Bull. Chem. Soc. Jpn., 76, 543–544 (2003)

Deswelling Kinetics of a Porous Poly(*N*-isopropylacrylamide/methacrylic acid) Gel Prepared by Freeze-Drying

Norihiro Kato,* **Yasuzo Sakai, and**
Atsushi Kanazawa

Department of Applied Chemistry, Faculty of Engineering,
Utsunomiya University, 7-1-2 Yoto, Utsunomiya 321-8585

(Received July 18, 2002)

A linear correlation between the enthalpy of activation ($\Delta H^{\ddagger}$) and the entropy of activation ($\Delta S^{\ddagger}$) was observed for the deswelling process of porous poly(*N*-isopropylacrylamide/methacrylic acid) gels. The free energy of activation ($\Delta G^{\ddagger}$) was nearly constant at $+84 \pm 2$ kJ mol^{-1} irrespective of the methacrylic acid content and pH of the solutions.

Since the response rate of gel deswelling is one of the critical factors concerning gel behavior, some approaches have been reported to accelerate the gel response for stimulation onto the gel.[1,2] The treatment of freeze-dry (FD) and hydration is a convenient method to prepare fast-responsive and porous gels. It was described in our previous papers that the acceleration of deswelling for a thermosensitive poly(*N*-isopropylacrylamide) gel, poly(NIPAAm) gel, was kinetically studied concerning the porous structure of the polymer network derived from a FD-treatment.[1,3] Gel deswelling, which results from heating above a lower critical solution temperature (LCST) of the polymers, is considered to be a water-expelling process followed by the aggregation of polymer chains due to a hydrophobic interaction in the gel.

According to Gehrke,[4] the interconnectivity of pores inside thermosensitive hydrogels play important roles in the water-expelling process. The principal hypothesis proposed was that deswelling in a porous gel involves two distinct mass-transfer steps: 1) diffusion in the polymer struts (diffusion through the pore walls) and 2) convection through interconnected pores. We have reported that a small portion of pores prepared by a FD-treatment was interconnected based on the result of SEM.[1,3] In this case, the deswelling rate should be controlled by step 1, as well as conventional gels without a FD-treatment, because the rate of diffusion is generally slower than the rate of convection.[3] The hydrophilic strut makes it easy to permeate water. On the other hand, the hydrophilic strut can possibly lower the deswelling pressure due to the aggregation of hydrophilic polymers. A low deswelling pressure was supposed to decrease the rate of water permeation through the strut.

It is worthwhile to clarify the relationship between the above-described two antagonistic effects by using methacrylic acid (MA) as a hydrophilic comonomer in the poly(NIPAAm) gel deswelling process. Since carboxylic acid groups in MA can dissociate under alkaline conditions, the circumstances of the polymer-network in the copolymer are expected to become more hydrophilic compared with poly(NIPAAm). Therefore, the purpose of this research was to study the effect of MA copolymerization on the deswelling kinetics of FD-treated poly(NIPAAm) gel. There are some papers on copolymers between NIPAAm and a compound containing a carboxylic acid group, such as acrylic acid.[5] However, these were not kinetic studies of gel deswelling on partially interconnected pores. The enthalpy of activation ($\Delta H^{\ddagger}$), the entropy of activation ($\Delta S^{\ddagger}$), and the free energy of activation ($\Delta G^{\ddagger}$) for gel deswelling were determined by altering the MA content and pH, and analysed concerning the hydrophilic circumstances of the copolymer.

Experimental

Gel Preparation. Cylindrical gel of poly(NIPAAm/MA) [NIPAAm/MA = 100/0–80/20 (mol/mol)] was prepared in a silicone tube as a mold (2 mm in inner diameter) with the addition of *N*,*N*′-methylenediacrylamide (MDA) [MDA/(NIPAAm + MA) = 4/96 (mol/mol)]. Gel synthesis was carried out as described in our previous papers.[1,3] The swollen gel at 295 K was put into a glass flask and cooled from 295 to 243 K with immersing the flask in a cool bath. The gel become cold up to 243 K within 3 min, of which the temperature was determined with a thermocouple inserted into the gel. After freeze-drying and rehydration of gels containing 20 mol% MA in 0.1 M (M = mol dm^{-3}) HCl or 0.1 M NaOH at 295 K, the length (L) of each gel returned up to 77 and 94% of the first length just after polymerization.

Kinetic Parameters. The kinetic parameters for the temperature-induced deswelling of the gel were obtained in the same way as described in our previous papers.[1,3] The deswelling rate of the gel was determined by the temperature-jump method from 295 to 313, 317, 322, and 327 K in solutions of pH 1 and 13. The time evolution of L was determined based on pictures recorded by video tape, and $(L/L_0)^3$ was calculated as the deswelling ratio, where L_0 is the initial length of a gel rod at 295K. Since the plots of $(L/L_0)^3$ against time fell on straight lines during an early stage of the deswelling process, the deswelling rate was defined as a zero-order reaction with respect to $(L/L_0)^3$. The initial deswelling rate, $-\mathrm{d}(L/L_0)^3/\mathrm{d}t$, should be equal to the deswelling rate constant (k).[1,3,6] The values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta G^{\ddagger}$ for gel deswelling were calculated from slopes and intercepts of straight lines obtained by Arrhenius plots.

Results and Discussion

The deswelling rates of poly(NIPAAm/MA) gels were accelerated after a FD-treatment, as were poly(NIPAAm) gels. Straight lines for the Arrhenius plots could be obtained irrespective of the MA content, and SEM microphotographs for the FD-treated poly(NIPAAm/MA) gel, of which the MA content was 0–20 mol%, showed macropores of 10–30 μm in diameter (data not shown). Similar results for poly(NIPAAm) gel were already reported in previous reports.[1,3] The porous hydrogels were fast-responsive to thermo-stimulation, whether or not the polymer contained MA. The polymer chains were gathered to make a heterogeneous network during a freezing

Table 1. The Values of k, $\Delta H^{\ne}$, $\Delta S^{\ne}$, and $\Delta G^{\ne}$ for the Freeze-Dried and Rehydrated Poly(NIPAAm/MA) Gels

MA/mol%	$k^{a)}$/s^{-1}		$\Delta H^{\ne}$/kJ mol^{-1}		$\Delta S^{\ne}$/JK^{-1} mol^{-1}		$\Delta G^{\ne}$/kJ mol^{-1}	
	pH 1	pH 13	pH 1	pH 13	pH 1	pH 13	pH 1	pH 13
0	0.10 ± 0.01	0.14 ± 0.01	55 ± 3	57 ± 2	−93 ± 9	−86 ± 7	85 ± 1	84 ± 1
4	0.13 ± 0.01	0.16 ± 0.01	38 ± 2	50 ± 2	−142 ± 7	−104 ± 7	83 ± 1	83 ± 1
6	0.12 ± 0.01	0.18 ± 0.01	29 ± 2	38 ± 2	−171 ± 7	−140 ± 7	83 ± 1	82 ± 1
8	0.14 ± 0.01	0.11 ± 0.01	31 ± 2	44 ± 3	−163 ± 7	−127 ± 9	82 ± 1	84 ± 1
16	0.14 ± 0.01	0.11 ± 0.01	58 ± 2	63 ± 3	−81 ± 7	−66 ± 9	84 ± 1	84 ± 1
20	0.14 ± 0.01	0.09 ± 0.01	66 ± 2	73 ± 4	−55 ± 7	−40 ± 12	84 ± 1	86 ± 2

a) The rate constant (k) was determined by the temperature-jump from 295 to 322 K.

process; it was deduced that the porous network remained due to a hydrophobic interaction after sublimation of the ice.[1,3] Although the morphology on gel rods of 2 mm in diameter did not change for the direction of depth, some large pores (> 60 μm) appeared in the center part of the gel when gel rods of 5 mm in diameter froze. This result means that the rate of cooling slows in the center part of large gels and the pore becomes larger with decreasing the rate of cooling. In this research, all of the data were obtained from gel rods of 2 mm.

According to our previous methods, $\Delta H^{\ne}$, $\Delta S^{\ne}$, and $\Delta G^{\ne}$ for gel deswelling were determined by thermodynamic calculations, as shown in Table 1. The minima of $\Delta H^{\ne}$ and $\Delta S^{\ne}$ appeared at 6 mol% MA. The polymer hydrophilicity was considered to increase with increasing MA content. In the region of less than 6 mol% MA, water easily permeated through the hydrophilic strut. However, the polymer chains seemed to become hard to aggregate in more than 6 mol% MA. Two different effects seemed to make the minima of $\Delta H^{\ne}$ and $\Delta S^{\ne}$. It was speculated from $\Delta S^{\ne} < 0$ in Table 1 that the rate-determining step in the deswelling process was controlled by the deswelling pressure due to the aggregation of polymer chains.[3] This is because a negative $\Delta S^{\ne}$ means that the rate-determining step should be a bond-formation process, such as a hydrophobic interaction.

Table 1 shows that the deswelling rates at pH 13 declined in more than 6 mol% MA, as compared with those at pH 1. Since COOH groups in MA dissociate at pH 13, it is probable that the electrostatic repulsion due to COO^- groups disturbs the aggregation of polymer chains.

A linear correlation between $T\Delta S^{\ne}$ and $\Delta H^{\ne}$ was obtained in the same way as those of the poly(NIPAAm) gels (Fig. 1).[6] The $T\Delta S^{\ne}$'s were calculated at $T = 313$ K. A linear correlation is well known for various aqueous solution processes.[7]

The $\Delta G^{\ne}$'s for both pH 1 and 13 were obtained to be constant at around +82–86 kJ mol^{-1}. This is the compensation effect of $\Delta G^{\ne}$ concerning the relationship between $\Delta H^{\ne}$ and $\Delta S^{\ne}$. According to our previous paper on the deswelling of poly(NIPAAm) gels,[6] the $\Delta G^{\ne}$'s before and after the FD-treatment were around +92–96 and +81–84 kJ mol^{-1}, respectively. The conventional gel is considered to need a larger $\Delta G^{\ne}$ in order to obtain a higher deswelling pressure, resulting from the destruction of water clusters around the isopropyl groups and the aggregation of polymers due to the hydrophobic interaction. The $\Delta G^{\ne}$'s (+82–86 kJ mol^{-1}) given in Table 1 are approximately in accord with those of FD-treated poly(NIPAAm) gels. Since the $\Delta G^{\ne}$'s are positive, the gel deswelling process is not spontaneous. This is because heating above the LCST is indispensable for gel deswelling.

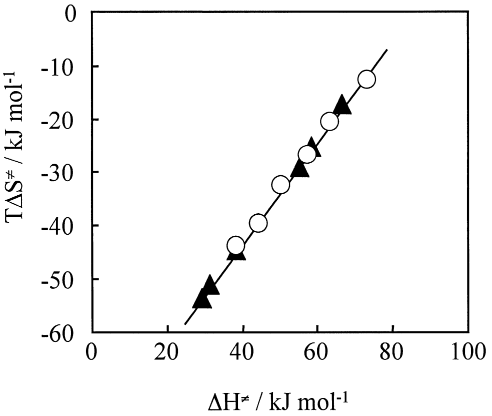

Fig. 1. Relationship between $T\Delta S^{\ne}$ and $\Delta H^{\ne}$ for deswelling of the FD-treated poly(NIPAAm/MA) gels. The gels containing 0–20 mol% MA deswelled in 0.1 M HCl (▲) and NaOH (○) aqueous solutions. The line is expressed as $T\Delta S^{\ne} = 0.94\,\Delta H^{\ne} - 81$.

In the processes for the poly(NIPAAm/MA) gel deswelling, the $\Delta H^{\ne}$ increase was always accompanied by a $\Delta S^{\ne}$ increase. Thereby, $\Delta G^{\ne}$ remained nearly constant. On the other hand, the $\Delta G^{\ne}$ of the non-porous gel without a FD-treatment was greater than that of the porous gel (+92–96 kJ mol^{-1}). $\Delta G^{\ne}$ might be controlled to be constant by the balance between the intensity of water permeation through the hydrophilic strut and the deswelling pressure due to polymer aggregation.

This work was partly supported by a Grant-in-Aid for Encouragement of Young Scientists (No. 14750613) from Japan Society for the Promotion of Science.

References

1 N. Kato and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **70**, 1289 (1997).

2 B. G. Kabra and S. H. Gehrke, *Polym. Commun.*, **32**, 322 (1991).

3 N. Kato, H. Hasegawa, and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **73**, 1089 (2000).

4 B. G. Kabra, S. H. Gehrke, and R. J. Spontak, *Macromolecules*, **31**, 2166 (1998).

5 J. Rička and T. Tanaka, *Macromolecules*, **17**, 2916 (1984).

6 N. Kato, Y. Sakai, and F. Takahashi, *Bull. Chem. Soc. Jpn.*, **74**, 2025 (2001).

7 R. Lumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).