Influence of Freely Mobile Grafted Chain Length on Dynamic Properties of Comb-Type Grafted Poly(*N*-isopropylacrylamide) Hydrogels

Yuzo Kaneko,[†] Kiyotaka Sakai,[†] Akihiko Kikuchi,[‡] Ryo Yoshida,[‡] Yasuhisa Sakurai,[‡] and Teruo Okano*,[‡]

Department of Chemical Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169, Japan, and Institute of Biomedical Engineering, Tokyo Women's Medical College, 8-1 Kawada-cho, Shinjuku-ku, Tokyo 162, Japan

Received June 2, 1995; Revised Manuscript Received August 21, 1995[⊗]

ABSTRACT: Amino semitelechelic poly(*N*-isopropylacrylamide)s (PIPAAm) with three different molecular weights were synthesized by telomerization of IPAAm monomer with 2-aminoethanethiol as a chain transfer agent, changing the molar ratio of monomer to chain transfer agent. Macromonomers of thermosensitive PIPAAm were synthesized by condensation reaction of amino semitelechelic PIPAAm with *N*-acryloxysuccinimide. The molecular weights of macromonomers determined by titration of the terminal amino groups were 2900, 4000, and 9000, respectively. The comb-type grafted PIPAAm hydrogels having different lengths of graft chains were synthesized by radical copolymerization of IPAAm monomer with PIPAAm macromonomer in the presence of *N,N'*-methylenebisacrylamide as a cross-linker. An important aspect of the graft-type gels is the construction of a molecular architecture different from PIPAAm normal type of gel even though the composition is same. Higher equilibrium swellings at lower temperatures were observed in graft-type gels in contrast to the normal-type gel, and longer graft chains resulted in higher equilibrium swelling due to the freely mobile grafted chains. Both the normal-type and the graft-type gels exhibited reversible swelling–deswelling changes in aqueous milieu in response to an alteration of temperature. The deswelling kinetics at 40 °C changed from equilibrium swelling states at 10 °C, however, exhibited remarkable differences, and rapid responses were observed for graft-type gels. The rapid dehydration of graft chains during gel shrinking was confirmed by analysis of DSC measurements. These dehydrated graft chains strongly aggregated with hydrophobic intermolecular forces, inducing the rapid deswelling of the gels. The attractive forces operating between dehydrated chains were larger in the gel having longer grafted chains, resulting in faster deswelling. A deswelling mechanism distinct from polymer network collective diffusion was demonstrated with these comb-type grafted hydrogels having freely mobile grafted chains in the network.

Introduction

Polymer gels responsive to solvent composition,[1] pH,[2,3] electric fields,[4,5] and temperature[6–10] are being utilized for potential new technical applications in chemical or mechanical engineering systems such as mass separation[11] and chemical valves,[12] as well as biomedical applications including artificial organs[13] and drug delivery systems.[7–9,14–17] For these hydrogel applications, a fast response is necessary for their practical usage. According to the reports of Tanaka and co-workers,[18,19] the response rate for the gels is inversely proportional to the square of the smallest dimension of the gel: the kinetics of gel movement are dominated by polymer network collective diffusivity. Due to this diffusion dependency, reducing gel size is one technique to achieve rapid kinetics. The other technique is to make the gel heterogeneous: a macroporous structure to increase the contact surface area between polymer and solvent was proposed by Hirasa *et al.*[20] in macroporous poly(vinyl methyl ether) or in phase-separated poly(*N*-isopropylacrylamide) (PIPAAm) hydrogels by Kabra and Gehrke[21] and Hoffman *et al.*[22] They achieved rapid swelling and deswelling volume changes in these gels in response to temperature. These proposed two technical methods—reducing gel size or introducing porosity—for rapidly responsive gels have also been developed to accelerate the diffusion process of polymer networks. In contrast to these reports, we have attempted to establish a novel mechanism to speed up gel deswelling dynamics rather than its diffusion mechanism.[6] We prepared a new thermosensitive PIPAAm hydrogel having PIPAAm chains grafted on the backbone network. This comb-type grafted hydrogel had the same chemical composition but different architecture from normal-type PIPAAm gels. This type of gel exhibited improved molecular mobility due to the existence of freely mobile grafted chains, and a rapid conformational change of graft chains in response to temperature was expected.

PIPAAm exhibits rapid hydration–dehydration changes (coil–globule transition[23]) in response to small temperature changes in aqueous media.[24,25] We previously observed drastic hydrophilic–hydrophobic changes of PIPAAm in fundamental applications, such as a cultured cell recovery system[26] and a reaction control system for enzymes,[27] both of which used surfaces or enzymes modified by terminally grafted PIPAAm chains that have freely mobile ends. Due to the mobile nature of the free chain ends, a dramatic response to temperature in cell detachment or enzyme reactivity is achieved. In contrast to the un-cross-linked chains, PIPAAm hydrogels in which both polymer ends are cross-linked and relatively immobile did not show these rapid kinetics due to the limiting collective diffusivity of the polymer network.[18,19] Rapid deswelling in response to temperature is not observed except on the surface portion of the gels. This temperature-induced surface shrunken layer (skin formation),[28–31] having high impermeability to water, disturbs the bulk network deswell-

* To whom correspondence should be addressed.
[†] Waseda University.
[‡] Tokyo Women's Medical College.
[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

0024-9297/95/2228-7717$09.00/0

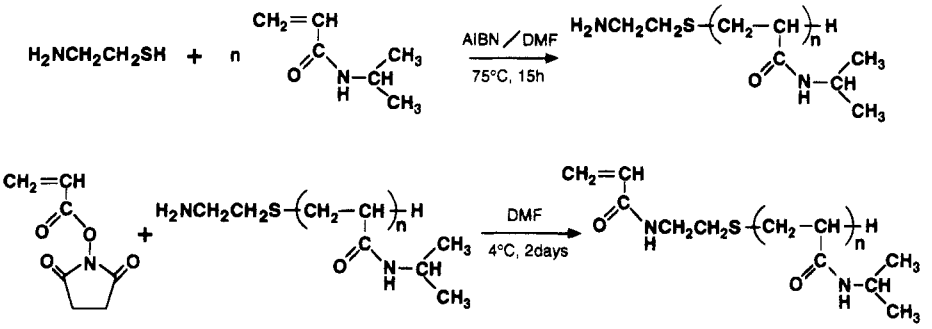

Figure 1. Preparation of PIPAAm macromonomer using telomerization and amide condensation reactions.

ing. To achieve rapid volume changes in PIPAAm gels, a quick deswelling of the bulk network is required to squeeze out entrapped water. In our novel comb-type grafted PIPAAm gel, a rapid bulk gel deswelling response together with a response at the surface region is achieved due to cooperative hydrophobic aggregation of dehydrated graft chains dispersed in the polymer network.[6] A rapid and size-independent thermoresponsive deswelling accompanied by strong aggregation of dehydrated graft PIPAAm chains was demonstrated.

Here, we introduce a discussion of the effect of graft chain length on the dynamic properties of this newly developed gel. Graft-type hydrogels having a grafted chain with different molecular weights are synthesized. The freely mobile grafted chain length can alter the mobility of the cross-linked main polymeric chains. Therefore, the responsive rate of the deswelling process for the graft-type gel might reflect the influence of graft chain lengths.

Experimental Section

Materials. *N*-Isopropylacrylamide (IPAAm; Eastman Kodak Co., Rochester, NY) was purified by recrystallization from toluene/*n*-hexane.[24,25] *N,N'*-Azobisisobutyronitrile (AIBN; Wako Pure Chemical Industries, Co., Ltd., Osaka, Japan) was recrystallized from methanol. *N,N*-Dimethylformamide (DMF; Kanto Chemical Co., Ltd., Tokyo, Japan) was distilled and obtained as a fraction boiling at 76 °C/39 mmHg. 2-Aminoethanethiol (AESH; Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan), *N*-acryloxysuccinimide (NAS; Eastman Kodak Co.), tetramethylethylenediamine (TEMED; Kanto Chemical Co.), ammonium persulfate (APS; Kanto Chemical Co.), *N,N'*-methylenebisacrylamide (MBAAm; Kanto Chemical Co.), and diethyl ether (Kanto Chemical Co.) were used as received.

Polymer Synthesis. IPAAm macromonomers having different molecular weights were prepared as follows.[32,33] First, a semitelechelic PIPAAm with a terminal amino end group was synthesized by radical telomerization of the IPAAm monomer using AESH as a chain transfer agent. This synthetic process is shown in Figure 1. Known amounts of IPAAm, AESH, and AIBN as an initiator were dissolved in DMF. The ampule containing the solution was degassed by freeze–thaw cycles and then sealed in vacuo and immersed in a water bath held at 75 °C for 15 h. After concentrating the reactant by DMF evaporation, the reactant was poured into diethyl ether to precipitate semitelechelic PIPAAm. PIPAAm was collected over a filter and purified by repeated precipitation in diethyl ether from DMF. Polymer product was then dried by freeze-drying from water solution. For the second step of preparation of PIPAAm macromonomer, a polymerizable end group was introduced into the amino semitelechelic PIPAAm using an amide condensation reaction between amino groups in PIPAAm and NAS (molar ratio 1:10) in DMF at 4 °C for 2 days. The purification process for macromonomers followed the same process for PIPAAm having terminal amino groups.

PIPAAm Molecular Weight Determination. The number-average molecular weights of PIPAAm having amino-terminated groups were determined by titration of amines. Polymer samples (0.1 g) were dissolved in 10 mL of acetic acid, and these solutions were titrated with 0.1 M perchloric acid–acetic acid standard solution using crystal violet as an indicator. The molecular weight of PIPAAm was calculated by dividing polymer mass samples by molar amount of added standard solution.[34]

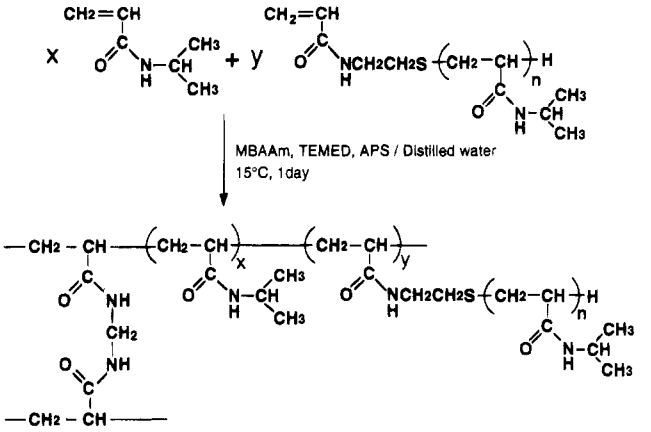

Figure 2. Synthetic procedure for comb-type grafted PIPAAm gels by radical copolymerization of IPAAm monomer with PIPAAm macromonomer using MBAAm as a cross-linking agent.

Table 1. Feed Composition for Preparation of PIPAAm Normal-Type Gel (NG) and Comb-Type Grafted PIPAAm Gel (GG)

	NG	GG
macromonomer (wt %)	0	30
IPAAm monomer (g)	1.5600	1.0920
macromonomer (g)		0.4680
MBAAm (g)	0.0266	0.0266
TEMED (μL)	48	48
APS (g)	0.0080	0.0080
distilled water (mL)	10	10

Synthesis of Cross-Linked Gels. To synthesize comb-type grafted PIPAAm gels, IPAAm monomer (70 wt %), PIPAAm macromonomers (30 wt %), MBAAm as a cross-linker (1.7 wt % with respect to monomers), and TEMED as an accelerator were dissolved in 10 mL of distilled water and bubbled with dry nitrogen gas for 10 min. After the addition of 8 mg of APS as an initiator (0.5 wt % with respect to monomers), the solutions were injected between two Mylar sheets separated by a Teflon gasket (2.0 mm) and backed by glass plates. The feed compositions of monomers and other chemicals are listed in Table 1. The solution was polymerized at 15 °C for 1 day. This synthetic procedure is illustrated in Figure 2. To remove unreacted compounds, the formed gel membranes were immersed in pure water for 1 week at room temperature with water changed every day. The swollen gel membranes were cut into disks (15 mm diameter) using a cork borer and dried under ambient conditions for 1 day followed by thorough drying under vacuum for 5 days at room temper-

Table 2. Preparation and Analysis of PIPAAm Macromonomers

sample no.	IPAAm (g)	AESH (g)	AIBN[a] (g)	DMF (mL)	[S]/[M][b]	conversion (%)	MW[c]
1	5.7950	0.2173	0.0887	22.3	0.055	71.7	2900
2	8.9621	0.0611	0.1314	33.4	0.010	86.8	4000
3	13.407	0.1279	0.0197	50.0	0.014	90.0	9000

[a] AIBN concentration, 0.1 mol % monomer. [b] [S], concentration of chain transfer agent (AESH); [M], monomer concentration (IPAAm). [c] Molecular weight determined by titration of terminal amino end group.

ature. For comparison, normal-type PIPAAm gel without PIPAAm macromonomer was synthesized by this same method.

Swelling Equilibria for Hydrogels. The equilibrium swelling ratio was defined as the weight of absorbed water per weight of dried polymer disk (W_{H_2O}/W_p). Equilibrium swelling weights for the gels in water over a series of temperatures were measured gravimetically after wiping excess water from the gel surface with filter paper. The gels were first equilibrated in pure water at higher temperature for 3 days. The temperature was lowered after weighing the gel mass and then the gels were equilibrated for swollen conditions. This process was repeated to a temperature of 10 °C.

Swelling and Deswelling Kinetics of Hydrogels. Both disk-shaped PIPAAm normal-type gel and the comb-type grafted PIPAAm gels were first equilibrated in pure water at predetermined temperatures. Gels were then quickly transferred into water at different temperatures. At specific time points, these gels were removed from the water and weighed after wiping with a filter paper to remove excess water from the gel surface. Swelling and deswelling kinetics were defined as temporal weight changes for the gels. The weight data from averages of three samples are converted to the normalized swelling which indicate the volume changes of hydrogels between equilibrium swollen (100%) and equilibrium shrunken (0%) states (or dry gel state).

DSC Measurements. Gel disks equilibrated at 10 °C (same sizes as for kinetics measurements) in pure water were quickly transferred into water at 40 °C. The sample for the DSC measurements was then cut into disks (4 mm diameter at center of gel) at predetermined time points using a cork borer. After excess water was wiped from each gel surface, the sample was sealed in an aluminum pan and placed in the DSC apparatus (Mettler TA-3000 system, Mettler Instrumente AG, Switzerland). After cooling to −20 °C within 5 min, the sample was heated to 40 °C at the rate of 1 K/min. The endothermal heat of water in the gels was measured using an empty aluminum pan as a reference. From the integral of the endothermal peak for water fusion (near 0 °C), gel freezable water content was determined. Total water content was determined by the weight difference between the swollen gel and the dried gel. Nonfreezable water content was calculated from the difference between total and freezable water content for these gels.

Results and Discussion

Polymer Synthesis. Three types of PIPAAm were prepared, and their molecular weights were determined by acid−base titration. Relationships between molar ratio of chain transfer agent to IPAAm monomer and molecular weight of synthesized PIPAAm are listed in Table 2. The prepared PIPAAm polymers have number-average molecular weights of 2900, 4000 and 9000, respectively.

Hydrogel Synthesis. Comb-type grafted gels were prepared by radical copolymerization of PIPAAm macromonomers with IPAAm in the presence of MBAAm as a cross-linker. The graft-type gels constructed with each length of macromonomer were designated as GG2900, GG4000, and GG9000, respectively. The weight conversions of graft-type gels from monomers were almost 60%. Normal-type PIPAAm gel without grafted PIPAAm chains was described as NG, having a weight conversion of about 80%. As the weight ratio of IPAAm to PIPAAm graft chains was kept constant, the number of polymer branches along the backbone networks was larger as the length of macromonomers was shorter.

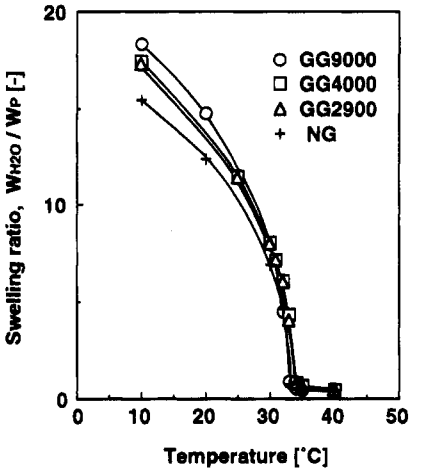

Figure 3. Equilibrium swelling ratio for the hydrogels as a function of temperature in pure water.

Equilibrium Swelling Measurements. Measurements of equilibrium swelling ratios for the gels in water, shown in Figure 3, indicate that the comb-type grafted PIPAAm gels have the same phase transition temperatures (32 °C) as the normal-type PIPAAm gel containing the same amount of IPAAm. The mobility of graft chains affects the gel swelling behavior. Below the phase transition temperatures, graft-type gels demonstrate slightly higher swelling than the normal-type gel. The longer PIPAAm chain gels show higher swelling at lower temperatures. As longer chains are structurally separated from the backbone cross-linked network, strong hydration is possible. This chain expansion may result in increased hydration in GG9000 over GG2900 or GG4000 hydrogels. Graft-type gels with different graft chain lengths may have different cross-linking density. The effect of different cross-linking density may not be excluded on the equilibrium swelling levels at lower temperature. Controlling the length of grafted chain freely mobile ends regulates the equilibrium properties of hydrogels.

Swelling Behavior of Hydrogels. Figure 4 shows the swelling kinetics for four types of hydrogels from dry conditions at 10 °C in pure water. Samples of comb-type grafted PIPAAm gels and normal-type PIPAAm gels with identical thicknesses and diameters demonstrate the same swelling kinetics. Generally, the swelling process of gels take three steps described as follows:[35−37] (1) diffusion of water molecules to the glassy gel matrix; (2) gel phase transition from glassy state to rubbery state due to hydration of polymers; and (3) collective diffusion of polymer networks toward the surrounding water. The gels change their structure from compact to expanding forms during the swelling. In the process of hydration and polymer expansion, rapid and strong graft chain hydration did not occur because these chains were frozen, surrounded by the

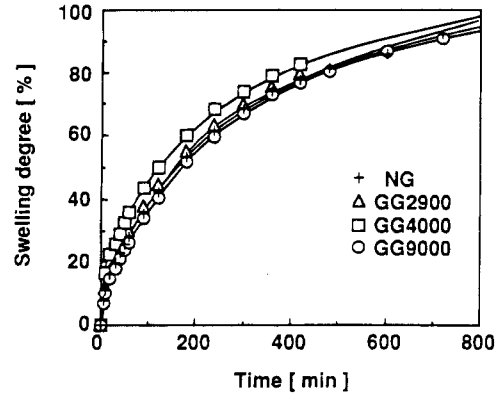

Figure 4. Time course of swelling for hydrogels undergoing swelling at 10 °C from dry conditions.

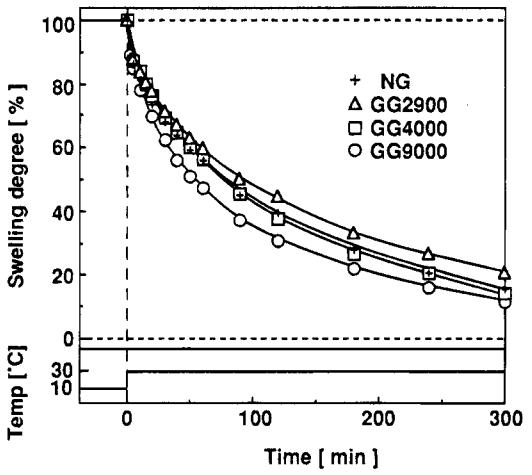

Figure 5. Time course of deswelling for hydrogels undergoing shrinking at 30 °C in response to stepwise temperature changes from 10 °C.

hydrophobic collapsed backbone network sterically hindering hydration and relaxation of grafted polymers. Due to this swelling behavior, the swelling kinetics of all gels were governed by polymer network diffusion. These similar swelling kinetics between four types of gels also suggested that graft-type gels maintained their homogeneous structure and did not exhibit porous structure. A porous structure is known to accelerate gel swelling dynamics.[20-22]

Deswelling Behavior of Hydrogels. Figure 5 shows the deswelling kinetics of hydrogels preequilibrated at 10 °C by elevating the temperature to 30 °C. The four types of gels decreased their water content similarly, gradually deswelling in response to temperature changes. At 30 °C, which is beneath the phase transition temperatures of the gels, the gels maintained slightly expanding structures. Hydrated graft polymers at lower temperature desorb water molecules to make more compact forms (swollen coils[38,39]) during gel shrinking. Graft chains could not form hydrophobic nuclei, and the strong hydrophobic elastic aggregation forces between hydrated chains did not occur. Therefore, beneath the phase transition temperature, the diffusion of the polymer network becomes the rate-determining step,[18,19,40] which is schematically illustrated in Figure 6.

In contrast, large differences in the deswelling behavior of hydrogels are seen during shrinking at 40 °C, above the gel phase transition temperature. The kinetics of gel shrinking are demonstrated in Figure 7. The normal-type PIPAAm gel shrunk slowly and took sev-

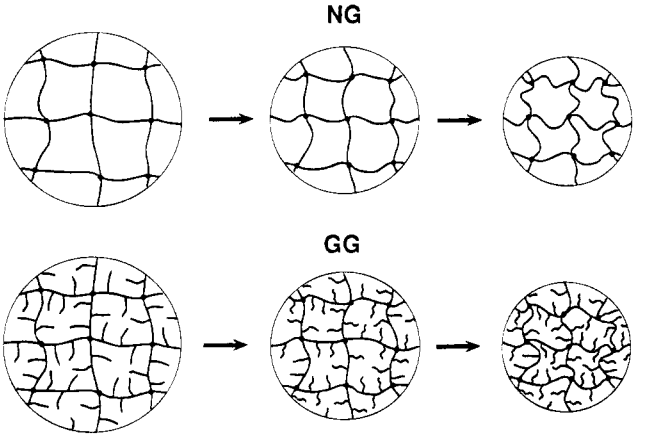

Figure 6. Schematic illustration for deswelling kinetics of hydrogels shrinking beneath their phase transition temperatures.

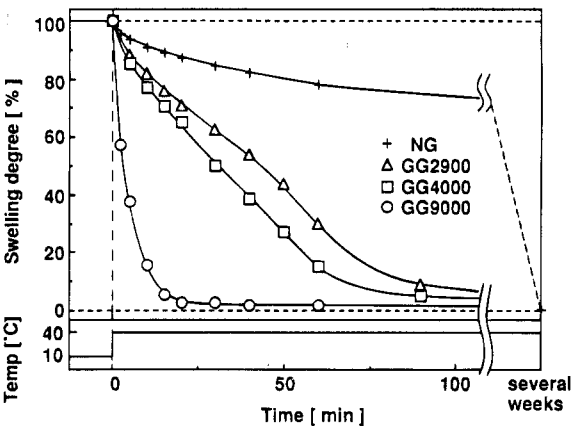

Figure 7. Time course of deswelling for hydrogels undergoing shrinking at 40 °C in response to stepwise temperature changes from 10 °C.

eral weeks to reach its equilibrium deswelling state. On the other hand, graft-type hydrogels shrunk rapidly on the minute time scale, and the quick response was ranked in the order of graft chain length in response to temperature changes. The actual shrinking processes of these disk-shaped gels are demonstrated in the series of photographs in Figure 8. The gels became opaque after stepwise temperature increase from 10 to 40 °C. This indicates that the polymer networks become heterogeneous immediately after the temperature jumps. At the molecular level, the polymers are phase-separated from water molecules. The normal-type PIPAAm gel formed skin layers.[28-31] These surface dense and stable polymer layers balanced the deswelling forces with internal pressure[19,40,41] during shrinking, preventing water release from the gel. This process of skin formation was mediated by diffusion of the collapsing polymer network at the interface.[18,19,40] Due to this skin formation, a slow release of entrapped water is observed. Therefore, the slow deswelling observed requires more than several weeks to its final equilibrium state, and this heterogeneous structure between the gel's inside and its surface causes the gel to be opaque.

The comb-type grafted PIPAAm hydrogels, GG2900 and GG4000, show the bubble formation common to the normal-type PIPAAm gel[19,29,40] immediately after the temperature increase during shrinkage. Larger bubbles are observed for hydrogels with shorter graft chain lengths. The heterogeneous structure of the polymers was rapidly and strongly formed on the surface of the gels. This temporal formation of surface layers ac-

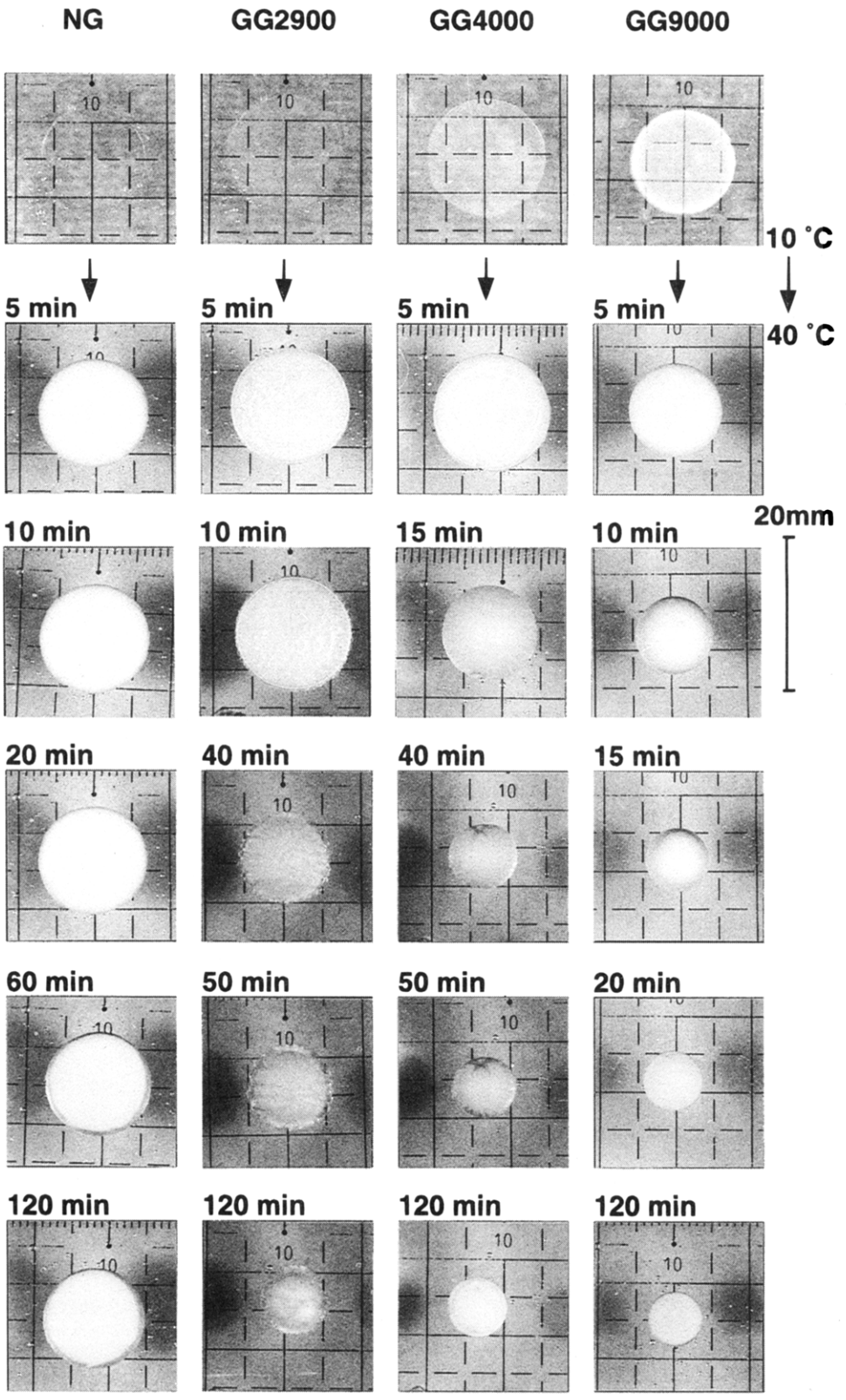

Figure 8. Photographs of the deswelling process of disk-shaped normal-type PIPAAm gel and comb-type grafted PIPAAm gels undergoing shrinking at 40 °C after elevated temperature from 10 °C.

cumulated the hydrostatic internal pressure within the gels.[19,40,41] The strong aggregation accumulated large internal pressure to create the bubble formation on the surface structure, and the entrapped water is squeezed out from the gel interior through this bubble formation on the surface. The gel GG2900 formed more stable, dense surface layers than GG4000, which result in larger bubble formation during the collapse.[40] Although gel deswelling starts from the surface, water is pushed out from inside the gel due to strong aggregation within the bulk polymer network in the case of GG4000. These strong aggregation forces of bulk network relatively weakened the influence of the surface layers on the gel collapse. In particular, GG9000 showed no formation of surface deswelling layers which results in no bubble appearance. GG9000 gel did exhibit mechanical buck-

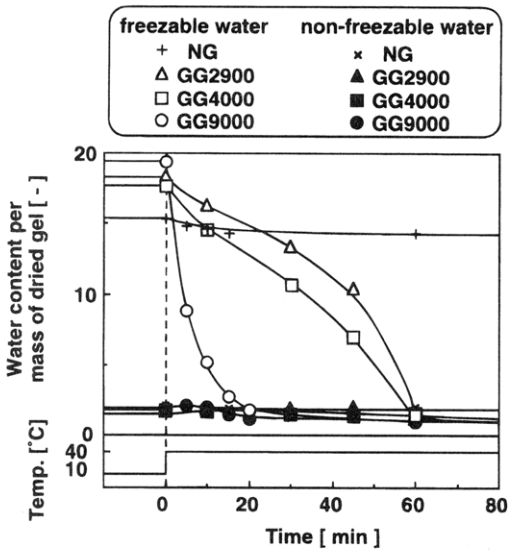

Figure 9. Time course of changes in water structure inside deswelling hydrogels determined by DSC measurements. The samples undergo deswelling at 40 °C after equilibrated swelling at 10 °C

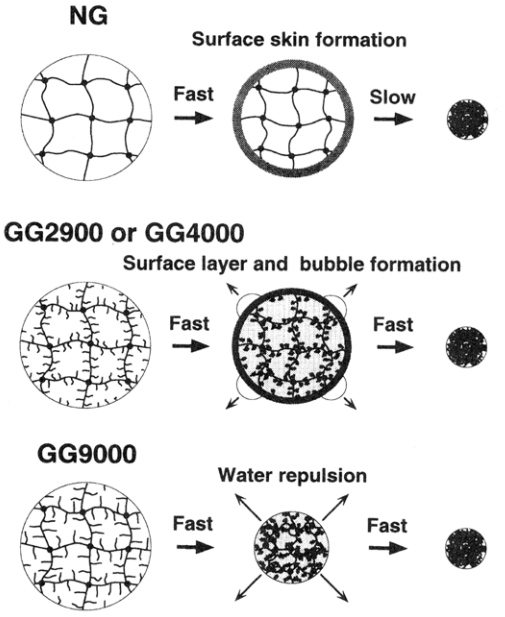

Figure 10. Schematic illustration of deswelling mechanism of comb-type grafted PIPAAm gels having different lengths of grafted chains above their phase transition temperature.

ling (10−15 min after temperature increase shown in Figure 8), demonstrating the strong chain aggregation forces inward in the hydrogels. The strong aggregation of bulk interior polymers creates large hydrostatic pressures within this gel, and the water is repulsed rapidly from the gel inside to external media without delay.

This strong repulsion phenomenon of entrapped water is readily observed by DSC measurements of the water structure inside the deswelling hydrogel networks. The changes in amount of freezable and nonfreezable water within the four types of gel matrices were determined and are shown in Figure 9. We define freezable water as water having the same physical properties of bulk water, and nonfreezable water as the water restricted in its molecular mobility due to interactions between water and the polymers. The time courses for decreasing water were comparable to those of volume change kinetics shown in Figure 7. As can be seen from Figure 9, the amount of freezable water in the GG9000 decreased dramatically within 20 min after the temperature was increased to 40 °C, although nonfreezable water content remained nearly constant at low levels. A gradual decrease in freezable water was also observed for both GG2900 and GG4000. In contrast to these graft-type PIPAAm gels, a slight decrease in freezable water content was observed for the PIPAAm normal-type gel up to 60 min. Therefore, dramatic swelling changes observed for the GG9000 gel are attributed to decreases in freezable water content in the gel. The gradual decreases of freezable water in GG2900 and GG4000 were also due to surface deswelling layers entrapping water inside gels for the initial state of deswelling.

Grafted chains maintain higher mobility as opposed to polymer networks cross-linked on each chain end because they are free end polymers. We have already observed dramatic surface property changes for grafted PIPAAm surfaces within a small temperature change from contact angle measurements.[34] The behavior of these systems is distinct from those PIPAAm molecules attached by anchoring at several points along the chain: the decrease in hydrophilicity with increasing temperature is less for the latter than for surfaces with terminally grafted chains. The grafted PIPAAm having freely mobile ends can hydrate sufficiently and contain a large amount of freezable water. When external temperature is elevated over its phase transition temperature, the grafted polymers are rapidly dehydrated, making tightly packed globule chains,[38,39] and almost freezable water is expelled. Due to this water release, rapid deswelling of graft-type PIPAAm gel is induced, followed by the subsequent hydrophobic intermolecular aggregation forces between dehydrated grafted chains. In the case of GG9000, rapid shrinking kinetics also resulted from the lack of collapsed polymer skin on the gel surface after temperature increases as described earlier. An increase in void volume within the GG9000 polymer network resulting from dehydration of grafted PIPAAm chains may also facilitate the rapid release of entrapped water to the gel exterior. Attractive forces between dehydrated graft chains are enhanced for the gel with longer grafted chains due to their larger molecular weight, and the hydrophobic aggregates were readily formed due to the size effect of these long chains. This may contribute the strong aggregation forces between dehydrated grafted chains within GG9000.

In contrast, aggregation forces between dehydrated graft chains were weakened for GG2900 and GG4000 due to their shorter length. Therefore, the effect of deswelling from the surface was relatively enhanced, which was always accompanied by surface deswelling layers and bubble formation. The deswelling rate of GG4000 became faster than for GG2900 due to the higher forces of aggregation and pressure for repulsing interior water. Entrapped freezable water was released gradually from inside the gels through the surface layers in GG2900. These deswelling mechanisms for graft-type hydrogels are schematically illustrated in Figure 10.

Hydrophilic comonomers are known to disrupt the skin barrier formation on the gel surface.[40,42] Thermosensitive PIPAAm gels having 2 mol% hydrophilic acrylic acid (AAc) as a comonomer shrunk rapidly because they did not form the surface stable dense shrunken layers due to decreased hydrophobic aggregation forces within polymer networks.[42] In P(IPAAm-

AAc) copolymer gels, the prevention of water flow did not occur and collective diffusion of the polymer network might determine the rate of gel volume transition above the phase transition temperatures. In contrast, our gel showed strong aggregation forces of the bulk network owing to rapid dehydration of the graft chains, resulting in strong water repulsion and rapid deswelling. A novel deswelling mechanism based on the inherent elastic forces of polymers rather than collective diffusion was introduced. Surface stable and dense skin structure could not form because the strong aggregation forces broke the balance between deswelling forces and internal pressure.

Due to the novel architecture of the polymer network, the rate of rapid gel deswelling is readily controlled by the length of freely mobile grafted chains exposed to water. This structure may allow an increasing contact opportunity between the water and polymers, causing rapid deswelling of hydrogels in contrast to normal-type gels lacking the grafted chains.

Conclusions

In this research, we synthesized thermosensitive comb-type grafted PIPAAm hydrogels having different graft chain lengths. These gels had the same chemical composition but different architecture from the normal-type PIPAAm gel. The molecular mobility of polymers in a graft-type gel was improved due to the existence of freely mobile grafted chains. The equilibrium properties and rate of volume changes of hydrogels were readily controlled by the chain length of the grafted polymers. A longer chain length allowed higher equilibrium swelling and rapid deswelling dynamics. Denser surface shrunken polymer layers were formed on the gel having shorter graft chains, and a larger magnitude of internal hydrostatic pressure during shrinkage accumulated within the gel having longer graft chains.

In contrast to the dynamic properties of hydrogels dominated by the diffusion-limited transport of polymeric components of the network in water (collective diffusion), we demonstrated a new concept for controlling gel swelling behavior by introducing rapid conformational changes of freely mobile, grafted polymers in response to temperature. We believe that using such intrinsic elastic forces of unhindered temperature-sensitive polymer chains within the network of a novel architecture can eliminate current limitations to achieve rapidly acting smart actuators.

Acknowledgment. The authors are grateful to Professor David W. Grainger, Department of Chemistry, Colorado State University, for valuable comments and discussions. This work was supported in part by Special Coordination Funds of the Science and Technology Agency of the Japanese Government.

References and Notes

(1) Hirokawa, E.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(2) Chen, G.; Hoffman, A. S. *Nature* **1995**, *373*, 49.
(3) Kiler, J.; Scranton, A. B.; Peppas, N. A. *Macromolecules* **1990**, *23*, 4944.
(4) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242.
(5) Kwon, I. C.; Bae, Y. H.; Kim, S. W. *Nature* **1991**, *354*, 291.
(6) Yoshida, R.; Uchida, K.; Kaneko, Y.; Sakai, K.; Kikuchi, A.; Sakurai, Y.; Okano, T. *Nature* **1995**, *374*, 240.
(7) Okano, T.; Bae, Y. H.; Kim, S. W. In *Pulsed and Self-Regulated Drug Delivery*; Kost, J., Ed.; CRC Press: Boca Raton, FL, 1990; p 17.
(8) Okano, T.; Yui, N.; Yokoyama, M.; Yoshida, R. *Advances in Polymeric Systems for Drug Delivery*; Gordon & Breach Science Publishers: Yverdon, Switzerland, 1994; p 67.
(9) Hoffman, A. S. *J. Controlled Release* **1987**, *6*, 297.
(10) Dusek, K., Ed. *Responsive Gels: Volume Transitions II*; Springer-Verlag: Berlin, 1993.
(11) Cussler, E. L.; Stoker, M. R.; Varferg, J. E. *AIChE J.* **1984**, *30*, 578.
(12) Osada, Y. *Advances in Polymer Science*; Springer-Verlag: Berlin, 1987; Vol. 82, p 1.
(13) Shiino, D.; Murata, Y.; Kataoka, K.; Koyama, Y.; Yokoyama, M.; Okano, T.; Sakurai, Y. *Biomaterials* **1994**, *15*, 121.
(14) Yoshida, R.; Kaneko, Y.; Sakai, K.; Okano, T.; Sakurai, Y.; Bae, Y. H.; Kim, S. W. *J. Controlled Release* **1994**, *32*, 97.
(15) Aoki, T.; Kawashima, M.; Katono, H.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. *Macromolecules* **1994**, *27*, 947.
(16) Hoffman, A. S.; Afrassiabi, A.; Dong, L. C. *J. Controlled Release* **1986**, *4*, 213.
(17) Peppas, N. A.; Korsmeyer, R. W. In *Hydrogels in Medicine and Pharmacy*; Peppas, N. A., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. III, p 122.
(18) Tanaka, T.; Fillmore, D. J. *J. Chem. Phys.* **1979**, *70*, 1214.
(19) Sato Matsuo, E.; Tanaka, T. *J. Chem. Phys.* **1988**, *89*, 1695.
(20) Hirasa, O.; Ito, S.; Yamauchi, A.; Fujishige, S.; Ichijo, H. In *Polymer Gels*; DeRossi, D., et al., Eds.; Plenum Press: New York; 1991; p 247.
(21) Kabra, B. G.; Gehrke, S. H. *Polym. Commun.* **1991**, *32*, 322.
(22) Wu, H. S.; Hoffman, A. S.; Yager, P. *J. Polym. Sci., Part A* **1992**, *30*, 2121
(23) Dusek, K.; Patterson, D. *J. Polym. Sci., Part A-2* **1968**, *6*, 1209.
(24) Heskins, M.; Guillet, J. E.; James, E. *J. Macromol. Sci. Chem.* **1968**, *A2*, 1441.
(25) Schild, H. G. *Prog. Polym. Sci.* **1992**, *17*, 163.
(26) Okano, T.; Yamada, N.; Okuhara, M.; Sakai, H.; Sakurai, Y. *Biomaterials* **1995**, *16*, 297.
(27) Matsukata, M.; Takei, Y. G.; Aoki, T.; Sanui, K.; Ogata, N.; Sakurai, Y.; Okano, T. *J. Biochem.* **1994**, *116*, 682.
(28) Bae, Y. H.; Okano, T.; Kim, S. W. *Makromol Chem. Rapid Commun.* **1988**, *9*, 185.
(29) Okano, T.; Bae, Y. H.; Jacobs, H.; Kim, S. W. *J. Controlled Release* **1990**, *11*, 255.
(30) Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. *J. Biomater. Sci., Polym. Ed.* **1992**, *3*, 243.
(31) Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. *J. Biomater. Sci., Polym. Ed.* **1994**, *6*, 585.
(32) Okano, T.; Katayama, M.; Shinohara, I. *J. Appl. Polym. Sci.* **1978**, *22*, 369.
(33) Takei, Y. G.; Aoki, T.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. *Bioconjugate Chem.* **1993**, *4*, 341.
(34) Takei, Y. G.; Aoki, T.; Sanui, K.; Ogata, N.; Sakurai, Y.; Okano, T. *Macromolecules* **1994**, *27*, 6163.
(35) Vrentas, J. S.; Jarzebski, C. M.; Duda, J. L. *AIChE J.* **1975**, *21*, 894.
(36) Okuyama, Y.; Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. *J. Biomater. Sci., Polym. Ed.* **1993**, *4*, 545.
(37) Yoshida, R.; Okuyama, Y.; Sakai, K.; Okano, T.; Sakurai, Y. *J. Membr. Sci.* **1994**, *89*, 267.
(38) Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, *93*, 3311.
(39) Kubota, K.; Fujishige, S.; Ando, I. *J. Phys. Chem.* **1990**, *94*, 5154.
(40) Kaneko, Y.; Yoshida, R.; Sakai, K.; Sakurai, Y.; Okano, T. *J. Membr. Sci.* **1995**, *101*, 13.
(41) Yoshida, R.; Sakai, K.; Okano, T.; Sakurai, Y. *Ind. Eng. Chem. Res.* **1992**, *31*, 2339.
(42) Gutowska, A.; Bae, Y. H.; Kim, S. W. *J. Controlled Release* **1992**, *22*, 95.

MA950763K