

Synthesis and Swelling/De-swelling Behavior of Core-Shell Type Gel Consisting of Two Different Poly(*N*-alkylacrylamide) Gel Layers

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ABSTRACT: When poly(acrylic acid) gel-1,8-diazabicyclo-[5,4,0]-7-undecene salt (DAA) was placed in *N*-methyl-2-pyrrolidone containing an excess of alkylamine and triphenylphosphine, selective amidation occurred from the surface to give the corresponding DAA-poly(*N*-alkylacrylamide) (PNAA) core-shell type gel, consisting of an unreacted DAA core and a quantitatively amidated shell layer. Further amidation of the DAA-PNAA core-shell type gel with a second alkylamine afforded a novel core-shell type gel consisting of two PNAA layers: PNAA(2) and PNAA(1). Thermal properties of the resulting core-shell type gels, such as swelling/de-swelling behavior, were measured in water at various temperatures. The resulting cylindrical PNAA(2)-PNAA(1) core-shell type gels were resistant to marked deformation caused by swelling/de-swelling because of their axial symmetry. In contrast, the semi-cylindrical double-layer gel prepared from the cylindrical poly(*N*-isopropylacrylamide)-poly(*N*-*n*-propylacrylamide) core-shell type gel was markedly bent in water at temperatures between the lower critical solution temperatures of both layers.

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KEY WORDS Thermosensitive Gel / Poly(*N*-alkylacrylamide) Gel / Amidation / Core-shell Type Gel / Swelling / De-swelling / Semi-cylindrical Gel /

Poly(*N*-alkylacrylamide) (PNAA) gels containing C2-C3 alkyl groups are thermosensitive with lower critical solution temperatures (LCST).¹ They swell in water at temperatures below the LCST and de-swell at temperatures above the LCST. The LCST varies, depending on the alkyl groups. Since poly(*N*-isopropylacrylamide) (PNIPA) gel has an LCST at a temperature slightly higher than room temperature,² it can be used in a variety of applications such as extraction,³ absorption,⁴ drug-delivery,⁵ and enzyme immobilization.⁶ Also, synthetic techniques for particles,⁷ porous gels,⁸ graft polymers,⁹ and comb polymers¹⁰ that are suitable for use in applications have been developed. However, conventional synthetic techniques are not always available for new applications of PNAA because the only known synthetic methods are based on the radical polymerization of the corresponding monomers. Another synthetic method is direct condensation of poly(acrylic acid) (PAA) with an alkylamine, using an activating agent. Activating agents and reaction systems for amidation have been developed for the direct polycondensation of dicarboxylic acids with diamines.¹¹ However, the application of these methods to the synthesis of thermosensitive polymers has been described in only a few papers.¹²

In recent studies, we reported a new synthetic method of core-shell type gels by the heterogeneous reac-

tion of the PAA-1,8-diazabicyclo-[5,4,0]-7-undecene (DBU) salt (DAA) with reagents, such as alkyl halides¹³ and alkylamines,¹⁴ and on the acetylation of poly(2-hydroxyethyl acrylate) gel.¹⁵ When triphenylphosphite (TPP) was used as the activating agent, the amidation of DAA with alkylamine started from the surface of the gel, yielding a new DAA-PNAA core-shell type gel that consisted of an unreacted DAA core and a chemically reacted PNAA shell (Figure 1, Figure 2).¹⁴ Finally, the reaction afforded PNAA gel. Since the unreacted DAA core in the core-shell type gel is the same as the original DAA, it can react with various reagents to give a wide variety of core-shell type gels. For example, neutralization of DAA-PNAA type core-shell type gels with acetic acid produced the corresponding PAA-PNAA type core-shell

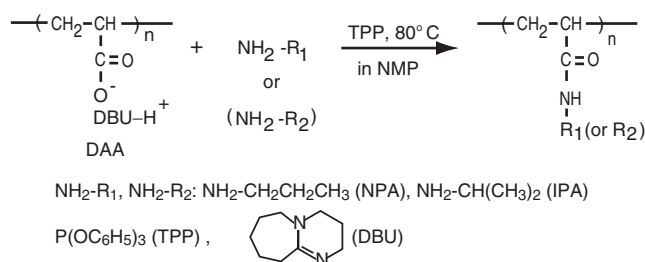


Figure 1. Synthesis of a PNAA gel via the reaction of DAA with NPA and IPA.

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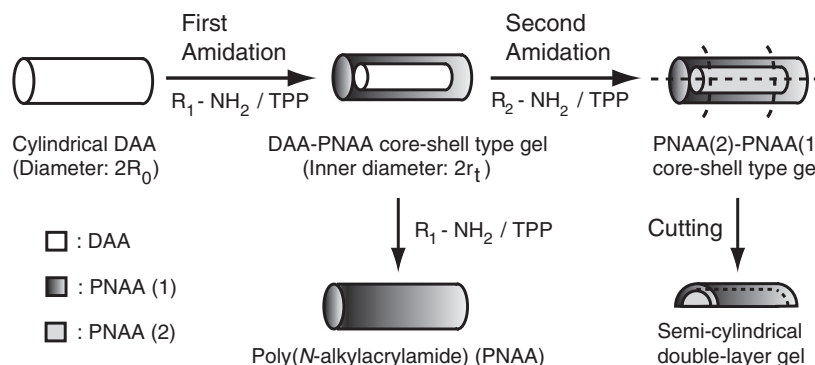


Figure 2. Synthesis of a PNAAs gel, DAA-PNAAs core-shell type gel, PNAAs(2)-PNAAs(1) core-shell type gel, and semi-cylindrical, double-layer gel.

type gels.^{14b,d} Although seed emulsion polymerization has been well-known for the synthesis method of fine core-shell type particles,¹⁶ this heterogeneous amidation possess great advantages over the polymerization method as follows; since the resulting core-shell type gels have essentially the same main chain structure and shape as the original DAA samples, 1) a desired shape and size of core-shell type gel can be prepared as well as fine particles, and 2) it has a defined structure—a continuous network and a boundary between both layers. These advantages prompt us to design a functional core-shell type gel which can hardly be prepared by the polymerization of the corresponding monomers.

This paper reports the successful synthesis of novel cylindrical core-shell type gels, consisting of two different PNAAs gel and poly(*N*-*n*-propylacrylamide) (PNNPA) gel layers as PNAAs(2) and PNAAs(1), by further amidation of the DAA-PNAAs core-shell type gels with another alkylamine, using TPP as the activating agent (Figure 2). Furthermore, we propose the preparation of semi-cylindrical, thermosensitive, double-layer gels; the long cylindrical core-shell type gels are cut into two halves. The unique structure—a continuous network and a boundary between both layers is of interest because the thermosensitive behavior may differ between the layers, and the structure may have strong resistance against destruction on the boundary.

EXPERIMENTAL

Materials

Acrylic acid and solvents were distilled prior to use. Commercial alkylamines such as *n*-propylamine (NNA) and isopropylamine (IPA) were used as purchased. *N,N'*-methylenebisacrylamide (MBAA), DBU, and TPP were used without further purification. Cylindrical DAA (diameter: about 5.3, length: about 20 mm) was prepared *via* a two-step procedure, in-

volving the copolymerization of acrylic acid with 0.5 mol % of MBAA in Teflon tubes (internal diameter: 6 mm), and neutralization of the resulting gel with excess DBU in methanol, as described previously.^{14a} The samples were washed extensively with methanol in a Soxhlet extractor, and then dried *in vacuo* at 60 °C to a constant weight. Nonporous cylindrical PNIPAA gels (PNIPAA-2) were prepared by the copolymerization of NIPAA with 0.5 mol % of MBAA in Teflon tubes (internal diameter: 6 mm) at a temperature below 5 °C according to Kayaman's paper.¹⁷ Porous spherical PNIPAA gel (PNIPAA-3) containing 2 mol % MBAA prepared by sedimentation polymerization was used.^{7b}

Synthesis of DAA-PNAAs core-shell type gels

A typical synthesis of DAA-PNAAs type core-shell type gels was as follows. 200 mL of a mixed solution of TPP (1.0 mol L⁻¹) and NPA (2.0 mol L⁻¹) in NMP was charged into a 300 mL Erlenmeyer flask in an 80 °C water bath. Dozens of DAA samples ($2R_0 = 5.3$ mm) were soaked in this solution for 200 min until the thickness of the shell layer ($1 - r_t/R_0$) reached 0.30, where $2R_0$ and $2r_t$ are the external diameters of the original DAA sample and core after $t = t$ min, respectively. The gels were taken out of the solution and put in a large quantity of methanol to terminate the reaction. The resulting G-2, DAA-PNNPA core-shell type gels were washed with methanol in a Soxhlet extractor. They were dried *in vacuo* at 60 °C to a constant weight.

Synthesis of PNAAs(2)-PNAAs(1) core-shell type gels

A typical synthesis of PNAAs(2)-PNAAs(1) core-shell type gels was as follows. 200 mL of a mixed solution of TPP (1.0 mol L⁻¹) and IPA (2.0 mol L⁻¹) in NMP was charged into a 300 mL Erlenmeyer flask in an 80 °C water bath. Dozens of G-2 samples were soaked in this solution for 24 h. The gels were taken out of the solution and placed in a large quantity of

methanol. The resulting **PNAA(2)-PNAA(1)** core-shell type gels were washed with a dilute acetic acid solution in methanol for 1 d, and then with methanol in a Soxhlet extractor for 1 d. They were dried *in vacuo* at 60 °C to a constant weight. The gel was dipped in triethylamine solution in methanol (10 mmol L⁻¹, 25 mL) at room temperature for 24 h. Free carboxylic acid in the gel was determined by neutralization titration of the filtrate with 0.01 mol L⁻¹ HCl solution. However, it was not detected.

Measurement of IR spectra of PNNPA-PNIPA core-shell type gels

A **PNNPA-PNIPA** core-shell type gel sample was swollen in water at 25 °C, and was cut into round slices. The swelled PNIPA shell layer was peeled off to divide into two groups, the swelled shell layer and unswelled core. After drying, every group was grinded down with an agate mortar. IR spectra (KBr) of the grinded powders were obtained using a Perkin Elmer model IR-700 spectrophotometer.

Measurement of Amidation Rate of DAA and DAA-PNAA core-shell type gels with Alkylamine

In a typical amidation of dried G-2, a mixed solution (50 mL) of IPA (2.0 mol L⁻¹) and TPP (1.0 mol L⁻¹) in *N*-methyl-2-pyrrolidone (NMP) was charged into a 50 mL cylindrical cell in an 80 °C water bath. Cylindrical **DAA** was immersed in this solution. The R_0 and r_t were determined at 10 min intervals using a digital video camera (Sony, DCR-TRV950, image of 640 × 480 pixels).

Measurement of Swelling/De-swelling Rate

A sample was placed in a 50 mL cylindrical cell at the desired temperature. The change in external radius (R'_t/R'_D or R'_t/R'_0), where $2R'_D$, $2R'_0$, and $2R'_t$ are the external diameters of the dried gel, the gel stored in water at 50 °C, and the gel swollen or de-swollen after $t = t$ min, respectively, was recorded using the digital video camera system described above.

Measurement of Equilibrium Swelling Ratio

A sample was immersed in water at the desired temperature (the initial temperature was 50 °C). The equilibrium swelling ratio was measured using a previously reported method.^{15b} The relationship $(W_s + W_p)/W_p$ was used, where W_s and W_p are the weights of the absorbed water and dried polymer, respectively.

RESULTS AND DISCUSSION

Amidation of DAA and DAA-PNAA core-shell type gels with Alkylamines

The heterogeneous reaction of **DAA** with IPA,

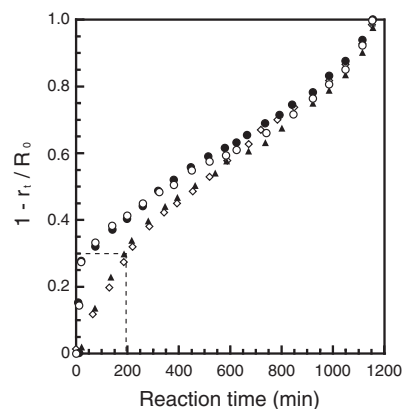


Figure 3. Typical amidation of a **DAA** gel and **DAA-PNAA** core-shell type gel with NPA or IPA; (\blacktriangle) reaction of **DAA** with NPA; (\diamond) reaction of **DAA** with IPA; (\circ) reaction of **G-5** with NPA; (\bullet) reaction of **G-2** with IPA.

using TPP, proceeded *via* a mechanism that was similar to the unreacted-model;¹⁸ the amidation occurred on the surface of the unreacted **DAA** core, since **DAA** did not swell in the solvent and the amidation reaction was very fast. The reaction from the surface gave **PNIPA** in the form of a core-shell type gel that consisted of an unreacted **DAA** core and a swelled shell (Figures 1 and 2). Based on these previous papers,¹⁴ the amidation of cylindrical **DAA** (length the same as the diameter; about 5.3 mm) with alkylamines (2.0 mol L⁻¹), such as **NNA** and **IPA**, was carried out in NMP, using TPP, at 80 °C. Typical disappearance rates for the core are shown in Figure 3. The rate was not affected by the type of alkylamine used, because the reaction rate was independent of the concentration.^{15b} The core disappeared after about 1200 min. The reaction of **DAA** with **IPA** and **NPA** gave **PNIPA (PNIPA-1)** and **PNNPA (PNNPA-1)** gels, respectively, when the core disappeared. The equilibrium swelling ratio for **PNIPA** gels prepared by several methods was measured in water over a wide temperature range (Figure 4). It is well known that the LCST in **PNIPA** was very sensitive to small amount of impurities.¹⁹ For example, copolymer gel of **NIPA** with 1 mol % acrylic acid has a LCST of 35 °C, where the LCST of pure **PNIPA** gel is 32 °C.^{14a} **PNIPA-1** prepared by this method had LCSTs of approximately 31 °C and showed much higher thermosensitivity than nonporous **PNIPA-2** and porous **PNIPA-3** prepared by radical polymerization. This results indicated that **PNIPA-1** had high purity, and nearly quantitative amidation was achieved, when **DAA** was placed in NMP containing an excess amount of alkylamine (2.0 mol L⁻¹) and TPP (1.0 mol L⁻¹). The thickness of the shell layer was controlled by the reaction time. Core-shell type gels **G-1-G-3** [**DAA-PNNPA** core-shell type gels, $r_t/R_0 = 0.10, 0.70,$ and 0.90] and **G-**

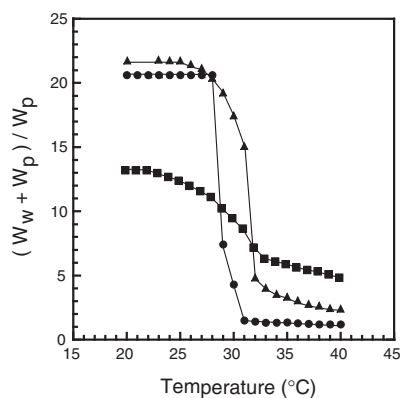


Figure 4. The equilibrium swelling ratio for **PNIPA** gels prepared by several methods in water as a function of temperature; (●) **PNIPA-1**; (▲) **PNIPA-2**; (■) **PNIPA-3**.

Table I. Synthesis of **DAA-PNAA** core-shell type gels by the first amidation of **DAA** with alkylamine^a

Run No.	Gel	Alkylamine	Solvent	Reaction time (min)	r_t/R_0
1	PNNPA-1	NPA	NMP	1160	0
2	G-1	NPA	NMP	1100	0.10
3	G-2	NPA	NMP	200	0.70
4	G-3	NPA	NMP	55	0.90
5	PNIPA-1	IPA	NMP	1160	0
6	G-4	IPA	NMP	1100	0.10
7	G-5	IPA	NMP	200	0.70
8	G-6	IPA	NMP	55	0.90

^aReaction of **DAA** was carried out in a solution of **TPP** (1.0 mol L^{-1}) and alkylamine (2.0 mol L^{-1}) in **NMP** (50 mL) at 80°C .

4-G-6 [**DAA-PNIPA** core-shell type gels, $r_t/R_0 = 0.10, 0.70,$ and 0.90] were synthesized by the first amidation of **DAA** with the corresponding alkylamine in **NMP**, using **TPP**, at 80°C for 1100, 200, and 55 min, respectively (Table I). The resulting **DAA-PNAA** core-shell type gels were washed with methanol in a Soxhlet extractor. They were dried *in vacuo* at 60°C to constant weight. The second amidation of the dried core-shell type gels with another alkylamine was carried out for 24 h under similar conditions to the first amidation. After rapid initial swelling of the amidated shell layer, the second amidation, which showed similar characteristics to the first amidation, occurred (Figure 3). The difference in the time required for complete disappearance of the unswollen core of the former compared with the latter was negligible, because the reaction proceeded under diffusion control of the unreacted-core model.^{14b,18} The amidation of **G-1-G-6** gave the corresponding **PNAA(2)-PNAA(1)** core-shell type gels, **GC-1-GC-6**, respectively. The results and conditions are summarized in Table II.

Table II. Synthesis of **PNAA(2)-PNAA(1)** core-shell type gels by the second amidation of **DAA-PNAA** core-shell type gels with various alkylamines^a

Run No.	PNAA(2)-PNAA(1) core-shell type gel	Alkylamine	DAA-PNAA core-shell type gel	r_t/R_0
9	GC-1	IPA	G-1	0.10
10	GC-2	IPA	G-2	0.70
11	GC-3	IPA	G-3	0.90
12	GC-4	NPA	G-4	0.10
13	GC-5	NPA	G-5	0.70
14	GC-6	NPA	G-6	0.90

^aReaction of **DAA-PNAA** core-shell type gel was carried out in a solution of **TPP** (1.0 mol L^{-1}) and alkylamine (2.0 mol L^{-1}) in **NMP** at 80°C for 24 h.

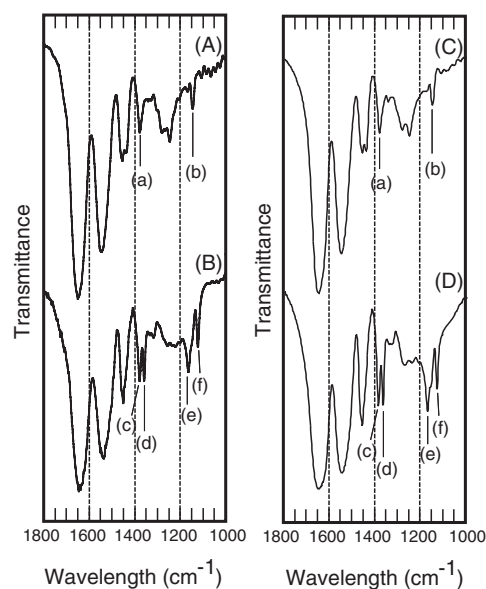


Figure 5. IR spectra (KBr) of **PNAA** gels; (A) **PNNPA** core in **GC-5**; (B) **PNIPA** shell in **GC-5**; (C) **PNNPA**^{7c} gel prepared by radical polymerization of *N-n*-propylacrylamide; (D) **PNIPA-2**.

Characterizations of the Core-Shell Type Gel Obtained by the Second Amidation

Typical IR spectra of **GC-5**, resulting from the amidation of a **DAA-PNIPA** core-shell type gel [$r_t/R_0 = 0.70$] with **NPA**, are shown in Figure 5. The **PNIPA** shell (B) and **PNNPA** core (A) of the gel showed strong absorption peaks at 3300 cm^{-1} (N-H, stretching), 1650 and 1545 cm^{-1} (amide I and amide II) with no absorption occurring at either 1710 cm^{-1} (C=O of carboxylic acid) or 1755 cm^{-1} (C=O of phenyl ester). Neutralization analysis showed that the amidated gels contained no carboxylic acid groups. The shell layer and core of the core-shell type gel showed absorption peaks characteristic of **PNIPA** at each of 1385 (c), 1368 (d), 1173 (e) and 1131 (f) cm^{-1} and of **PNNPA** at each of 1384 (a) and 1153 (b) cm^{-1} ; the absorption

spectra were clearly consistent with those of **PNIPA-2** (**D**) and **PNNPA**^{7c} (**C**) gels prepared by the radical polymerization of the corresponding monomers respectively, as well as **PNIPA-1** and **PNNPA-1**.^{15d} These results indicated that the second amidation of **DAA-PNAA** core-shell type gels with an alkylamine was nearly quantitative, giving the corresponding **PNAA(2)-PNAA(1)** core-shell type gels. Since unreacted DAA cores in the core-shell type gels can react with various reagents, they are useful for their chemical modification and the synthesis of a wide variety of core-shell type gels.

Thermal Swelling/De-swelling Behavior of the core-shell type gels

In the synthesis of the **PNAA(2)-PNAA(1)** core-shell type gels, attention was paid to the thermal swelling/de-swelling behavior of **PNNPA-1** and **PNIPA-1** gels. **PNNPA-1** and **PNIPA-1** gels had LCSTs of approximately 21 and 31 °C, respectively, and the difference in the equilibrium swelling ratios of **PNNPA-1** and **PNIPA-1**, at temperatures below and above the LCST, was negligible.^{14d} Thermal swelling/de-swelling behavior of **PNNPA-1** and **PNIPA-1** gels was divided into three regions: 1) at a lower temperature region (< 21 °C), **PNNPA-1** and **PNIPA-1** swelled, 2) at a middle temperature region (between 21–31 °C), **PNNPA-1** and **PNIPA-1** de-swelled and swelled, respectively, and 3) at a higher temperature region (> 31 °C), both **PNNPA-1** and **PNIPA-1** de-swelled. The differences among the three regions were so large that the properties of **PNNPA-PNIPA** and **PNIPA-PNNPA** core-shell type gels would be expected to change dramatically in response to changing temperatures. The swelling/de-swelling behavior of **PNAA(2)-PNAA(1)** core-shell type gels was measured in water at temperatures (15, 25, and 35 °C) in the three regions.

When dried **GC-3**, **PNIPA-PNNPA** core-shell type gels ($r_t/R_0 = 0.90$) were placed in water at 15 °C, the de-swelled gels began to swell from the surface. The swelling behavior in water for t min was described using the expression, R'_t/R'_D , where R'_D and R'_t were the external radii of the dried gel and swelled in water for t min, respectively (Figure 6). The gel swelled slowly, but maintained its cylindrical shape, and reached the equilibrium swelling ratio after 50 h; no significant swelling occurred at temperatures above the LCST of PNIPA. The swelling behavior of the **PNIPA-PNNPA** core-shell type gels was nearly the same as that observed for **PNNPA-1** and **PNIPA-1** gels at 15 °C. A boundary between the two layers was not observed in the swollen core-shell type gel because there was hardly any difference of optical properties between them. The thermosensitive

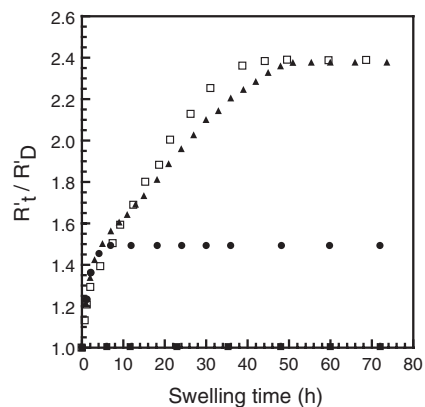


Figure 6. Swelling of **PNIPA-1** gel and **GC-3** in water; (□) **PNIPA-1** at 15 °C; (▲) **GC-3** at 15 °C; (●) **GC-3** at 25 °C; (■) **GC-3** at 35 °C.

PNNPA shell layer change from being hydrophilic to hydrophobic at 25 °C and the equilibrium swelling ratio was reached at 2 h. The equilibrium swelling ratio (R'_t/R'_D) was 1.5 at 25 °C compared with 2.4 at 15 °C. Previous papers^{14b,d} reported that the hydrophobic **PNNPA** or **PNIPA** shell layer of the **PAA-PNAA** core-shell type gels functioned as a permeability barrier to water when the gel was placed in water at temperatures higher than the LCST. The **PNIPA-PNNPA** core-shell type gel swelled only slightly, and the dense shell layer suppressed swelling of the core. In **PNNPA-PNIPA** core-shell type gels, only the **PNIPA** shell layer swelled in water at 25 °C. Therefore, the swelling of the cores in the **PNAA(2)-PNAA(1)** core-shell type gels was affected by the hydrophilic/hydrophobic properties of the shell layers, where the shell swelled independently when the water temperature is lower than the LCST.

De-swelling of the gels swelled in water at 15 °C was carried out at various temperatures above the LCST of **PNNPA**. When swelled gels were immersed in water at 25 °C, the R'_t/R'_0 values, where R'_0 and R'_t are the radii diameters of the gel stored in water at 50 °C and de-swelled in water for t min, respectively, decreased since only the **PNNPA** regions shrunk. The **PNNPA-1** gel rapidly reached the equilibrium swelling ratio (Figure 7). However, the de-swelling rate for the **PNNPA** shell in **GC-2** ($r_t/R_0 = 0.70$) and the core in **GC-5** ($r_t/R_0 = 0.70$) was lower than that of **PNNPA-1**. De-swelling of the **PNNPA** core and shell layer appeared to be structurally inhibited by the swollen **PNIPA** shell layer and core, respectively. Especially, the de-swelling rate for **GC-5** was low because water must diffuse from the core to surface. When the core-shell type gels and **PNIPA** stored at 25 °C were placed in water at 35 °C, the gels shrunk again due to the de-swelling of the **PNIPA** regions. After 1200 min, all core-shell type gels and the

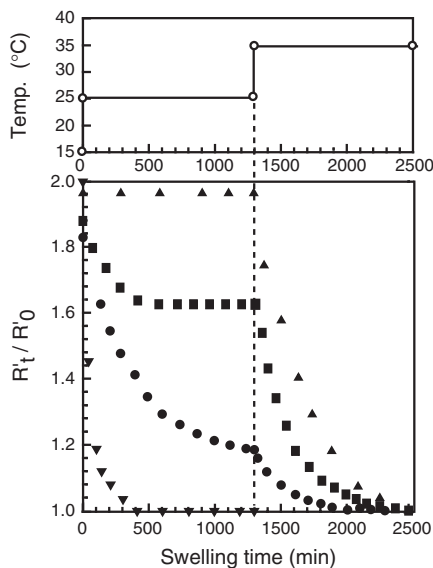


Figure 7. De-swelling of gels previously swelled in water in response to stepwise changes in temperature; (∇) **PNNPA-1**; (\blacktriangle) **PNIPA-1**; (\blacksquare) **GC-2**; (\bullet) **GC-5**.

PNIPA-1 gel reached the original size of the gels stored in water at 50 °C. Therefore, the de-swelled **PNNPA** shell layer in **GC-2** did not function effectively as a permeability barrier to water during de-swelling, and the two-step de-swelling of the core-shell type gels, due to the independent de-swelling of the core and shell in response to stepwise temperature changes, was observed. In addition, the thin shell layers were not burst when the stepwise temperature changes were repeated.

Typical images of de-swelling of **GC-4**, a **PNNPA-PNIPA** core-shell type gel [$r_i/R_0 = 0.10$], are shown in Figure 8. The **PNIPA** shell in **GC-4** swelled and the **PNNPA** core de-swelled in water at 25 °C. When the gel was immersed in water at 40 °C, the surface

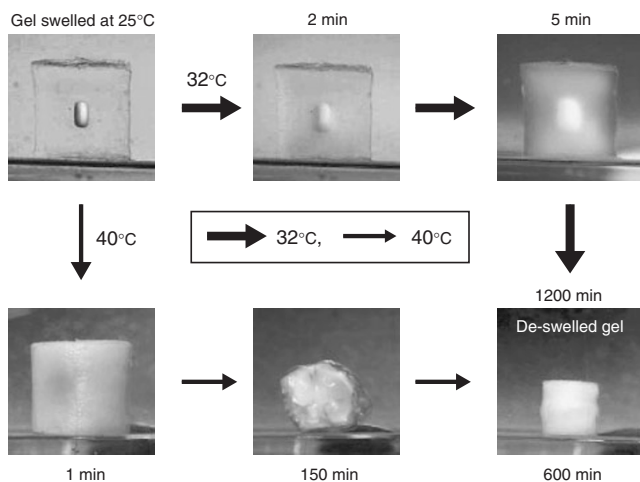


Figure 8. Typical pictures of de-swelling of **GC-4** previously swelled in water at 32 and 40 °C.

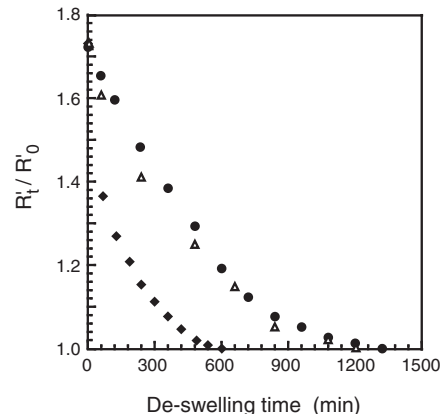


Figure 9. De-swelling of **GC-4** previously swelled in water at various temperatures; (\bullet) 25 \rightarrow 32 °C; (\triangle) 25 \rightarrow 35 °C; (\blacklozenge) 25 \rightarrow 40 °C.

was heated locally, and a dense surface skin layer was produced. The shrinkage force was so strong that water was ejected from the gel. Although the skin layer functioned as a permeability barrier to water, the de-swelling rate at 40 °C was higher than those observed at 32 and 35 °C (Figure 9). This result suggested that the shrinkage force was so strong that water was ejected from the gel. The rapid shrinking was well-known as a squeeze effect of **PNIPA** gel,¹⁹ forcing water from the gel. On the other hand, the clouding of the **PNIPA** shell layer occurred near the **PNNPA** core, and then the entire gel turned milky at 32 and 35 °C slightly higher than the LCST, where the swelled **PNIPA-1** became uniformly milky. Similar phenomenon was not observed in the de-swelling of **PNNPA** shell layers and cores in the **PNA(2)-PNA(1)** core-shell type gels. The local shrinking might be attributed to a slight composition gradient in the shell layer and a neighboring effect of hydrophobic properties of the cores. The local shrinking was observed in a matter of minutes, and the de-swelling rate was the same as that of **PNIPA-1** gel (Figure 7). Therefore, the de-swelling of shell layers and cores in the **PNA(2)-PNA(1)** core-shell type gels was hardly affected by the local shrinking, and occurred almost independently in response to the temperature changes. The shell layers showed almost the same thermosensitive behavior as those in the corresponding **PAA-PNA** core-shell type gels,^{14b,d} which showed on-off chemical release characteristics in response to stepwise temperature changes. However, the thermal swelling/de-swelling behavior of the **PNA(2)-PNA(1)** core-shell type gels can be controlled more multiply than that of **PAA-PNA** core-shell type gels, since the core also showed thermosensitivity. This behavior may be useful for design of fine functional polymers.

Preparation of Semi-cylindrical Double-layer Gels

The resulting cylindrical **PNA(2)-PNA(1)** core-shell type gel cannot be markedly deformed by swelling/de-swelling because of the axial symmetry. Cylindrical **PNIPA-PNNA** and **PNNA-PNIPA** core-shell type gels ($r_i/R_0 = 0.70$, $2R'_D$: 4.2 mm, length: about 16 mm) were prepared by two-step amidation of the corresponding long **DAA**. The core-shell type gels were cut laterally approximately 2 mm from the edge and into two halves, resulting in semi-cylindrical, long, double-layer gels **GC'-2** and **GC'-5** (Figure 2). The semi-cylindrical gels obtained could be bent markedly in response to stepwise temperature changes since they were not symmetric with respect to the axis.

Thermal Swelling/De-swelling Behavior of Semi-cylindrical Double-layer Gels

The semi-cylindrical dried **GC'-2** (A) ($2R'_D$: 4.2 mm, length: 12 mm), containing a **PNNA** shell layer and **PNIPA** core, slowly swelled in water at 15 °C, but maintained its semi-cylindrical shape, reaching the equilibrium swelling ratio after 40 h (Figure 10). The swollen gel (B) de-swelled slowly in water at 35 °C (Figure 11). The swelling/de-swelling behavior was the same as those of the **PNIPA-1** and **PNNA-1** gels. On the other hand, when the swollen gel (B) was immersed in water at 25 °C, the transparent **PNNA** shell layer immediately turned milky and shrank independently of the core, curling towards the shell side. After 2 h, the gel (C) was markedly bent and was inside-out. Although the shape of the bent gel was extremely distorted, the destruction on the boundary hardly occurred because it had a defined structure—a continuous network and a boundary between both layers. As the water temperature was raised from 25 to 35 °C, the swelled core of the bent gel (C) slowly shrank. After 20 h, the de-swelled gel (D) was almost the same size as the original dried gel (A). However, direct change from the original gel to the opaque gel

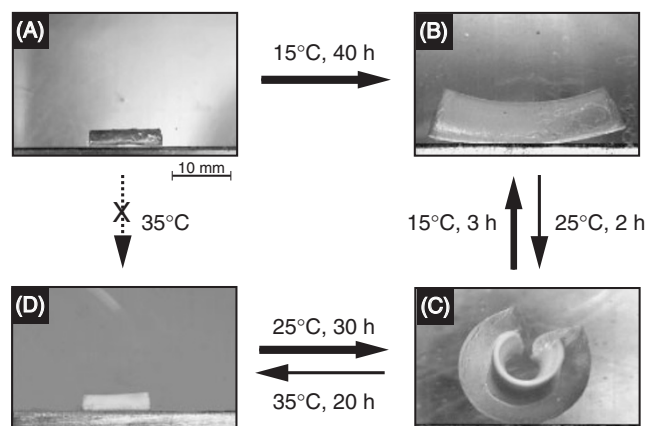


Figure 10. Typical pictures of swelling/de-swelling of **GC'-2** in water; (A) dried gel; (B) swelled gel at 15 °C; (C) bent gel at 25 °C; (D) deswelled gel at 35 °C.

(D) did not occur when the original gel was stored in water at 35 °C for a long time. When the water temperature was lowered from 35 to 25 and to 15 °C in a stepwise fashion, the de-swelled gel (D) was transformed into the swelled gel (B) through the bent gel (C). The deformation between the swelled gel (B) and the bent gel (C) was faster than that between the de-swelled gel (D) and the bent gel (C) because the shell layer was thinner than the core. Deformation induced by heating was slightly faster than that caused by cooling. The swelled and de-swelled shapes of semi-cylindrical **GC'-5** were the same as those of **GC'-2** in water at 15 and 35 °C, respectively. The **PNIPA** shell swelled and the **PNNA** core shrank at 25 °C; however, the gel (C') did not bend to the core side because the semi-cylindrical structure inhibited axial shrinking of the core sufficiently, such that radial shrinking preferentially occurred. These deformations occurred reversibly in response to the stepwise temperature changes, even though the deformation of **GC'-2** was so large. However, the shell layer of **GC'-2** peeled off gradually, although both layers com-

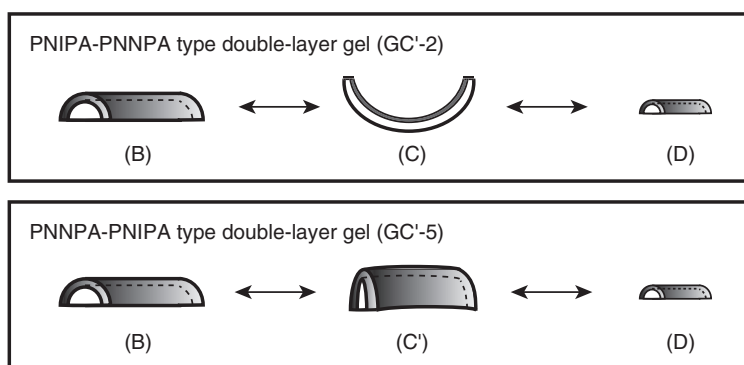


Figure 11. Deformation of semi-cylindrical, double-layer gels in response to stepwise changes in temperature; (B) swelled gel at 15 °C; (C) and (C') bent gel at 25 °C; (D) deswelled gel at 35 °C.

bined with each other by a continuous network when the stepwise temperature changes were repeated. The differences in deformations between **GC'-2** and **GC'-5** are interesting in terms of the design of novel functional polymers for use as actuators and temperature sensors.

CONCLUSION

1. The first amidation of **DAA** with alkylamines proceeded nearly quantitatively at 80 °C in the presence of TPP to give the corresponding **DAA-PNAA** core-shell type gels. The thickness of the shell layer was controlled by the reaction time. **PNAA(2)-PNAA(1)** core-shell type gels were prepared by the second amidation of **DAA-PNAA** core-shell type gel with another alkylamine under the similar conditions as the first amidation.
2. Although **PNNPA** and **PNIPA** differed in LCST, the difference between them in equilibrium swelling ratio at temperatures below and above the transition was negligible.
3. The swelling of the cores in the **PNAA(2)-PNAA(1)** core-shell type gels was affected by the hydrophilic/hydrophobic properties of the shell layers, where the shell swelled independently when the water temperature is lower than the LCST.
4. The de-swelling of shell layers and cores in the **PNAA(2)-PNAA(1)** core-shell type gels occurred almost independently in response to the temperature changes.
5. The semi-cylindrical, double-layer gels were prepared by laterally cutting the cylindrical **PNIPA-PNNPA** and **PNNPA-PNIPA** approximately 2 mm from the edge and by cutting the cylinders into halves.
6. The semi-cylindrical, double-layer gels prepared from **PNIPA-PNNPA** core-shell type gels were markedly bent in water at temperatures between the LCSTs of **PNIPA** and **PNNPA**.

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