA and poly(DMAEMA-co-EAAm) with a semi-IPN structure. For this purpose, a novel semi-IPN has been prepared. The system consisted of two chemically independent polymers in which the proportions and properties of both polymers can be independently varied. The first network consists of SA which provides the crosslinked network. The other is poly(DMAEMA-co-EAAm) which imparts temperature sensitivity into the polymer network. SA is a polysaccharide which is obtained from marine brown algae. It forms gel in the presence of divalent ions at concentrations of >0.1% w/w. Based on this property of SA, the solution mixture of SA and poly(DMAEMA-co-EAAm) was treated with calcium chloride to form a gel matrix. It could be expected

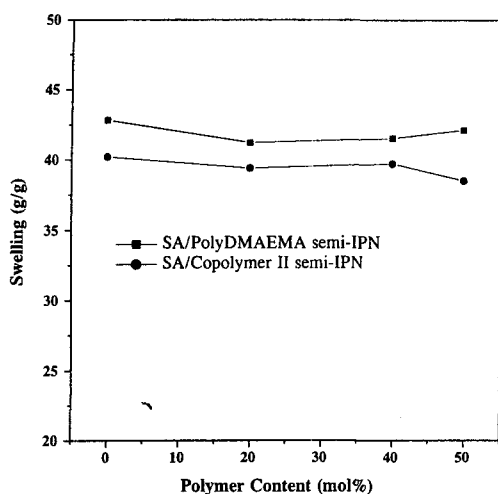


Figure 3. The swelling change of semi-interpenetrating networks as a function of poly(DMAEMA-co-EAAM) content.

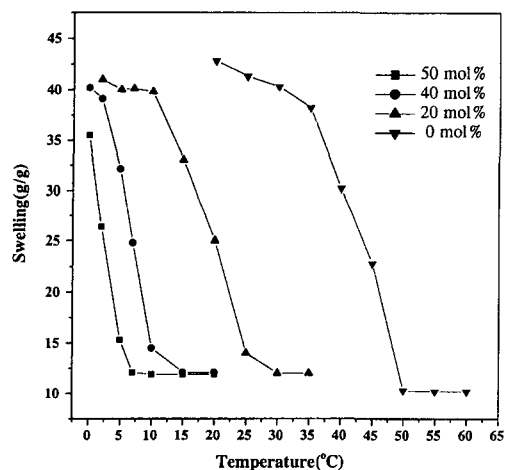


Figure 4. The temperature dependence of equilibrium swelling of semi-IPN as a function of chemical composition of poly(DMAEMA-co-EAAM) (as a function of EAAM content).

that SA formed a gel matrix (calcium alginate) and poly(DMAEMA-co-EAAM) chains entangled through the calcium alginate matrix, resulting in semi-IPN.

Figure 3 shows the swelling behavior of semi-IPN as a function of poly(DMAEMA-co-EAAM) content. The swelling was measured below the LCST of poly(DMAEMA-co-EAAM) used in the preparation of semi-IPN gel to observe the swell-

ing state of semi-IPN gel before the temperature-induced swelling transition. The swelling change was not observed with the variation of poly(DMAEMA-co-EAAM) content. The semi-IPN with 20 wt% of poly(DMAEMA-co-EAAM) was used throughout the experiment.

Figure 4 shows the temperature dependence for the equilibrium swelling of semi-IPN gel with the variation of chemical composition of poly(DMAEMA-co-EAAM). The transition temperature between the shrunken and swollen state was changed from 10 and 45 °C with the variation of chemical composition of poly(DMAEMA-co-EAAM). The transition temperature was defined as the temperature at the inflection point in the swelling versus temperature curve. This is in accordance with the LCST change of poly(DMAEMA-co-EAAM) aqueous solution as a function of EAAM content as shown in Figure 1. However, this is contrary to the change of transition temperature of poly(DMAEMA-co-EAAM) gel as shown in Figure 2. Our previous reports show that the hydrogen bond between ethylamide and *N,N*-dimethylamino group is the major factor to control the phase transition in poly(DMAEMA-co-EAAM) and the hydrogen bond was changed significantly with the formation of poly(DMAEMA-co-EAAM) gel. This led to temperature-sensitive swelling change of poly(DMAEMA-co-EAAM) gel which was contrary to the LCST change of poly(DMAEMA-co-EAAM) aqueous solution as a function of EAAM content. However, with the formation of semi-IPN, the intra/intermolecular interactions via hydrogen bond in poly(DMAEMA-co-EAAM) were not altered and played a major role in the temperature-induced swelling transition of semi-IPN gel.

The kinetics of swelling and de-swelling of polymer gels in response to external stimulus have been studied and several strategies have been explored for increasing the response dynamics for technological applications such as smart actuator and sensors.¹² To increase the response dynamics, the crosslinking density of semi-IPN was changed by manipulating SA network of semi-IPN and the swelling kinetics of semi-IPN was observed as shown in Figure 5. In alkaline aqueous solution, calcium alginate network disintegrates into SA

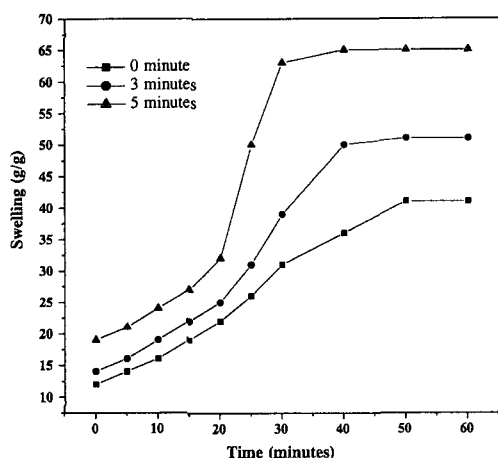


Figure 5. The swelling kinetics of semi-IPN (SA/Copolymer I) in response to temperature change as a function of decoupling time.

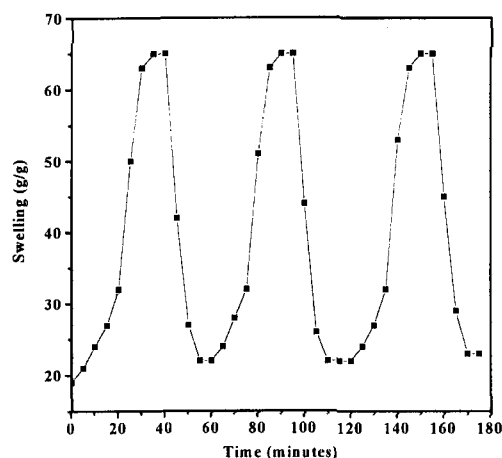


Figure 7. The swelling change of semi-IPN (SA/Copolymer I) in response to pulsatile temperature change (decoupling time: 5 min).

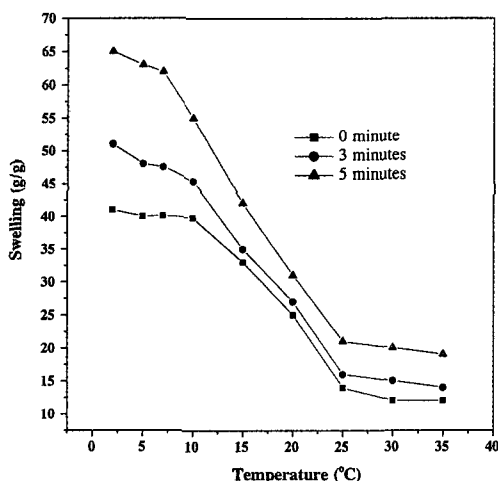


Figure 6. The temperature dependence of equilibrium swelling of semi-IPN (SA/Copolymer I) as a function of decoupling time.

(decoupling). Therefore, the crosslinking density of a polymer network might be regulated by the control of decoupling time. Firstly, the temperature of polymer network was maintained at 40°C. With the change of temperature from 40 to 5°C, the swelling increase was observed. The rapid swelling increase with increased equilibrium swelling was observed with the increase of decoupling time. This is due to the decrease in the crosslinking density caused by the decoupling indicating that the crosslinking density and swelling kinetics

of semi-IPN gel can be regulated reproducibly by the control of decoupling time.

Figure 6 shows the temperature dependence of equilibrium swelling of semi-IPN as a function of decoupling time. With the increase of decoupling time, the temperature-induced swelling change was significant indicating that the extent of temperature-induced swelling change could be regulated by the variation of decoupling time of the semi-IPN.

The swelling behavior of semi-IPN in response to pulsatile temperature change was measured to investigate the reversible swelling change. Firstly, the temperature was maintained at 40°C for equilibrium and decreased to 5°C. When we applied to the step function of temperature change, reversible swelling change was observed as shown in Figure 7.

Conclusions

With the formation of semi-IPN composed of SA and poly(DMAEMA-co-EAAM), polymer system with rapid response to temperature change has been demonstrated. The transition temperature of swelling change was mainly dominated by the chemical composition of poly(DMAEMA-co-EAAM) indicating that the temperature-induced phase transition of poly(DMAEMA-co-EAAM) played a major role in temperature-induced swell-

ing transition of semi-IPN. The response dynamics of semi-IPN to temperature change could be regulated effectively by the control of crosslinking density of semi-IPN.

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