Characteristic Swelling−Deswelling of Polymer/Clay Nanocomposite Gels

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Ⓢ *Supporting Information*

ABSTRACT: Swelling behavior of nanocomposite hydrogels (NC gels) having organic polymer/inorganic clay network structures were systematically investigated, focusing on the role of exfoliated clay platelets with sodium counterions in the network and effects of various swelling conditions. NC gels in water exhibited characteristic swelling−deswelling behavior, i.e., initial large swelling, maximum swelling, and subsequent deswelling toward an equilibrium state, under conditions where the water was changed frequently. Effects of swelling conditions, such as the frequency of changing the water, amount of water per unit gram of gel, salt concentration, and pH of the swelling solvent, gel composition (e.g., kind of polymer, clay concentration (C_{clay}), and polymer concentration (C_p)), swelling temperature, and gel size, were clarified. NC gels with different polymers were all found to exhibit swelling−deswelling behavior except at very low C_{clay} and high C_p. Spontaneous deswelling of the gels was attributed to the combined effects of high swelling capability of the NC gel as a polyelectrolyte gel and continuous release of sodium ions from the network during swelling. Furthermore, the swelling−deswelling behavior could be reversed by reintroducing sodium ions into the network. These characteristic swelling behaviors of NC gels with polymer/clay networks are completely different from those of hydrogels with chemically cross-linked polymer network structures.
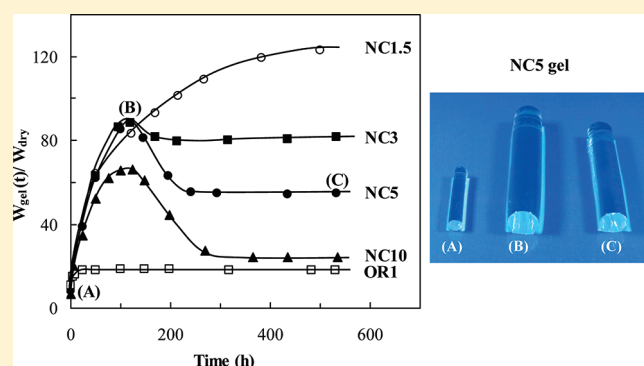
■ INTRODUCTION

Since the first synthesis of nanocomposite hydrogels (NC gels) having a unique organic (polymer)/inorganic (clay) network structure by Haraguchi et al. in 2002,[1] who reported their extraordinary optical, mechanical, and swelling/deswelling properties, these gels have attracted great interest from both academic and practical viewpoints. In particular, NC gels show ultrahigh mechanical toughness when compared with chemically cross-linked polymer hydrogels (OR gels) prepared using an organic cross-linker in place of the clay;[2,3] furthermore, their tensile and compressive mechanical properties can be controlled over a wide range by modifying their composition.[4] NC gels have also been found to exhibit a number of new functions such as rapid stimuli-responsive properties (e.g., transparency, gel volume, and reversible force generation), circumstance-dependent sliding frictional behavior, optical anisotropy and its change upon uniaxial deformation, cell cultivation with thermoresponsive cell detachment, and ultrahigh surface hydrophobicity.[5]

NC gels are usually composed of nonionic polymers, such as poly(*N*-isopropylacrylamide) (PNIPA) and poly(*N,N*-dimethylacrylamide) (PDMAA), and ionic inorganic clay minerals, such as hectorite (e.g., Laponite XLG) or montmorillonite (e.g., Kunipia F).[2,3,6] The unique polymer/clay networks can be established by

fully exfoliating inorganic clay in an aqueous reaction solution and uniformly incorporating the resulting thin disklike platelets (ca. 1 nm thickness) within the networks through in-situ free-radical polymerization;[7] these platelets act as multifunctional cross-linkers for polymer chains. The detailed structure of the polymer/clay networks was previously clarified by analytical measurements such as X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), dynamic viscoelasticity, dynamic light scattering, and small-angle neutron scattering (SANS).[1−4,8,9] In particular, contrast-variation SANS measurements showed that PNIPA chains interacted with clay via hydrogen bonding formed a thin dense layer (ca. 1 nm thick) on each side of the clay platelets.[9] Furthermore, by selective decomposition of clay in the network and subsequent gel permeation chromatography measurements,[10] it was found that PNIPA in NC gels has a high molecular weight, $M_w = 5.5 \times 10^6$ g/mol, without self-cross-linking,[11] and this molecular weight is almost independent of the clay concentration.

Usually, NC gels are prepared from water-swellable clay minerals, e.g., clays belonging to the smectite group, with negative charges on their surface along with positive metal counterions. The most typical example of such a mineral is Laponite XLG (synthetic hectorite), which has a cation exchange capacity (CEC) of 104 mequiv/100 g of clay and sodium counterions.[7,12] NC gels composed of polymer and exfoliated Laponite XLG should belong to a class of polyelectrolyte gel with negatively charged groups in the network. It is known that polyelectrolyte gels with positive or negative charges on the polymer chains generally show high swelling capabilities in water and exhibit large volume transitions in response to changes in their environments, such as temperature,[13] pH and salt concentration in the solvent,[14,15] solvent composition,[16] and electrical field.[17] Tanaka et al.[18] reported the quantitative relationship between the Donnan theory and the swelling of weakly charged ionic gels and predicted the changes in swelling and swelling extrema observed for acrylamide-co-acrylic acid gels at specific ion concentrations in the aqueous media. To date, most studies on polyelectrolyte gels with interpenetrating[19−21] or semi-interpenetrating[22,23] network structures, as well as chemically cross-linked copolymer networks,[13−17] have described their equilibrium swelling or transition behaviors in response to external stimuli such as pH and temperature. However, very few studies have investigated the swelling kinetics of polyelectrolyte gels. English et al.[24] reported the swelling behavior of a polyampholyte gel composed of both positive and negative monomeric groups and underscored the importance of counterions in establishing equilibrium in polyampholyte hydrogels. Hirashima et al.[25] reported the deswelling of ionized PNIPA (a copolymer of N-isopropylacrylamide and sodium acrylate) gel under conditions in which the surrounding water is frequently changed. The shrinking of the ionized PNIPA gel in water was attributed to an increase in the number of nonionized carboxyl groups and the formation of additional hydrogen bonds. Sato et al.[26] reported on the swelling behavior of poly(sodium acrylate) gels cross-linked by aluminum ions. When the surrounding water was changed at a regular interval, this gel underwent swelling to a maximum volume followed by very slow shrinking; finally, the gel shrank to a volume smaller than its original volume. These behaviors were attributed to the diffusion of aluminum ions and the formation of hydrogen bonds owing to the replacement of sodium ions by protons.

With regard to NC gels, Can et al.[27] reported the abnormal swelling behavior of NC gels consisting of PNIPA or PDMAA and inorganic clay (Laponite XLS with a dispersing agent, pyrophosphate-Na). They concluded that the swelling–deswelling behavior observed in NC gels is attributable to an irreversible rearrangement of the network structure; that is, the aggregated clay in the original, as-prepared gel (optically opaque) was gradually exfoliated in the early stage of swelling, and subsequently, additional cross-links were formed between the resulting exfoliated clays and polymer chains in the later stages of swelling. However, we show in the present study that this explanation is possibly incorrect.

Here, we report the characteristic swelling behavior of NC gels with excellent optical transparency and mechanical properties. We identify the specific conditions and network structures that enable NC gels to undergo extensive swelling and to undergo spontaneous swelling–deswelling transitions in aqueous media. We also discuss the reversibility and mechanism of the swelling–deswelling process of NC gels in comparison with OR gels with a chemically cross-linked network structure.

■ EXPERIMENTAL SECTION

Materials. The monomers N,N-dimethylacrylamide (DMAA) and N-isopropylacrylamide (NIPA) were provided by Kohjin Co., Japan. DMAA was purified by filtering through activated an alumina column, and NIPA was purified by recrystallization from a toluene/hexane mixture and dried under vacuum at 40 °C. Other reagents were purchased from Wako Pure Chemical Industries, Japan, and used without further purification. Potassium persulfate (KPS), N,N,N′,N′-tetramethylethylenediamine (TEMED), and N,N′-methylenebis(acrylamide) (BIS) were used as the initiator, catalyst, and organic cross-linker, respectively. The synthetic hectorite, Laponite XLG (Rockwood, Ltd., UK, [$Mg_{5.34}Li_{0.66}Si_8O_{20}$-$(OH)_4$]$Na_{0.66}$, with platelets ca. 30 nm in diameter and 1 nm thick, CEC of 104 mequiv/100 g), was used as inorganic clay after washing and freeze-drying. Ultrapure water supplied by a PURIC-MX system (Organo Co., Japan) was used for all experiments. To prepare gels, oxygen in the water was removed by bubbling nitrogen gas for more than 3 h prior to use. Aqueous solutions with different salt concentrations (0.0001−0.9 wt %) and acidities (pH 3−11) were prepared using sodium chloride, hydrochloric acid, and sodium hydroxide, respectively.

Sample Nomenclature. Sample codes for NC and OR gels are generally defined by the kind of monomer (D- and N- for DMAA and NIPA, respectively) and the concentrations of clay and monomer relative to the amount of water. For example, D-NCn-Mm gel refers to an NC gel prepared using n mol % of clay (which is equal to 0.76 × n wt % based on the formula $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4$) and m mol of DMAA in 1 L of water. When m is 1, the last symbol (M1) is usually omitted for simplicity. Further, D-ORn′ gel represents an OR gel prepared using n′ mol % of BIS relative to the monomer (1 M of DMAA). However, in the present study, since DMAA was mainly used for preparing NC and OR gels, the prefix (D-) is omitted for all PDMAA-based gels, and the prefix (N-) is used only for PNIPA-NC gels, as in N-NC gel. The clay, polymer, and BIS concentrations in NC and OR gels ($C_{clay} = n \times 10^{-2}$ mol/L of H_2O, $C_p = m \times 10^{-2}$ mol/L of H_2O, and $C_{BIS} = n′$ mol % relative to monomer) are expressed using simplified numerical values of n, m, and n′, respectively. In the present study, C_{clay}, C_{BIS}, and C_p varied in the range of n = 1.5−15, n′ = 0.01−1, and m = 0.5−8, respectively.

Syntheses of Hydrogels. The synthetic procedure used to prepare NC gels is the same as that reported previously.[3,4b] In brief, to synthesize D-NC3-M1 gel, a transparent aqueous solution consisting of water (28.5 mL), Laponite XLG (0.686 g), and DMAA (2.97 g) was first prepared. Next, the catalyst (24 μL) and an aqueous solution of the initiator [30 mg in H_2O (1.5 mL)] were added to the reaction mixture at 0 °C while stirring. The solution was then transferred to a tubular glass vessel with an interior diameter of 5.5 mm and a length of 300 mm. Free-radical polymerization was then allowed to proceed in a water bath at 20 °C for 20 h. Oxygen was removed from the solutions and the system throughout the syntheses. The same procedure was used to synthesize OR gels, except that an organic cross-linker (BIS) was used instead of clay.

Measurements. *Swelling Ratio.* In this study, the time-dependent swelling ratio is denoted by $W_{gel}(t)/W_{dry}$. Here, $W_{gel}(t)$ is the weight of the gel at swelling time t and W_{dry} is the weight of the dried gel. The change in gel weight relative to the weight of the original gel(W_0), $W_{gel}(t)/W_0$, was also used on some occasions (effects of C_p). Kinetic swelling experiments of NC gels were conducted under the following conditions unless otherwise noted. A sample of the NC or OR gel in the form of a rod with an initial diameter and length of 5.5 mm and 30 mm, respectively, was immersed in 200 mL of the swelling solvent at 20 °C. In most cases, ultrapure water was used as the swelling solvent, and in the

remaining few cases, aqueous solutions of NaCl, NaOH, and HCl were used as the swelling solvents. This solvent was changed each time the gel weight was measured unless otherwise noted. The swelling temperature (T_s) was kept at 20 °C throughout, except when studying its effect on the swelling behavior, when it was varied between 4 and 40 °C. To verify the data reproducibility, at least three swelling experiments were carried in for each swelling test.

pH and Electroconductivity. pH and electroconductivity of the swelling solvent were measured using a pH meter (B-212, Horiba, Ltd., Japan) and electroconductivity meter (D-24, Horiba, Ltd., Japan), respectively.

Inductively Coupled Plasma Atomic Emission Spectroscopy and Atomic Absorption Spectroscopy. To identify the precise ionic species released from NC gels into the swelling solvent (water), five rod-shaped samples of D-NC10 gels were first washed three times with 10 mL of water. The samples were then immersed in clean plastic bottles filled with 125 mL of water which was changed each time the weight was measured. The amounts of sodium, magnesium, and lithium ions in the swelling solvents were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima 3300DV, Perkin-Elmer Inc., Japan). When the swelling reached equilibrium, gels were dried at room temperature for 48 h and at 50 °C in a vacuum for 10 h. The sodium contents of the dried gels were determined by solid atomic absorption spectrometer (AAS: ZEEnit 600, Analytic Jena Inc., Japan). The same measurements were conducted for OR0.1 gel and blank pure water in a similar manner.

■ RESULT AND DISCUSSION

All NC gels, including N-NC gels prepared in the present study, had high transparency and excellent mechanical properties. Typical tensile stress—strain curves for NCn gels are shown in Figure S1 of the Supporting Information. From the XRD, DSC, and TEM measurements of dried NC gels and the tensile and dynamic-mechanical properties of NC gels, we confirmed the formation of a uniform organic polymer (PDMAA)/inorganic clay (Laponite XLG) network, as reported in previous papers.[1−3,7]

Characteristic Swelling Behavior of NC Gels in Water. Curves i and ii of Figure 1a show changes in the swelling ratio $W_{gel}(t)/W_{dry}$ for two types of PDMAA hydrogels, viz. NC5 and OR1 gels, in water at 20 °C as a function of swelling time. Here, the solvent (pure water) was changed after each measurement of the gel weight ($W_{gel}(t)$). The chemically cross-linked OR1 gel showed normal swelling behavior; that is, its swelling ratio initially increased with time and eventually attained a constant value (equilibrium degree of swelling (EDS) = 18). EDS is generally determined by a balance between water absorption (due to the hydrophilicity of polymer chains) and network elasticity (proportional to the cross-link density ν), which, according to the Flory—Rehner theory,[16,28] are represented by the first and the second terms, respectively, of eq 1

$$\Pi = \Pi_{mixing} + \Pi_{elastic} + \Pi_{ion} \qquad (1)$$

where Π is the osmotic pressure of the hydrogel, and Π_{mixing}, $\Pi_{elastic}$, and Π_{ion} are the contributions from mixing, network elasticity, and mobile ion concentration. In contrast, the NC5 gel used in this study showed a quite different swelling behavior, particularly when undergoing swelling for long times (Figure 1a(i)). That is, this gel initially swelled extensively until after attaining a transient maximum ($W_{gel}(t)/W_{dry}$ = 93) after about 120 h it started to deswell, finally reaching an EDS of 55 after about 300 h.
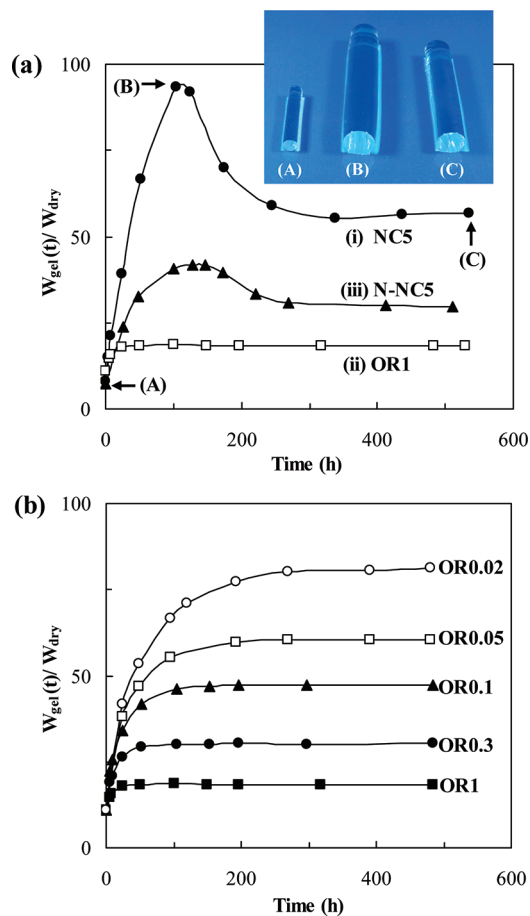

Figure 1. Changes in swelling ratio ($W_{gel(t)}/W_{dry}$) of NC and OR gels in water as a function of swelling time. Swelling conditions: initial gel size, 5.5 mm diameter and 30 mm length; amount of water, 200 mL; frequent exchanges of water; and swelling temperature T_s = 20 °C. (a) Swelling behaviors of (D-)NC5 gel, N-NC5 gel, and (D-)OR1 gel. Insets show images of NC5 gel in as-prepared (A), maximum swelling (B), and equilibrium swelling states (C). (b) Swelling behaviors of (D-) ORn' gels (n' = 0.02−1).

In many cases NC gels have been reported to swell more extensively than OR gels.[1−3] This is mainly because ν for NC gels is lower than for the most commonly used OR gels (OR1 gel). In this study, to first determine whether the abnormal swelling behavior, i.e., maximum swelling and subsequent deswelling, observed for NC5 gel was due to its high swelling capability, the swelling behavior of ORm gels with lower ν than usual was examined. Figure 1b shows the effect of low C_{BIS} (m = 0.02−1) on the swelling behavior of the OR gels. All ORm gels exhibited a simple swelling behavior regardless of m, although the EDS of the gels increased with decreasing m. For example, OR0.02 gel showed a monotonous increase in $W_{gel}(t)/W_{dry}$ with an EDS of about 80, which is close to the maximum degree of swelling (DS$_{max}$) of NC5 gel. Thus, OR gels consisting of chemically cross-linked PDMAA networks do not exhibit any abnormal swelling behavior, regardless of ν or the EDS.

With regard to other kinds of NC gels, e.g., N-NC gel having a PNIPA/clay network, we found that N-NC5 gel also exhibited characteristic swelling—deswelling behavior, similar to (PDMAA-) NC5 gel, as shown in Figure 1a(iii). The values of DS$_{max}$ and EDS for N-NC5 gel were smaller than those of NC5
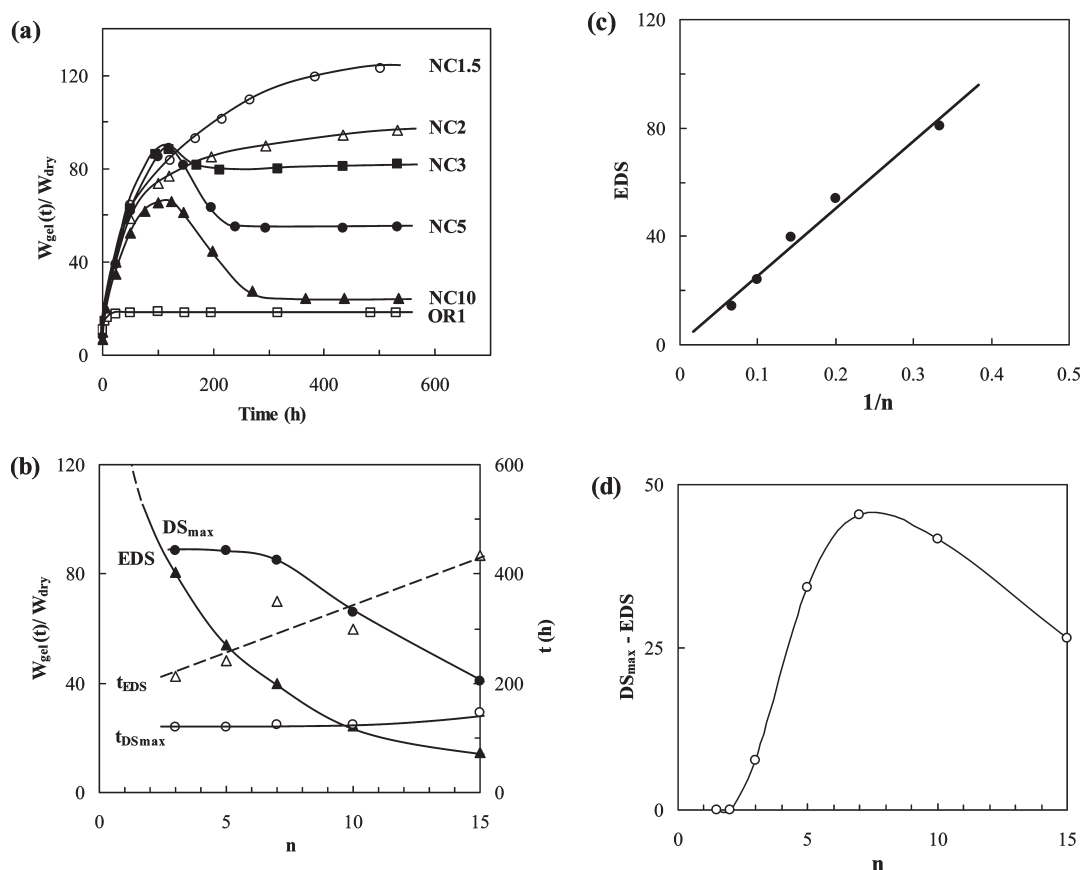
Figure 2. Effects of C_{clay} and C_p on the swelling behavior of NC gels. (a) Swelling behaviors of NCn (n = 1.5−15) gels in water. (b) C_{clay} dependences of the equilibrium degree of swelling (EDS), the maximum degree of swelling (DS$_{max}$), the time of maximum swelling (t_{max}), and the time of EDS (t_{EDS}). (c) Relationship between EDS and $1/n$. (d) Dependence of the absolute value of deswelling (DS$_{max}$ − EDS) on C_{clay}. Swelling conditions: initial gel size, 5.5 mm diameter and 30 mm length; amount of water, 200 mL; frequent water change; and swelling temperature (T_s) = 20 °C.

gel because of the relatively high ν of the former.[2,3] Here, it should be noted that the volume transition from swelling to deswelling in N-NC5 gel occurred as a spontaneous process in the course of swelling, which is completely different from the rapid volume transition of N-NC5 gel caused by the thermosensitive coil-to-globule transition at its lower critical solution temperature.[2]

Thus, we found that transparent NC gels with a polymer/clay networks exhibited characteristic swelling behavior, i.e., initial large swelling followed by deswelling, regardless of the kind of alkyl group in the poly(N-alkyl acrylamide). Furthermore, as shown in the inset to Figure 1a, NC gels in all swelling states, e.g., as-prepared, maximum swelling, and equilibrium swelling states, were uniform and transparent without having any heterogeneity or wrinkles. On the basis of these results and the high reproducibility of data shown in Figure 1a, we concluded that the abnormal swelling−deswelling behavior observed in NC gels is not caused by any kind of irregular swelling or heterogeneous morphology but by the unique polymer/clay network structure in which the exfoliated clay nanoparticles are uniformly incorporated.

Effect of Network Composition of NC Gel. Figure 2a shows the swelling behavior of NCn gels with different C_{clay} (n = 1.5−15). In these measurements, C_p was fixed at 1 M. It was observed that except at very low C_{clay} (e.g., n = 1.5), NCn gels exhibited characteristic swelling−deswelling behavior over a

wide range of n. Furthermore, a critical value of n was found to be between 2 and 3. NCn gels with $n \leq 2$ showed the usual large swelling but did not exhibit a DS$_{max}$ and subsequent deswelling. In contrast, NCn gels with $n \geq 3$ showed clear maximum swelling at around 120 h and subsequent deswelling to an EDS. The dependences of DS$_{max}$ and the EDS on C_{clay} (n) are summarized in Figure 2b. Both DS$_{max}$ and the EDS decreased gradually with increasing n, although their profiles were quite different from each other. Values of EDS were almost inversely proportional to n (Figure 2c) as expected from EDS $\propto \nu$ and $\nu \propto n$, whereas DS$_{max}$ decreased more rapidly at higher values of n ($n > 7$). Then, the absolute change in the deswelling process ($\equiv$ DS$_{max}$ − EDS) of NCn gels attained a maximum at an intermediate value of n (about 7) (Figure 2d). Furthermore, as shown in Figure 2b, the time at which DS$_{max}$ was attained (t_{max}) was almost constant (120 h) regardless of n, whereas the time at which the EDS was attained (t_{EDS}) gradually increased with increasing n.

Figure 3 shows the swelling behavior of NC5-Mm gels with different C_p in water. In these measurements, C_{clay} was fixed at a value of n = 5 and C_p (=mM) was varied over a wide range (m = 0.5−8). To obtain a better understanding of the swelling behavior of these gels, we consider two parameters to describe the degree of swelling, namely the gel weight relative to the dried weight (W_{dry}) and to the original gel weight (W_0), as shown in Figures 3a and 3b, respectively. In both cases, a well-defined DS$_{max}$ was observed for NC5 gels with low C_p (m = 0.5 and 1)
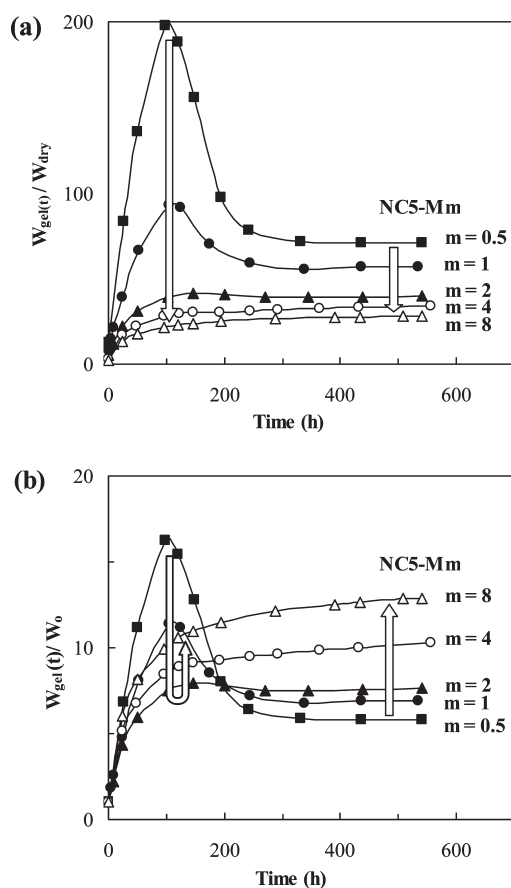
(a)

(b)

Figure 3. Swelling behaviors of NC5-Mm (m = 0.5−8) gels in water. (a) Variation in $W_{gel(t)}/W_{dry}$ with swelling time. (b) Variation in $W_{gel(t)}/W_0$ with swelling time. W_0 is the initial weight of gel. Swelling conditions: initial gel size, 5.5 mm diameter and 30 mm length; amount of water, 200 mL; frequent water change; and T_s = 20 °C.

and a slight DS_{max} at m = 2. NC5 gels with higher C_p (m > 2) did not exhibit a maximum swelling and subsequent deswelling. Furthermore, it is interesting to note that the two parameters showed completely opposite tendencies in the approach to EDS. That is, at equilibrium $W_{gel}(t)/W_{dry}$ decreased with increasing m (Figure 3a), whereas $W_{gel}(t)/W_0$ increased with increasing m (Figure 3b). Furthermore, the degree of swelling at 120 h (corresponding to DS_{max} for m = 0.5 and 1) decreased monotonically in the case of $W_{gel}(t)/W_{dry}$ (Figure 3a), whereas for $W_{gel}(t)/W_0$ it initially decreased and then increased after attaining a minimum at m = 2 (Figure 3b), as indicated by the arrows in these figures.

The disappearance of a maximum swelling (and loss of the deswelling process) in the NC gels at high C_p is attributed to the increase in ν, which in turn is caused by the increase in C_p at a fixed clay concentration (NC5 gel). The increase in ν (proportional to the modulus) with C_p was confirmed by tensile measurements in a previous study.[3] Because values of ν at high C_p are high, the swelling capability should be largely suppressed. In addition, since the number of sodium ions per polymer chain is small in NC gels with high C_p, the deswelling behavior attributed to the release of sodium ions (see the next section) becomes negligible. Thus, the degree of swelling, expressed as W_{gel}/W_{dry}, decreases with increasing C_p (m) at all times (Figure 3a). However, in contrast, the degree of swelling expressed by W_{gel}/W_0

increases with increasing C_p in the equilibrium state (Figure 3b) because the absolute amount of water absorbed increases with the increase in C_p as a result of the strong hydrophilicity (i.e., water absorption ability) of the polymer chains. Consequently, at the swelling time at which DS_{max} was attained (∼120 h) the swelling expressed by W_{gel}/W_0 was minimal at m = 2 due to the combined effects of enhanced swelling due to the hydrophilicity along with its weakening due to the change in network elasticity.

Effects of Changing the Aqueous Environment on the Swelling Process. Throughout the experiments shown in Figures 1−3, the swelling solvent (water) was replaced with fresh water when each measurement of the gel weight was made. Figure 4a-1 shows the effect of changing the water on swelling NC5 gel under two conditions: (i) the water was changed at every measurement, and (ii) the water was not changed. In case ii, NC5 gel showed normal swelling behavior, except for a slight decrease from a shallow maximum at long swelling times of more than 200 h. On the other hand, in case i, NC5 gel showed large swelling with a well-defined maximum and subsequent deswelling. As shown in Figure 4b-1, the swelling of OR0.1 gel was completely unaffected by changing the water, although the degrees of swelling for both OR0.1 and NC5 gels are comparable. Thus, the swelling followed by deswelling was only observed for NC gels under conditions where the water was changed frequently. These results suggest that some substance released from the NC gel into the surrounding water strongly affects the swelling behavior. This is reasonable because the NC gel is a kind of polyelectrolyte gel consisting of charged inorganic clay platelets with sodium counterions.

Changes in pH and electroconductivity (ρ) in the surrounding aqueous environment during the swelling of NC5 and OR0.1 gels under conditions (i) frequent water change and (ii) no water change are shown in Figures 4a-2 and 4a-3 (for NC5) and in Figures 4b-2 and 4b-3 (for OR0.1). In the case of (i) for NC5 gel, pH and ρ increased steeply to 9.1 and 1.2 ms/m, respectively, in the first water sample (8 h), and then, they decreased during subsequent swelling stages; thereafter, they maintained constant low values (pH = 7.2 and ρ = 0.08 ms/m) at ≥120 h. In case ii, pH and ρ increased in the first stage of swelling, and thereafter, ρ gradually increased to 1.8 ms/m and pH remained almost constant at a high value (9 ± 0.3). These trends indicate that ionic or dipolar chemicals were released from the NC gel into the surrounding water, particularly in the early stage of swelling. On the other hand, in the case of swelling of OR0.1 gel, the change in pH was quite different from that of NC5 gel. As shown in Figure 4b-2, the pH was almost constant in case i (pH = 7.2) and decreased only slightly (to 6.5) with time in case ii. The nature of the change in ρ of OR0.1 gel was very similar to that for NC5 gel, although the absolute values were about half of those for NC5 gel. In the present study, since the NC and OR gels were used for the swelling test without any purification (washing) after synthesis, some chemicals such as residual fragments of KPS, TEMED, and unreacted monomer were expected to be released from the gels. In addition, in the case of the NC gel, sodium ions could be released into the surrounding water. The resulting changes in the pH and ρ indicate that the chemicals remaining after the synthesis mainly affect ρ and that they are rapidly released in the early stages of swelling for both the NC and the OR gels. On the other hand, the sodium ions, which are counterions on clay platelets, affect pH as well as ρ, and they are released on a longer time scale. Here, it should be noted that the time (120 h) at which
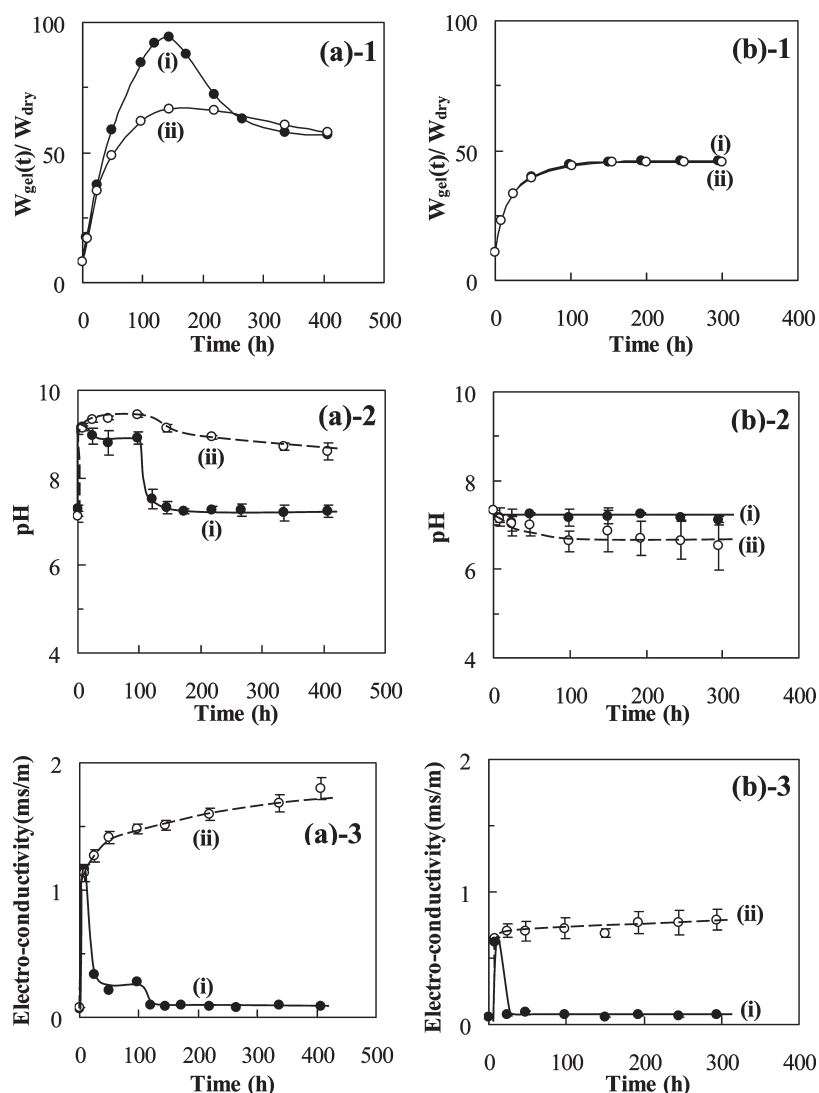
Figure 4. Effects of changing the water during the swelling test on (a) NC5 gel and (b) OR0.1 gel, under two conditions: (i) water changed at every measuring point and (ii) no change of water. (a-1) and (b-1): change in degree of swelling. (a-2) and (b-2): change in pH of swelling solvent (water). (a-3) and (b-3): change in electroconductivity of swelling solvent (water). Other swelling conditions: initial gel size, 5.5 mm diameter and 30 mm length; amount of water, 200 mL; and T_s = 20 °C.

the surrounding water changes to final pH and ρ values is consistent with t_{max} for the swelling of NC5 gel.

Release of Sodium Ions from NC Gel. In order to detect the precise amount of sodium ions released during swelling, we performed measurements for NC10 gel with high C_{clay} under specific swelling conditions, as described in the Experimental Section. In brief, five rod-shaped samples of as-prepared NC10 gel were swollen in pure water (125 mL), while changing the water frequently. The change in $W_{gel}(t)/W_{dry}$ as a function of swelling time is shown in Figure 5 (open circles). Similar to the result shown in Figure 2a, NC10 gel showed a well-defined maximum swelling and subsequent deswelling. Because the swelling behavior of the NC gel strongly depends on the swelling conditions (refer to the later section "Factors Affecting the Swelling−Deswelling"), t_{max} in Figure 5 was observed to be at 273 h, which is about twice the time shown in Figure 2a. Further, t_{EDS} was longer (>1000 h) than that in Figure 2a. These differences in swelling behavior can be attributed to the different swelling conditions, specifically, the amount of water used per

gram of gel and the frequency changing the water; both factors were selected in order to determine the quantity of sodium ions released precisely.

The change in the quantity of sodium ions released from NC10 gel into the surrounding water is shown in Figure 5 (closed circles). Sodium ions were found to be released primarily in the early stage of swelling, and their release decreased steeply with increasing swelling time. When the degree of swelling was maximum, only 8.9 wt % of sodium ions relative to the initial state remained in the gel. Further, after 1350 h, when the swelling had almost reached equilibrium, 99 wt % of sodium ions was found to have been released. The release of 99 wt % of sodium ions was also confirmed by an AAS measurement for an NC10 gel dried after swelling for 1350 h. Thus, it was found that the sodium counterions contained in clay platelets are released quite rapidly from the NC gel into the surrounding water throughout the swelling process, but at the time that DS_{max} was attained (273 h), there was no abrupt change in the sodium-ion release curve. This observation indicates that DS_{max} is not attained by an

irregular change in the release of sodium ions or other chemicals, but by a combination of factors that affect the swelling capability in different ways.

Swelling–Deswelling Mechanism in NC Gels. NC gels are composed of a nonionic polymer (PDMAA) and ionic inorganic clay containing sodium counterions (Laponite XLG). The change in the PDMAA/clay network structure during swelling is schematically depicted in Figure 6. In the as-prepared state (Figure 6(i)), exfoliated clay platelets with a negative surface charge and sodium counterions were uniformly dispersed in aqueous media (thus, the original NC gel contained a stoichiometric amount of sodium ions, e.g., 700 μg/g of gel for NC5 gel),

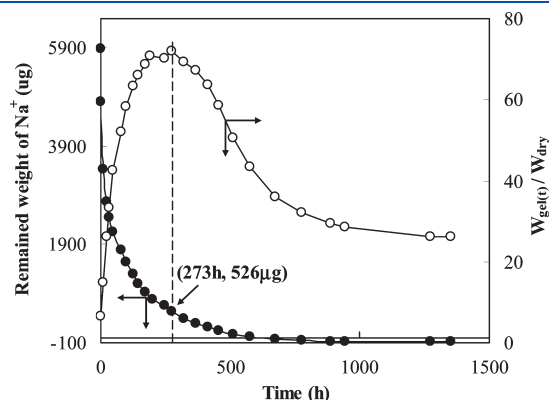**Figure 5.** Swelling behavior of NC10 gel and the release of sodium counterions during swelling. The open circles show the change in $W_{gel}(t)/W_{dry}$, and the closed circles show the concentration of sodium ions remained in the gel, measured by ICP-AES. Swelling conditions: initial gel, 5 samples each with a 5.5 mm diameter and 30 mm length; amount of water, 125 mL; water changed at each measurement; and $T_s =$ 20 °C. NC10 gel was first washed three times, each time using 10 mL water for 5 min.

and neighboring clay sheets were linked to each other through a number of flexible PDMAA chains. When the NC gel is immersed in a swelling solvent (pure water), water molecules move into the network (i.e., the NC gel absorbs water), and simultaneously, the mobile sodium ions diffuse from inside the network to the surrounding water, probably by replacing with hydrogen ions. The kinetics of swelling (absorption of water) and the diffusion of sodium ions from the NC gel into the surrounding water depend on the swelling conditions.

In cases where the water was not changed, the samples initially swelled extensively and gradually attained equilibrium (Figure 4a-1(ii)), at which point the concentrations of ionic species (sodium ions, etc.) inside and outside the gel were almost equal. On the other hand, when the water was changed frequently, the release of ionic species from the network and the absorption of water from its surroundings were more rapid because there was a large difference between the ion concentrations in the interior of the gel and in its surroundings (fresh water). In particular, the sodium ions in the network were continuously released until they were completely removed (Figure 5). The change in the PDMAA/clay network upon the release of sodium counterions is depicted in Figures 6(ii) and 6(iii). With the removal of sodium ions, the dissociated pair of clay and the counterion $(X_{clay}{}^- + Na^+)$ may change to a hydrogen ion associated state $(X_{clay}{}^- - H^+)$, which is analogous to the change in the sodium carboxylic group $((COO^- + Na^+)$ $\leftrightarrow$ COOH$)$. Here, $X_{clay}{}^-$ refers to the formula for the clay $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]^{0.66-}$. Thus, NC gels lose their large swelling ability as a polyelectrolyte gel as the swelling proceeds with frequent changes of the surrounding water. Therefore, in the early stage of swelling, the NC gel absorbs a large amount of water owing to the osmotic pressures (Π_{ion} as well as Π_{mixing}). Then, at a particular swelling time (when ~10 wt % of sodium ions remains), the gel shows maximum swelling (DS$_{max}$) (Figure 6(ii)), after which it starts to contract as further sodium
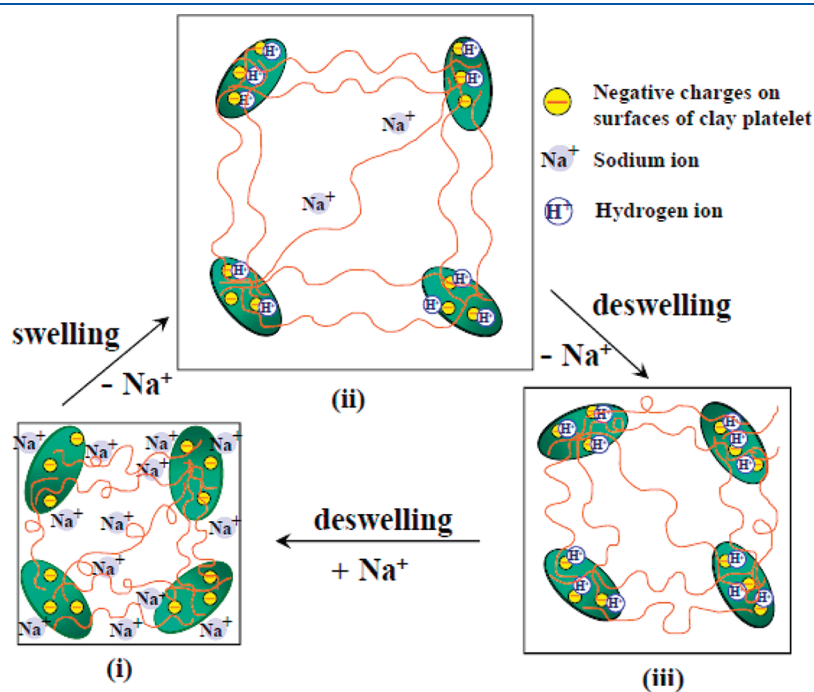
Figure 6. Change in polymer (PDMAA)/clay (Laponite XLG) network structure during swelling: (i) as-prepared state; (ii) maximum swelling (DS$_{max}$) state; (iii) equilibrium swelling (EDS) state. Only a few polymer chains and counterions are depicted for simplicity.

ions are released into the refreshed water. DS_{max} corresponds to the point where the contributions from the Donnan swelling pressure and elastic contracting force are balanced. Finally, the NC gel with no residual sodium ions reaches an equilibrium swelling state, which depends on ν of the gel and the hydrophilicity of the PDMAA chains (Figure 6(iii)). Since values of
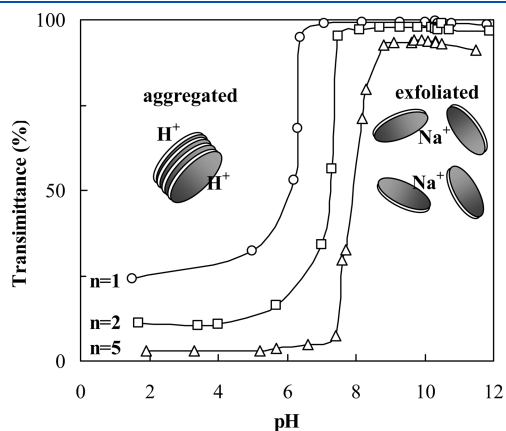

Figure 7. Change in clay dispersion ($C_{clay} = 1 \times 10^{-2} - 5 \times 10^{-2}$ mol/L of H_2O) in water with a change in pH. The clay is exfoliated at high pH and aggregated at low pH.

ν for NC gels are generally lower than those of conventional OR1 gel, the EDS of the NC gel is still higher than that of OR1 gel.

In NC gels with high C_p, the effect of the sodium ion release (i.e., maximum swelling and subsequent deswelling) was not clearly observed (Figure 3). This is because the degree of swelling is primarily suppressed owing to the high cross-link density ($\nu \propto C_p$) and also owing to the relatively low content of sodium ions at high C_p. Similarly, in the case of NC gels with very low C_{clay} at fixed C_p (=1 M), e.g., NC1.5 gel (Figure 2a), the gels did not show deswelling because (i) the EDS is very large owing to the low clay (cross-linker) concentration and (ii) the effect of the sodium ion release is small owing to the low sodium ion concentration (proportional to C_{clay}).

With regard to the clay shown in Figures 6(iii), it should be noted that $X_{clay}{}^{-}-H^{+}$ is not soluble in water and may no longer contribute to the water absorption by the NC gel. Figure 7 shows the pH dependence of clay (Laponite XLG) dispersion in water. The clay was molecularly dispersed (exfoliated) in water and the pH of the aqueous dispersion was 10.2, almost irrespective of the clay concentration ($C_{clay} = 1 \times 10^{-2} - 10 \times 10^{-2}$ mol/L of H_2O). It was found that the clay is molecularly dispersed in a high pH range, e.g., pH $\geq$ 8 for $C_{clay} = 5 \times 10^{-2}$ mol/L of H_2O; hence, for a low pH, the once-exfoliated clay platelets tend to aggregate in the aqueous medium (Figure 7). However, in an NC gel, since the exfoliated clay platelets are fixed at positions separated by PDMAA chains, the clay platelets do not aggregate
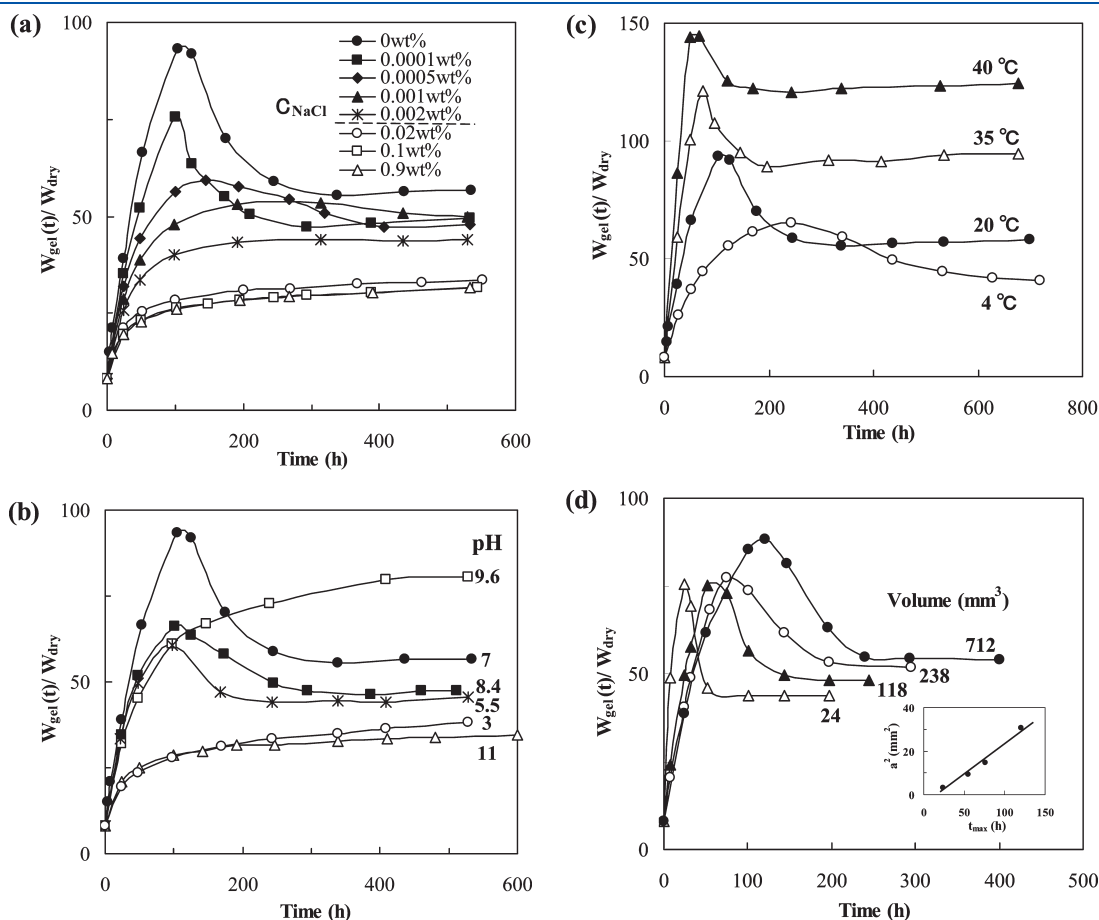

Figure 8. Changes in swelling of NC5 gel with changes in conditions of surrounding solvent. (a) Effect of NaCl concentration in the swelling solvent. (b) Effect of pH of the swelling solvent. (c) Effect of temperature of the swelling solvent. (d) Effect of gel size. The inset shows the relationship between a^2 and t_{max}. Other swelling conditions: initial gel size, 5.5 mm diameter and 30 mm length; amount of water as swelling solvent, 200 mL; and $T_s = 20\,°C$.
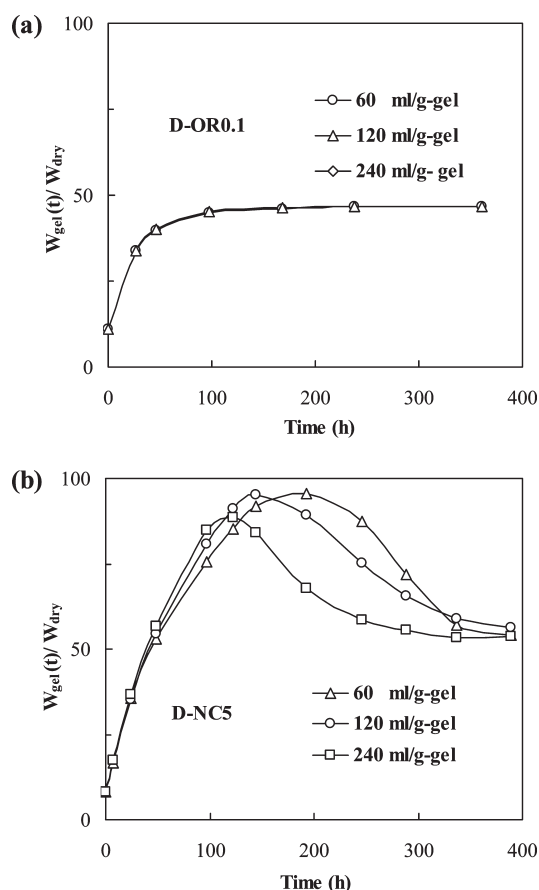
(a)

(a)

(b)

(b)

Figure 9. Difference in the swelling behavior of (a) OR0.1 gel and (b) NC5 gel with the amount of solvent (water) used per unit gram of gel (W_{H_2O}/g of gel = 60, 120, and 240 mL/g of gel). Other swelling conditions: initial gel size, 5.5 mm diameter and 30 mm length; frequent water change; T_s = 20 °C.
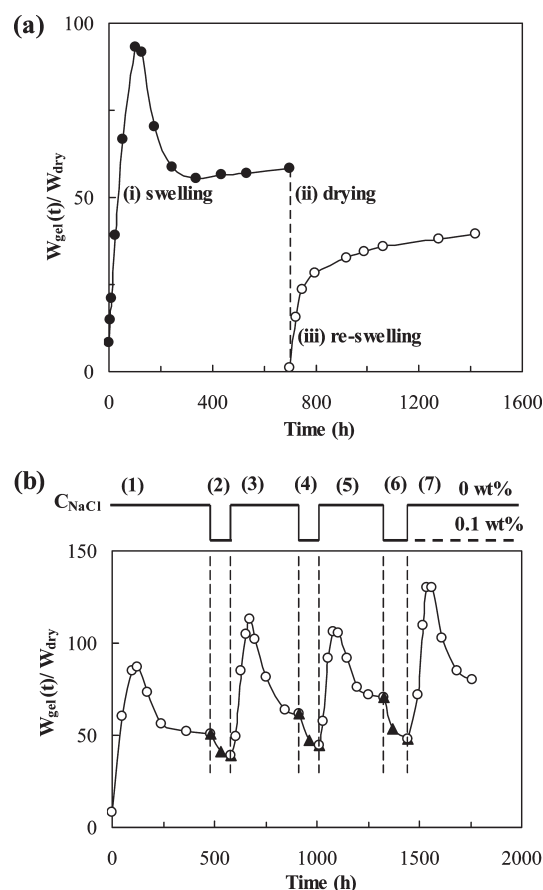
Figure 10. Effects of repeated swelling tests on an NC5 gel. (a) Swelling in water (i) and drying (ii) followed by reswelling (iii). (b) Cyclic swelling tests for an NC5 gel alternating between pure water and aqueous NaCl solutions (C_{NaCl} = 0.1 wt %). Other swelling conditions: initial gel size, 5.5 mm diameter and 30 mm length; amount of water, 200 mL; frequent water change; and T_s = 20 °C.

(accordingly, the NC gel maintains its high transparency) even at pH = 7, but only change to a nonionic state by losing the sodium counterions.

Factors Affecting the Swelling–Deswelling Behavior of NC Gel. Other factors that were considered to affect the characteristic swelling behavior of the NC gel were investigated, such as the addition of salt, pH, temperature, gel size, and amount of water per unit gram of gel. The effect of salt concentration on the swelling of chemically cross-linked polyelectrolyte gels has thus far been widely studied. It is known that, in general, the degree of swelling is largely suppressed by adding salt to the solvent, e.g., polyelectrolyte gels based on sodium methacrylate; EDS decreases in a NaCl aqueous solution.[29] The effect of NaCl concentration (C_{NaCl}) on the swelling behavior of the NC5 gel is shown in Figure 8a. It was observed that with the increase in C_{NaCl} from 0 to 0.9 wt % the degree of swelling of the NC5 gel was strongly suppressed, particularly at very low C_{NaCl}. For example, DS_{max} decreased greatly on addition of only 0.0001– 0.0005 wt % of NaCl and almost disappeared after the addition of 0.002 wt % NaCl, whereas EDS gradually decreased from 56 (0 wt %) to 45 (0.002 wt %) and 33 (0.02 wt %). When C_{NaCl} was further increased from 0.02 to 0.9 wt %, the EDS hardly changed (Figure 8a). These observations indicate that the degree of swelling due to the Donnan swelling pressure is largely suppressed by the very low C_{NaCl} in the surrounding water; these

observations also indicate that when C_{NaCl} in the surrounding water is greater than the sodium ion concentration in the original NC5 gel (0.083 wt %), then C_{NaCl} hardly affects the swelling of the NC5 gel.

The effect of solvent pH on the swelling behavior of the NC gel is shown in Figure 8b. Over a wide range of pH values (3–11), maximum swelling was observed between 5.5 and 8.4. The highest DS_{max} was observed when pure water (pH 7) was used. Deswelling and DS_{max} did not occur in cases of higher ion concentration, e.g., pH = 9.6, 11, or 3.

The effect of swelling temperature T_s (4–40 °C) on the swelling behavior of the NC5 gel is shown in Figure 8c. Since PDMAA is not a thermosensitive polymer, the NC5 gel exhibited swelling–deswelling behavior at all T_s and the overall degree of swelling, including the EDS, increased with T_s. DS_{max} also increased with T_s, but t_{max} reduced. The reduction in t_{max} may be due to the fast release (i.e., large diffusion rate) of sodium ions at high temperature.

With regard to the influence of size of gel sample on the swelling behavior, Tanaka et al.[30] reported that the swelling time (t) is proportional to the square of a linear dimension (a) of a gel, as expressed in eq 2.

$$t \propto a^2/D \qquad (2)$$

Here, t is the characteristic swelling time, a is the radius of the gel, and D is the diffusion coefficient of the gel. Figure 8d shows the effect of size on the swelling behavior of an NC5 gel under conditions where the water was changed frequently. All NC5 gels exhibited characteristic swelling—deswelling behavior regardless of the sample size, and the swelling occurs rapidly if the size is small. In other words, t_{max} reduces with a decrease in sample size. The relationship between t_{max} and the square of the gel size (a), which is obtained from $V_{gel} = 4\pi a^3/3$ (where V_{gel} is the gel volume), is shown in the inset of Figure 8d. In agreement with eq 2, t_{max} and a^2 show a good linear relationship. In the present study, in order to clarify the simultaneous release of sodium ions and the effects of other factors on the swelling, we used an NC gel of quite a large size to study its swelling.

With regard to the amount of solvent (water) per unit gram of gel (W_{H_2O}/g of gel), we normally used the excess water relative to the original hydrogel and did not consider the exact value of W_{H_2O}/g of gel. In fact, in the case of the conventional OR0.1 gel, W_{H_2O}/g of gel hardly affected the swelling if it was larger than 60, as shown in Figure 9a. However, in the case of NC gels, W_{H_2O}/g of gel was found to have a stronger effect on the swelling behavior. Figure 9b shows the effect of W_{H_2O}/g of gel 60, 120, and 240 mL/g of gel) on the swelling—deswelling behavior of NC5 gels under conditions where the water was change frequently. Unlike the present case (240 mL/g of gel), deswelling was not observed in the case of 60 mL/g of gel within 200 h. This is the reason why deswelling was not observed in our previous studies.[3] Although W_{H_2O}/g of gel of 60—120 and swelling times of 200 h are supposed to be quite large, they are insufficient for the NC gel with sizes of a few tens of millimeters to exhibit true swelling behavior that includes deswelling.

Reversibility of Swelling—Deswelling Behavior. As mentioned in the Introduction, Can et al.[27] reported the swelling—deswelling behavior of an opaque NC gel prepared using Laponite XLS and concluded that the reported abnormal swelling behavior was due to further exfoliation of the clay and the subsequent formation of additional cross-links during swelling. However, this explanation cannot be accepted as the reason for the swelling behavior, because in the present study swelling—deswelling behavior is observed in various NC gels, all of which have a definite uniform network (high transparency) and very strong mechanical properties in their as-prepared state, and in which the exfoliation of clay was confirmed through XRD and TEM. Further, as discussed in the previous sections, the occurrence of deswelling was dependent on the compositions of the NC gels and the swelling conditions. Therefore, it is concluded that the swelling—deswelling behavior originates from the nature of the NC gel as a polyelectrolyte gel. In addition, if the swelling—deswelling behavior is due to the exfoliation of clay and subsequent formation of additional cross-links, as proposed by Can et al., then this behavior should be irreversible. Hence, we next investigated the reversibility of the swelling—deswelling behavior.

Figure 10a shows the swelling behavior of a once-swollen and dried NC5 gel. NC5 gel was first swollen in pure water for about 700 h, during which the gel was observed to swell and deswell and attain an EDS of 58. Next, the swollen NC5 gel was carefully (slowly) dried at room temperature for 48 h at 50 °C in vacuum for 10 h. The once-swollen and dried NC 5 gel thus obtained was subsequently subjected to the swelling test under exactly the same conditions as those imposed during the first swelling. As shown in Figure 10a(iii), the once-swollen and dried gel

exhibited normal swelling behavior (without deswelling) and attained an EDS of ~40. Here, the relatively small EDS in (iii) is because of the formation of additional cross-links as a result of the rearrangement of the PDMAA/clay network during the drying process, as reported in a previous paper.[31] Thus, under simple swelling conditions (Figure 10a), the swelling—deswelling behavior was not reversible. It was confirmed through solid atomic absorption spectroscopy that sodium ions were rarely contained in the dried NC5 gels after both (ii) and (iii). This indicates that the characteristic swelling—deswelling behavior is only observed for as-prepared NC gels containing a sufficient content of sodium ions.

Figure 10b shows the results of cyclic swelling tests conducted on an NC5 gel by means of repeated introduction of sodium ions into the gel network from the surrounding aqueous NaCl solution. As shown in Figure 10b, after the first swelling—deswelling process (1) was completed (~480 h), the gel was immersed in a 0.1 wt % NaCl aqueous solution for 100 h (2). As expected, the NC5 gel was deswollen in the aqueous NaCl solution. During this process, sodium ions would diffuse into the PDMAA/clay network. The NC5 gel was again immersed in pure water (3) and subjected to another swelling test under the same conditions (pure water) as in the first swelling test. The NC5 gel exhibited characteristic swelling—deswelling behavior, similar to the first swelling of the original NC5 gel. Thus, swelling—deswelling behavior could be reverted by reintroducing sodium ions into the network and was successfully reproduced even after several successive treatments (Figure 10b).

■ CONCLUSION

NC gels with excellent optical transparency and mechanical toughness were found to exhibit spontaneous swelling—deswelling behavior in water. NC gels initially exhibited strong swelling, then started to deswell after attaining a transient maximum degree of swelling, and finally reached an equilibrium state. A characteristic swelling behavior was observed in different types of NC gels (e.g., PDMAA- and PNIPA-NC gels) and in most NC gels at varying C_{clay} and C_p values, except at very low C_{clay} ($n \leq 2$) and high C_p ($m \geq 3$). Further, the swelling—deswelling behavior was observed under specific swelling conditions. The effects of various swelling conditions such as the frequency of changing the water, the amount of water per unit gram of gel, salt concentration and pH of the swelling solvent, and gel size were clarified. The characteristic swelling—deswelling mechanism was attributed to the polymer/clay network structure, particularly to the combined effects of the high swelling capability of NC gels as polyelectrolyte gels and the continuous release of sodium ions from the network in the course of swelling. Furthermore, although the deswelling process is normally irreversible, a reversible swelling—deswelling behavior could be achieved by reintroducing sodium ions into the network. Thus, variations in the swelling behavior of NC gels under different conditions, and the role of exfoliated clay platelets in combination with sodium counterions in the network, were identified. The characteristic swelling behaviors of polymer/clay networks (NC gels) described in this paper, which are completely different from those of chemically cross-linked polymer networks, provide important and interesting information that is useful for basic research on organic/inorganic NC gels and their potential applications.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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