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이온성 고분자 젤(I) : pH에 의존하는 수팽윤 현상

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Polyelectrolyte Gels(I) : pH-Dependent Swelling Behaviors

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요 약 : 두 종류의 이온성 고분자 젤(Random Copolymer Networks(RCNs) and Interpenetrating Networks(IPNs))이 그 젤의 물리적, 화학적 성질에 따라 어떻게 pH에 의존하는 수팽윤 현상을 나타내는지 알아보았다. 이온성 작용기(Sulfonic group)의 pH변화에 따른 이온화 형태가 젤의 pH의존성 수팽윤 변화를 주도하였으나 RCNs와 IPNs의 구조적 차이에서 나타나는 pH의존성 수팽윤 변화도 관찰되었다. 이는 수팽윤 변화를 주도하는 이온성 작용기의 이온화 형태가 구조적 차이가 있는 두 종류의 젤 네트워에 의하여 다른 형태로 영향을 받았기 때문으로 추측된다.

Abstract : Random copolymer networks(RCNs) and Interpenetrating Networks(IPNs) were prepared as model networks in an attempt to investigate the pH-dependent swelling behaviors depending on physical and chemical natures of gel networks. Although the ionization profiles of sulfonic groups in the gel networks played the major role in pH-dependent swelling behaviors, the changes in pH-dependent swelling behaviors caused by the structural difference between RCNs and IPNs was observed. This might be attributed to the differences in the intermolecular interaction between sulfonic groups and gel networks.

INTRODUCTION

A gel is the crosslinked polymer networks which show significant swelling in water. It has a variety of potential applications for artificial organ components, sensors, switches and controlled drug delivery system. Especially, much interest has been focused on the charged gel(polyelectrolyte gel) and a number of polyelectrolyte gel have been reported to show the reversible changes in their structures and functions in response to external stimulus such as pH,[1~2] temperature,[3~4] and electric current.[5~8] These properties of polyeletrolyte gels can be explained in terms of phase transition

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and critical phenomena in swelling.[9] The swelling of polyelectrolyte gels is an important factor for their physical and biological properties, specially in the swelling-controlled drug delivery systems.

In this study, random copolymer networks (RCNs) and interpenetrating networks(IPNs) were prepared as model networks in an attempt to investigate the pH-dependent swelling behavior depending on physical and chemical properties of gel network. Copolymers of 2-acrylamido-2-methyl-1-propane sulfonic acid(AMPSA) and butyl methacrylate(BMA) were prepared as model networks for RCNs and those of acrylamide(AAm) and AMPSA were prepared as model networks for INPs. pH-Dependent swelling behaviors of model gel networks were observed in the view points of chemical composition and structural difference between RCNs and IPNs.

EXPERIMENTAL

Materials. Acrylamide(AAm) monomer was purchased from Junsei chemical(Japan). N,N′-methylenebisacrylamide(NMBAAm), ammonium persulfate(APS), sodium pyrosulfite(SPS), ethyleneglycol dimethacrylate(EGDMA), 2-acrylamido-2-methyl-1-propane sulfonic acid(AMPSA), butyl methacrylate(BMA), and poly AMPSA aqueous solution(10 wt %) were purchased from Aldrich Chemical Co.(USA). Azobisisobutyronitrile(AIBN) was purchased from Sigma Chemical Co.(USA). BMA was purified by distillation with reduced pressure under nitrogen and all other chemicals were used without further purification.

Preparation of Gel Networks. RCNs was synthesized using EGDMA as a crosslinker and AIBN as an initiator. AMPSA was dissolved in DMF followed by the addition of BMA, EGDMA and AIBN. Polymerization was performed between two Mylar® sheets(15 cm×15 cm) separated by a silicone rubber gasket and backed by glass plates at 60℃ for 24 hours. After polymerization, the gel network was removed from the mold and soaked in a water/acetone(50/50 volume %) solvent mixture which was replaced daily for 1 week to extract the unreacted compounds. After extraction, the polymer was immersed in distilled-deionized water until use.

IPNs were prepared by free radical polymerization using redox initiators. AAm monomer, NMBAAm as a crosslinker, and poly AMPSA were dissolved in distilled water, to which redox initiators were added to initiate the polymerization. The aqueous solutions of SPS(3.5 g/25 ml) and APS(10 g/25 ml) were used as redox initiators and 0.25 ml of each component of redox initiators was added to solution mixture. Polymerization was performed between the two Mylar® sheet separated by a silicone rubber gasket and backed by glass plates at 40℃ for 12 hours. Although the solution mixture was converted to gel network within 3 hours, the polymerization was carried out for 12 hours to obtain the complete gel network. After polymerization, the gel network was removed from the mold and immersed in distilled water for 12 hours to remove the unreacted compound. The feed composition of gel networks is presented in Table 1.

Swelling Measurement. The water uptake(swelling) of gel network was measured as a function of environmental pH. The water uptake was measured by weighing the gel network after wiping the excess water on the surface. The number of experiment(n) was 3. The swelling is defined as the weight of water uptake per unit weight of dried polymer. The pH of aqueous media was controlled by the addition of HCl and NaCl. The total ionic strength of each aqueous media was adjusted to 0.1 M with a calculated amount of NaCl. Nitrogen was purged into the aqueous media at a flow rate of 10 l/min and the aqueous media was stored in sealed bottle to prevent the pH change caused by CO_2 in the atmosphere until use.

Differential Scanning Calorimetry. Thermal characterization of polymer(ca. 10 mg) was conducted with a differential scanning calorimeter(DSC) (Du pont DSC-9900 Computer/Thermal Analyzer). The heating rate was 10℃/min. and nitrogen was used as the sweep gas(30 ml/min.).

Table 1. Feed Composition for Polyelectrolyte Gel Networks

(unit ; g)

Category	Sample dode	Composition								
		AAm	Poly AMPSA	AMPSA	BMA	NMBAAm	EGDMA	AIBN	Water	DMF
Homopolymer	Poly AAm	3.88	–	–	–	0.12	–	–	40	–
RCNs	AMPSA/BMA(I)	–	–	0.70	4.70	–	0.01	0.01	–	10
	AMPSA/BMA(II)	–	–	1.46	3.94	–	0.01	0.01	–	10
	AMPSA/BMA(III)	–	–	2.70	2.70					
IPNs	AMPSA/AAM(I)	3.88	0.39	–	–	0.12	–	–	40	–
	AMPSA/AAM(II)	3.88	1.16	–	–	0.12	–	–	40	–
	AMPSA/AAM(III)	3.88	0.39	–	–	0.06	–	–	40	–

RESULTS AND DISCUSSION

RCNs and IPNs were used as model networks for the study of pH-dependent swelling behaviors caused by the change of chemical composition and the structural difference between RCNs and IPNs.

RCNs is the random copolymer of AMPSA and BMA. The role of AMPSA is to provide the ionic functional groups into the gel network and that of BMA is to provide the mechanical strength into the gel network.

IPNs is the copolymer of AAm and AMPSA which has the interpenetrating networks. With the initiation of polymerization, AAm is easily converted to a gel network without the chemical interaction of poly AMPSA chains in the reaction solution. Therefore, it could be expected that AAm formed a gel network and poly AMPSA chains entangled through the gel network resulting in IPNs as shown in Fig. 1. To observe the leakage of poly AMPSA from IPNs, AMPSA/AAm(II) was stored in distilled water for 1 month and the pH change of aqueous media was measured. In this experiment, the volume of aqueous media was 20 ml and the weight of gel network immersed in the aqueous media was 1.0 g. The pH of aqueous media decreased from 7.0 to 3.1 during the storage of gel network in distilled water for 1 week and minimal pH change was observed during the first day of 1 week. This indicated the leakage of poly AMPSA from the gel network.(pH of 0.2 wt % of poly AMPSA aqueous solution was 2.54) But noticeable swelling change was not observed during one month while replacing the distilled water with fresh one every three days.

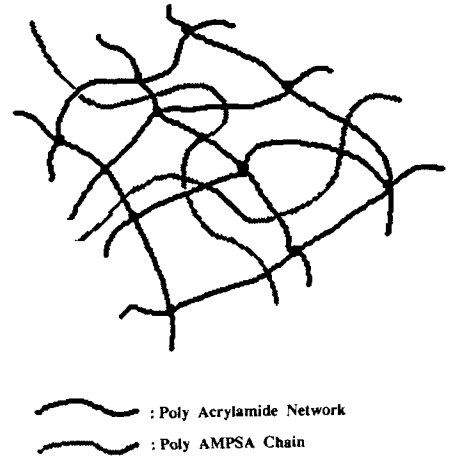

Fig. 1. Schematic diagram of interpenetrating networks of AMPSA/AAm.

Fig. 2 shows the calorimetric thermograms of swollen gels. Poly AAm and AMPSA/BMA(II) did not exhibit any noticeable peaks in the temperature range between 25℃ and 250℃. With the formation of IPNs, the endothermic peaks were observed at 136.29 and 210℃ in the case of AMPSA /AAm(II), which was equilibrated with distilled water for one month. The endothermic peak observed at 210℃ might be attributed to the intermolecular interaction between poly AMPSA and AAm network in IPNs and the presence of poly AMPSA in the gel network was confirmed by the

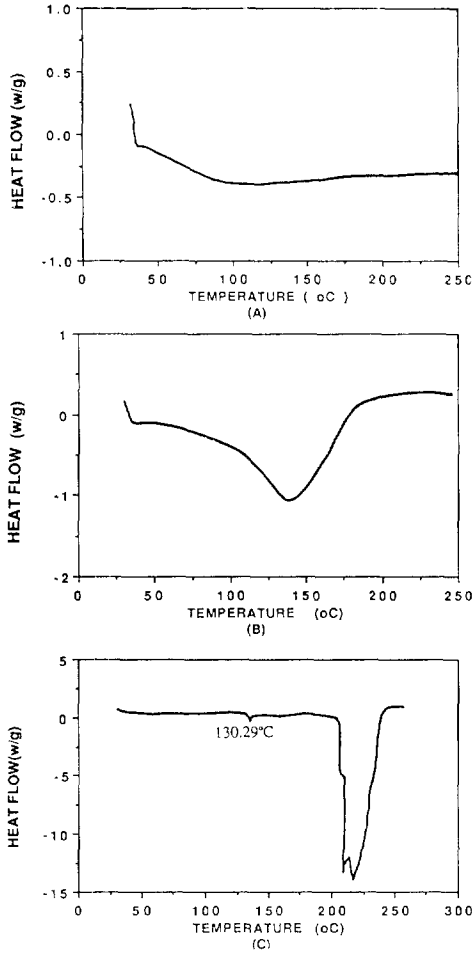

Fig. 2. Calorimetric thermograms : (A) swollen poly AAm gel, (B) swollen poly AMPSA gel, (C) swollen AMPSA/AAm (II).

endothermic peak at 130.29C.

Fig. 3 shows the pH-dependent swelling behaviors of RCNs. At acidic condition(pH=1), sulfonic groups were protonated and the gel matrix was deswelled. As the pH of aqueous media was increased from pH 1, the concentration of negatively charged sulfonic groups in the gel matrix was increased resulting in a drastic swelling increase. The maximum swelling change of these gels occurred at pH 1.5~2.0 which reflected the ionization of sulfonic group in the gel network and the pKa of these gels was approximated as 1.5 from the inflection point in Fig. 3. Similar results were reported elsewhere[6]. It was also observed that the range of swelling change could be regulated with the variation of the content of AMPSA in the gel network.

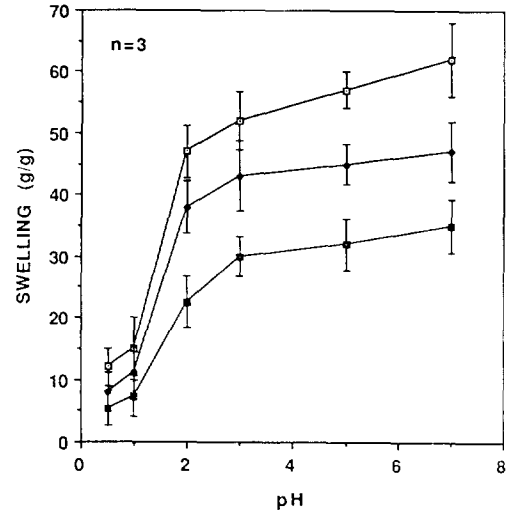

Fig. 3. pH dependent swelling behavior : AMPSA/BMA(I) (□), AMPSA/BMA(II) (◆), AMPSA/BMA (III) (▣).

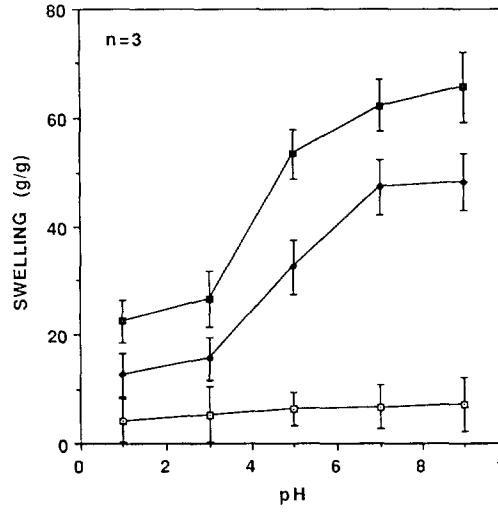

Fig. 4. pH dependent swelling behavior : Poly AAm (▣), AMPSA/AAm(I) (◆), AMPAS/AAm(II) (□).

Fig. 4 shows the swelling behaviors of IPNs. With the formation of IPNs, the increased swelling

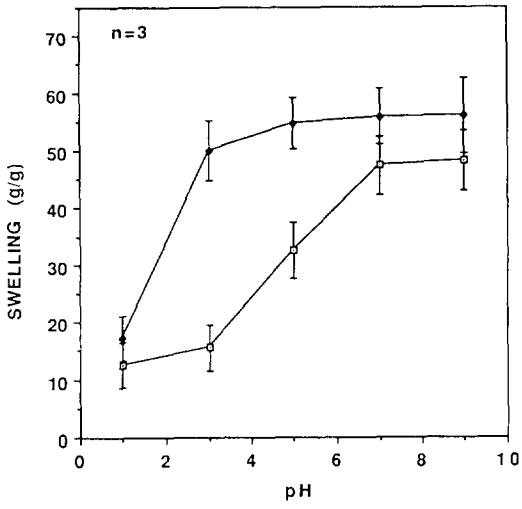

Fig. 5. pH dependent swelling behavior as a function of crosslinking density : AMPSA/AAm(I) (▣), AMPAS/AAm(III) (◆).

and apparent pH dependence of swelling were observed comparing with poly AAm and the maximum swelling change occurred at pH 3.5~4.0. Although sulfonic groups in poly AMPSA played a major role in the pH-dependent swelling behaviors of RCNs and IPNs, the maximum swelling change was observed at pH 1.5~2.0 in the case of RCNs but was observed at pH 3.5~4.0 in the case of IPNs. Therefore, the difference in pH points at which the maximum swelling change occurred might be closely related to the structural difference between RCNs and IPNs. To examine the effect of the structural difference on pH-dependent swelling pattern, AMPSA/AAm(I) and (III) were prepared with the variation of the crosslinking density of poly AAm gel network. As shown in Fig. 5, the pH point at which maximum swelling change occurred shifted from 3.5~4.0 to 1.5~2.0 with the decreased crosslinking density of poly AAm gel network. This might be due to the fact that the degree of freedom of poly AMPSA increased and the intermolecular interaction of poly AMPSA chains and poly AAm network decreased with the decreased crosslinking density of poly AAm gel matrix.

CONCLUSIONS

AMPSA/BMA and AMPSA/AAm were prepared as model polymer networks in an attempt to investigate the pH-dependent swelling behaviors of polyelectrolyte gels. pH-Dependent swelling behaviors of gel network was closely related to the ionization profile of sulfonic groups in AMPSA. Although sulfonic groups in poly AMPSA played a major role in the pH-dependent swelling behaviors of RCNs and IPNs, the maximum swelling change was observed at different pH point indicating the importance of structural difference between random copolymer networks and interpenetrating networks in pH-dependent swelling behaviors.

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