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Effects of Clay Content on the Properties of Nanocomposite Hydrogels Composed of Poly(*N*-isopropylacrylamide) and Clay

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ABSTRACT: For two different types of poly(*N*-isopropylacrylamide) (PNIPA) hydrogels, i.e., nanocomposite type PNIPA hydrogels (NC gel) and conventional chemically cross-linked PNIPA hydrogels (OR gel), the effects of cross-linker contents on various physical properties were investigated. In NC gels composed of a unique organic (PNIPA)/inorganic (clay) network, the inorganic clay acts as a multifunctional cross-linker in place of an organic cross-linker (BIS) as used in OR gels. In NC gels, which generally exhibit extraordinary mechanical toughness, the tensile moduli and tensile strengths are almost proportional to the clay content (C_{clay}), while the elongation at break tends to decrease slightly with increasing C_{clay}. On the other hand, in OR gels, which always exhibit weak and brittle natures, there was no detectable change in properties on altering the concentration of BIS (C_{BIS}). The deswelling rate was affected markedly by the cross-linker content in both gels though in opposite directions. On increasing cross-linker contents NC gels exhibit decreases and OR gels exhibit increases in rates of deswelling. In NC gels, high deswelling rates and high structural homogeneities (transparencies) were achieved simultaneously. Also, volume changes related to the phase transition of PNIPA at LCST were also inclined to decrease on increasing cross-linker contents in both gels, although swelling ratios at temperatures below LCST were generally larger in NC gels than those in OR gels. As for transparency changes at LCST, in OR gels changes in transparency decrease on increasing C_{BIS}, because below the LCST the transmittances themselves decrease steeply with increasing C_{BIS}. On the contrary, NC gels exhibit large transparency changes regardless of C_{clay} and show a tendency to increase their transmittances above LCST in the high C_{clay} region. All results obtained were consistent with the proposed model structure for NC gels. On the basis of the theory of rubber elasticity and using tensile mechanical data, the number of effective cross-links and the molecular weight between cross-linking points were evaluated for all NC gels.

Introduction

Poly(*N*-isopropylacrylamide) (abbreviated as PNIPA) is one of the most attractive environmentally sensitive polymers and has been studied extensively from both basic and application points of view.[1] PNIPA undergoes a fast and reversible coil-to-globule transition around its lower critical solution temperature (LCST) in aqueous media.[2] At temperatures below the LCST, PNIPA chains are hydrated and adopt flexible and expanded random-coil conformations in water. Above the LCST, PNIPA chains become dehydrated and collapse into a tightly packed globular conformation. Currently, PNIPA is widely utilized in functional hydrogels. PNIPA hydrogels exhibit a clear volume phase transition in response to external stimuli such as temperature,[3−6] pH,[7] solvent composition,[3,8] salt concentration,[7,9] light,[10] mechanical stress,[11−13] and magnetic field.[14] Many potential applications such as biotechnological devices,[15] tissue engineering,[16] immobilization of enzymes,[17] and drug-delivery systems[18] stem from the stimuli-responsive properties of PNIPA described above.

PNIPA hydrogels are commonly prepared by chemical cross-linking using an organic cross-linker such as *N*,*N*′-methylenebis(acrylamide). In conventional PNIPA hydrogels (hereinafter, abbreviated as OR gels), it was reported that many properties such as volume (swelling ratio)[19] along with optical transparency, mechanical modulus,[20] surface properties,[21] and electrophoretic mobility[22] change significantly as a consequence of the hydrophilic/hydrophobic transition at the LCST. However, it is also true that OR gels have several important limitations. For example, OR gels often become turbid when the polymerization conditions, such as cross-linker content,[23] polymerization temperature,[24,25] and pressure,[26] are changed. Typically, OR gels prepared with high cross-linker concentrations become opaque even at temperatures below LCST. This is attributed to the development of permanent structural inhomogeneities on an optical-wavelength scale created by a high cross-link density. Regarding swelling in water, OR gels exhibit a quite low equilibrium swelling ratio in the range of cross-linker concentrations commonly used.[5,24,27,28] Also, OR gels generally exhibit very slow deswelling behavior, often taking more than a month to approach equilibrium,[27] although higher deswelling rates are required for many potential applications. Furthermore, OR gels always exhibit very weak mechanical properties and are easily broken by applying external stresses.[11,13] Therefore, OR gels cannot be used where they are extended or bent. Since all these disadvantages of OR gels arose from the inherent problems of chemically cross-linked polymer networks, they were considered inevitable. That is, these limitations are observed in any OR gel having a broad distribution of polymer chain lengths between cross-linking points.

Among these disadvantages, slow rates of deswelling have been studied most extensively. As a result, fast deswelling has been achieved by introducing

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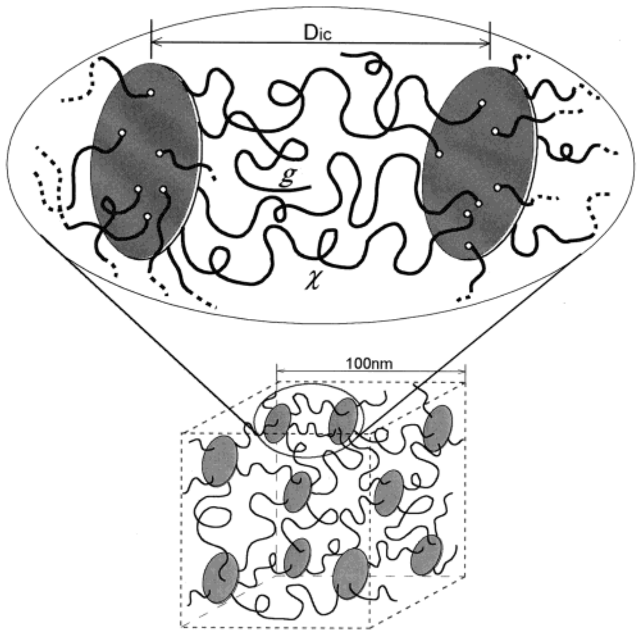

Figure 1. Schematic representation of the organic/inorganic network in the NC gel, which consists of uniformly dispersed (exfoliated) inorganic clay sheets and two primary types of flexible polymer chains, χ and g, grafted to two neighboring clay sheets and one clay sheet, respectively. In the NC3 gel, the number of clay sheets and cross-linked polymer chains in a 100 nm cube are estimated as approximately 10 and 620, respectively. In the model, only a small number of polymer chains are depicted for simplicity.

porosities,[24,29−31] structural inhomogeneities,[23,32] or a tailored graft structure[27] into OR gels. The modified OR gels were prepared, for example, by polymerization using selected conditions such as high and low polymerization temperatures[32,33] or high cross-linker concentration,[23] and also by polymerization in the presence of other components having a siloxane linkage,[31] a carboxylate group,[34] etc.[24,30,35] However, in most cases, other properties such as mechanical properties, swelling ratio, and optical transparency were not improved and were often made worse. Therefore, it was a dream to develop a new material that could overcome all these disadvantages simultaneously. In an ideal PNIPA hydrogel, desirable properties in structural homogeneity (i.e., high transparency), mechanical properties (high strength and toughness), and swelling/deswelling behaviors (high swelling ratio and fast deswelling rate) should be achieved simultaneously.

Recently ,we succeeded in synthesizing a new type of PNIPA hydrogel with almost ideal properties.[36] The novel hydrogel was a nanocomposite type hydrogel (hereinafter abbreviated as NC gel). The NC gel is composed of PNIPA, inorganic clay, and water, in which the exfoliated inorganic clay acts as an effective multifunctional cross-linker. We proposed the model structure for NC gel depicted in Figure 1. The model is based on a uniform dispersion of exfoliated inorganic clay in an aqueous medium and PNIPA chains grafted on the clay surface at one or both ends. NC gels mainly consist of polymer chains connecting neighboring clay sheets. In other words, polymer chains are effectively cross-linked by clay sheets. Also, because of the large distance between the clay sheets, all polymer chains in NC gels are long and flexible, adopting random conformations. Thus, the chain lengths between clay sheets may be proportional to the clay−clay interparticle distance (D_{ic}) and with a fairly narrow distribution of chain lengths. In contrast, PNIPA chains in OR gels are randomly cross-linked by a large number of organic cross-linking units and the chain lengths between cross-linking points are short on average and have a wide distribution of chain lengths between random cross-linking points.

NC gels could be prepared by in situ free-radical polymerization of *N*-isopropylacrylamide (NIPA) in the presence of a water-swollen inorganic clay and without using any organic cross-linker. We found that because of their unique organic (polymer)/inorganic (clay) network structure, NC gels exhibit extraordinary mechanical, optical, and swelling/deswelling properties. In this paper, we present the characteristics of NC gels in more detail, focusing on the effect of cross-linker content, i.e., clay content (C_{clay}), in comparison with the characteristics of conventional OR gels. We show that all characteristics of NC gels exhibit strong dependencies on C_{clay} and that the effects of cross-linker content on the properties of NC and OR gels are totally different.

Experimental Section

Raw Materials. *N*-Isopropylacrylamide (NIPA) monomer, provided by Kohjin Co., was purified by recrystallization from a toluene/*n*-hexane mixture and dried in a vacuum at 40 °C. Other reagents were purchased from Wako Pure Chemical Industries, Japan, and used without further purification. Deionized water was distilled for all experiments including swelling/deswelling experiments. For preparations of hydrogels, nitrogen gas was bubbled through the distilled water for more than 3 h prior to use. As an inorganic clay, synthetic hectorite “Laponite XLG” (Rockwood Ltd.: $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$, layer size = 20−30 nm $\phi \times 1$ nm, cation exchange capacity = 104 mequiv/100 g) was used. Here, the term inorganic clay is used in contrast to organophilic clay, which contains substantial amounts of organic surfactant and is widely used in the preparation of polymer−clay nanocomposites.[37]

Synthesis of PNIPA Hydrogels. NC and OR gels were prepared using initial solutions consisting of monomer (NIPA), cross-linker (clay or *N*,*N*′-methylenebis(acrylamide) (BIS)), solvent (H_2O), initiator (potassium peroxodisulfate (KPS)), and catalyst (tetramethylenediamine (TEMED)). The molar ratio of monomer, initiator, and catalyst was 100:0.426:0.735. Since the initial solution contained 10 times as much H_2O as monomer by weight in all cases, the water/polymer ratio in the resulting hydrogels was fixed at 10/1 (w/w). The synthetic procedure of NC gel formation is simple and versatile. First, a transparent aqueous solution consisting of water (28.5 mL), inorganic clay (0.198−1.782 g), and NIPA (26.52 mmol) was prepared. Next, the catalyst (TEMED, 24 μL) and subsequently the aqueous solution of initiator (KPS 0.03 g in H_2O 1.5 mL) were added to the former solution with stirring at iced-water temperature. Then, free-radical polymerization was allowed to proceed in a water bath at 20 °C for 20 h. In the preparation of OR gels, BIS (0.014−0.126 g) was used as a cross-linker. Throughout the experiments, oxygen was excluded from the system. Both NC and OR gels were synthesized in two kinds of glass vessels, one a columnar shape (interior size = 27 mm $\phi \times 50$ mm length) and the other a rod shape (interior size = 5.5 mm $\phi \times 200$ mm length). Here, ϕ represents a diameter. For analytical and swelling measurements, NC and OR gels were purified prior to use by immersing them in an excess of water at 5 °C and then 60 °C for 48 h at each temperature, changing the water several times. For measurements of mechanical properties, transparencies, and some volume changes, hydrogels were used as-prepared in order to retain the water/polymer ratio of that in the initial gel samples.

Sample Nomenclature. In the present study, both OR and NC gels are expressed as ORX gel and NCY gel, using a simplified numerical value of each cross-linker content. For OR gels, cross-linker (BIS) content is expressed as *X*, which corresponds to the mole percent of BIS against NIPA monomer. As an actual weight, 0.14 × X g of BIS is used with 10 g of NIPA monomer for ORX gel; Here, 0.14 = {10/(molecular weight of NIPA)} × (molecular weight of BIS)/100. For NC gels, the clay content for the solution of (0.66 g clay/100 g H_2O) is simply expressed as 1 according to {(weight of clay per 1000 mL of water)/(molecular weight of $Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4$} × 100. Then, the hydrogel containing (0.66 × Y g clay/100 g of H_2O/10 g of PNIPA) is expressed as NCY gel. In this study, the X and Y are varied within the range 1−9.

Characterization. Analytical measurements such as TG, IR, TEM, SAXS, and DSC measurements are performed using dried NC and OR gels in order to analyze their composition and structures. Dried NC and OR gels were prepared by drying purified NC and OR gels under atmospheric conditions for 3 days and then at 70 °C in a vacuum oven for 24 h. Thermogravimetric (TG) analyses were carried out using a TG/DTA 220 (Seiko Denshi Industries Inc.) instrument, heating samples from 30 to 1000 °C at a heating rate of 10 °C min^{-1} in an air flow. The clay content in the NC dried gel was evaluated from the residual weight at 1000 °C. Fourier transform infrared (FTIR) spectra were obtained using a FT/IR-550 (Nihon Bunko Inc.) with milled NC and OR dried gels by the conventional KBr disk tablet method. Transmission electron microscopy (TEM) was undertaken using a JEM-200CX (Nihon Denshi Co.) instrument at 100 kV for NC dried gels. Ultrathin films (ca. 50 nm thick) were prepared for TEM observation by cutting dried gels embedded in epoxy resin, using an ultramicrotome (Reichert Ultracut S). Differential scanning calorimetry (DSC) measurements were performed using a DSC-7 (Perkin-Elmer Inc.) in a nitrogen gas atmosphere with milled NC and OR dried gels, heating from 30 to 250 °C at a heating rate of 1 °C min^{-1}. Glass transition temperatures were obtained from the second run after heating to 250 °C in the first run.

Measurements. (a) Swelling Ratio. Swelling experiments were performed by immersing purified gels (initial size of 5.5 mm ϕ × 30 mm length) in a large excess of water at 5 °C for ∼1000 h until the gel weight approached saturation. Swelling ratios are represented by the ratio of weights of the swollen hydrogel (W_{gel}) to the corresponding dried gel (W_{dry}).

(b) Transparency and Its Changes. Transparencies were measured using a NDH-300 (Nippon Denshoku Inc.) turbidimeter with a white halogen light, for NC and OR gels (gel size = 27 mm ϕ × 30 mm length) synthesized in a columnar glass vessel. All hydrogels within the glass vessels were maintained in a water bath for 30 min prior to each measurement. Bath temperatures used varied from 1 to 50 °C. The total transmittance and its components (parallel and diffuse) were measured within a few seconds after removing the gel from the water bath.

(c) Temperature Dependence of Gel Volume. To measure the temperature dependence of gel volume, NC and OR gels (initial size 5.5 mm ϕ × 30 mm length) were kept in a large volume of water at 20 °C for 48 h. After the size (length and diameter) and weight were measured at 20 °C, they were transferred to water baths at specific temperatures (∼50 °C) and maintained for 8 h prior to further measurements. In the measurement, the hydrogel was weighed and measured after excess water was removed.

(d) Swelling and Deswelling Kinetics: To measure the deswelling kinetics of NC and OR gels, as-prepared hydrogels of the same size (5.5 mm ϕ × 30 mm length) and same water/polymer ratio (10/1 (w/w)) were used. The time dependence of the gel weight was measured after moving the original hydrogel into a water bath at 40 °C. In each measurement, which took about 10 s, the hydrogel was removed from the water bath and weighed after excess water was removed from the surface.

To determine the swelling/deswelling behaviors with alternating temperature changes, NC1-5 gels and OR1-5 gels with the same size and water/polymer ratio as described above were used. At first, the original NC and OR gels were retained at 50 °C for 24 h. Then the hydrogels were alternately moved into water at 20 and 50 °C. The hydrogels were retained for 48 h at each temperature and weighed at specific times after removing the excess water from the surface. The time dependences of swelling ratio were represented by $W_{gel}(t)/W_{50}(24)$, where $W_{gel}(t)$ is gel weight at specific time t (h) and $W_{50}(24)$ is the gel weight after retention of the first 24 h at 50 °C.

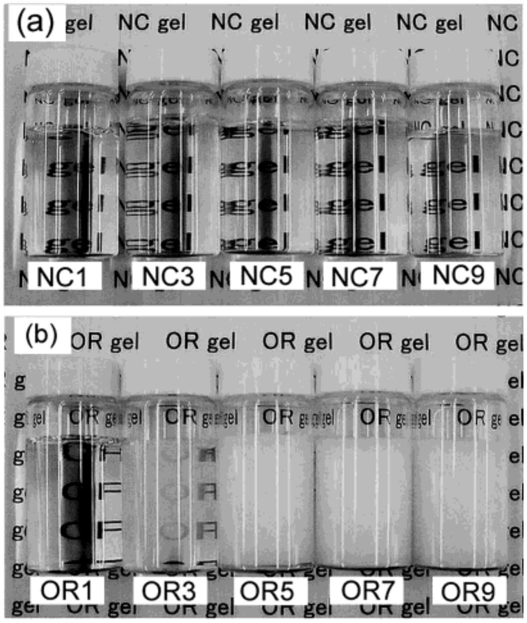

Figure 2. NC and OR gels with different cross-linker contents: (a) NC1−9 gels and (b) OR1−9 gels. All gels were polymerized at 20 °C at water/polymer = 10/1 (w/w).

(e) Mechanical Properties: Tensile mechanical measurements were performed on NC and OR gels of the same size (5.5 mm ϕ × 70 mm length) and the same water/polymer ratio (10/1 (w/w)) using a Shimadzu Autograph AGS-H. Tensile properties of NC gels were obtained under the following conditions; sample length between jaws 35 mm; crosshead speed 100 mm min^{-1}; test temperature 25 °C. The initial cross section (23.75 mm^2) was used to calculate the tensile strengths and the tensile moduli. The tensile modulus was calculated from the increase in load detected between elongations of 100% and 200%.[38] The permanent (irreversible) elongation was evaluated by measuring the increase of sample length on the second run after NC gels were elongated up to 500% and returned to the original length. Since recoveries show time dependencies, the once-elongated sample was relaxed to a stress-released state for a fixed time (3 min) before the second run. On the other hand, tensile mechanical properties of OR gels could not be obtained using the same test method. This is because OR gels were too weak to carry out the measurements, and in particular, it was too difficult to hold OR gels tightly enough for the tensile tests. OR gels always broke before obtaining precise mechanical data. Approximate mechanical data for OR gels were obtained using a simple elongation method with a ruler and weight.

Results and Discussion

Preparation of NC Gels. Uniform PNIPA hydrogels (NC gels) were prepared by in situ free radical polymerization in solutions containing different amounts of clay, in all cases without any phase separation or precipitation. Figure 2 shows the appearances of NC gels (NC 1−9 gels) and OR gels (OR 1−9 gels), synthesized in columnar glass vessels. In both NC and OR gels, it was found that the shape of the resulting hydrogel was the same as that of the vessel used.

Polymerization yields, evaluated from the weights of dried gels, were nearly 100% in all cases. FTIR spectra of the dried NC gels show the characteristic absorptions of both PNIPA (2970, 2920, 1650, 1550, and 1460 cm^{-1})

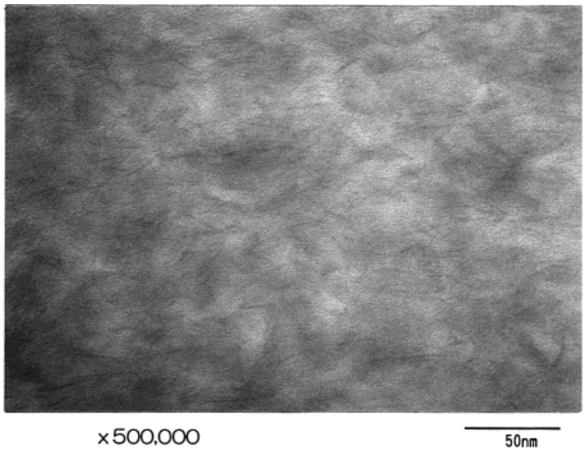

Figure 3. Transmission electron micrograph of dried NC5 gel at a magnification of 500 000. In the dried NC5 gel, the clay/polymer ratio is 33 wt %.

and clay (1005, 650, and 1005 cm^{-1}). The weight ratios of clay/polymer in NC gels, evaluated by TG measurements for the corresponding NC dried gels, were in accord with those calculated from the solution composition. Thus, regardless of C_{clay}, PNIPA hydrogels consisting of PNIPA, clay, and water were formed with the same compositions as the starting solution. The dispersion of clay was observed by TEM on the dried NC gel. Figure 3 shows a transmission electron micrograph of an ultrathin film of dried NC5 gel. Although the clay was concentrated in the dried gel (33 wt % against polymer), in comparison with the hydrogel (2.9 wt % against gel), it was found that the clay was substantially exfoliated and dispersed homogeneously throughout the polymer matrix. It was therefore concluded that fine and homogeneous clay dispersions are achieved in the hydrogel state, consistent with the high optical transparency of NC gel.

When kept in large volumes of water for a long time, none of the NC gels dissolved but swelled extensively while retaining a similar shape. This result shows that PNIPA and clay formed network structures without any organic cross-linker.[39] The degrees of swelling of NC gels were, on the whole, higher than those of conventional OR gels. The near equilibrium swelling ratios expressed by W_{gel}(weight of swollen gel)/W_{dry}(weight of dried gel) were 110, 51, and 48 for NC1, -3, and -5 gels, respectively, whereas the swelling ratios for OR1 and -5 gels were 29 and 14, respectively. Thus, in both a series of NC and OR gels, the swelling ratio gradually decreased as the cross-linker content increased.

Optical Transparency. As shown in Figure 2, NC1−9 gels were all transparent, whereas OR1−9 gels exhibited different transparencies depending on the cross-linker content. Note that all these samples were polymerized and photographs taken at 20 °C which is below the LCST. Extensive studies correlating light scattering intensities to the structural inhomogeneities in the polymeric hydrogels have been reported.[25,26,42] It is considered that the optical transmittance of NC and OR gels reflects the spatial cross-link inhomogeneity in the polymer networks. In the case of thermosensitive PNIPA hydrogels, the structural inhomogeneity is readily changed by the temperature at observation. Therefore, the transparencies should be measured at temperatures sufficiently lower than the LCST. Figure 4 shows the effects of cross-linker contents on transparencies measured at 1 °C for NC and OR gels.

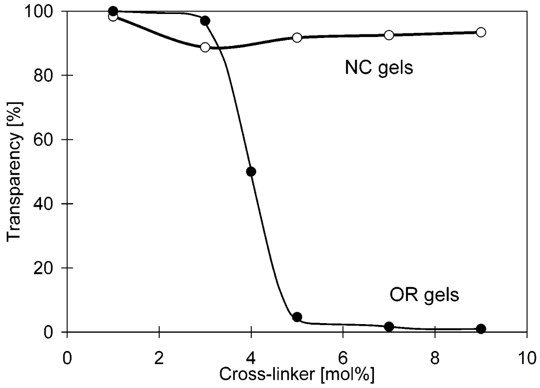

Figure 4. Changes in optical transparency of NC and OR gels produced by altering the cross-linker contents. Optical transmittance was measured at 1 °C for hydrogels (26 mm ϕ × 35 mm in length in a glass vessel) synthesized at 20 °C.

In OR gels, it was observed that BIS increases correlate with decreases in transparency. When BIS concentration equaled or exceeded 5 mol %, the resulting OR gels were totally opaque, i.e., total transmittance (TT) $\approx$ 0. This is ascribed to topological frozen inhomogeneties, introduced by locally concentrated cross-linking. Such inhomogeneity generally occurred in all polymeric hydrogels prepared with organic cross-linkers. Therefore, in PNIPA hydrogels, it seemed that increasing the cross-linker content always caused decreases in transparency. However, it was found that all NC gels from NC1 to NC9 exhibited high transparency almost regardless of C_{clay}. TT was higher than 90% even for NC9 gel, although the NC9 gel contained a large amount of clay (ca. 60 wt %) with respect to polymer. Note that values of TT are mainly composed of parallel transmittance components, e.g., PT = 87% out of TT = 92% for NC5 gel. These results suggest that the cross-linking reactions occurred uniformly in NC gels regardless of C_{clay}, which is distinct from the behavior of OR gels.

Mechanical Properties of NC Gels. NC gels and OR gels differ markedly in regards to their mechanical properties. Here, it should be noted that all NC and OR gels used for mechanical tests have same size (5.5 mm ϕ × 70 mm length) and same water/polymer ratio (10/1 (w/w)); that is, the polymers were far removed from conditions corresponding to equilibrium swelling. OR gels were always weak and exhibited brittle fracture (Figure 5). In contrast, NC gels were very tough and could withstand high levels of deformation such as elongation (Figure 6a), bending (Figure 6b) and compression. NC gels could be elongated to more than or close to 1000%. Also, NC gels can even be made into a knot without damage, as shown in Figure 6c,d. In tensile tests using knotted NC gel samples, it was often observed that the samples broke at a different point than the knot. Furthermore, it was found that NC gels were hardly damaged by compressive deformation. Normal tensile measurements could be performed without problem for all NC gels. Figure 7 shows the load-strain curves for NC1−9 gels. In contrast, it was difficult to perform normal tensile testing on OR gels, because they were too brittle to be held tightly enough between the clamps. OR gels were readily broken at low deformations in elongation (Figure 5a), bending (Figure 5b) or compression. Needless to say, OR gels could not be knotted. The mechanical weakness of OR gels was little affected by the BIS content (Figure 5). To make a rough estimate of the mechanical properties of OR gels, we

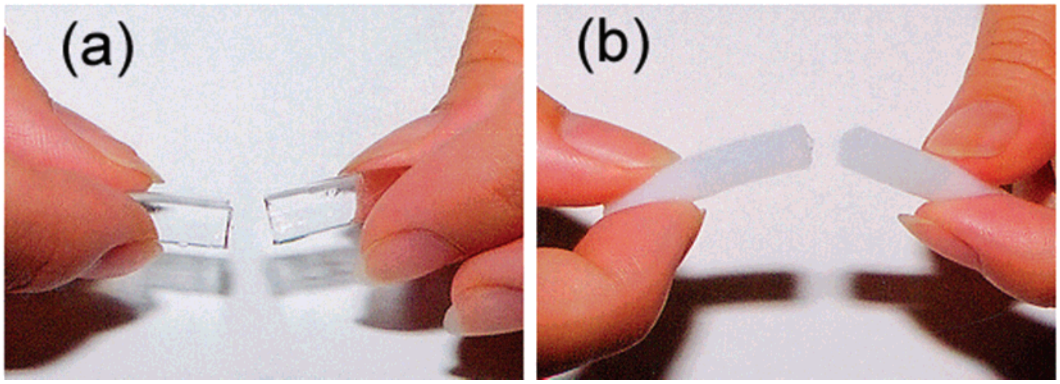

Figure 5. All OR gels, irrespective of the C_{BIS}, exhibit weak and brittle fracture. (a) OR1gel and (b) OR5 gel were broken by elongation and bending, only to a small extent.

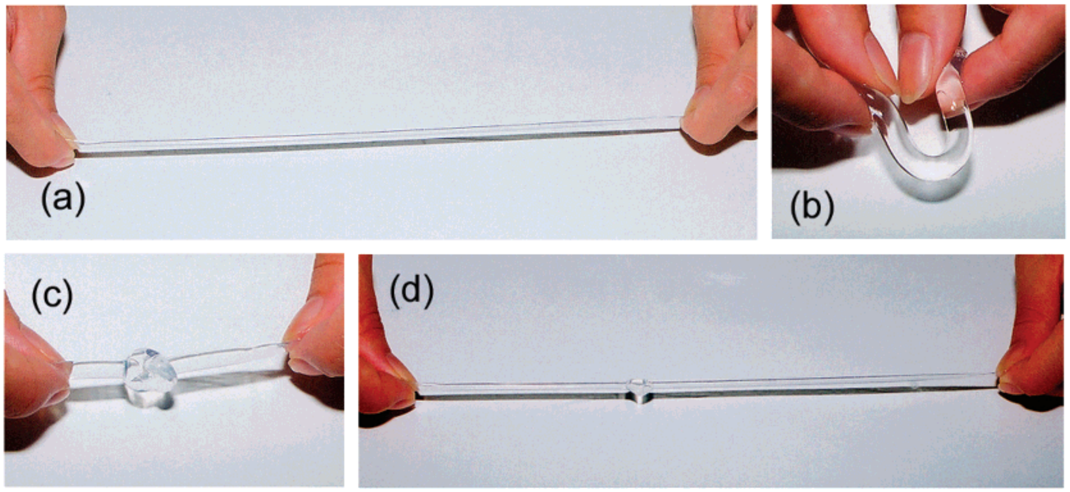

Figure 6. All NC gels exhibit extraordinary mechanical toughness. NC5 gel can withstand high levels of deformations in such as (a) elongation and (b) torsion. (c) and (d) show a knotted NC5 gel.

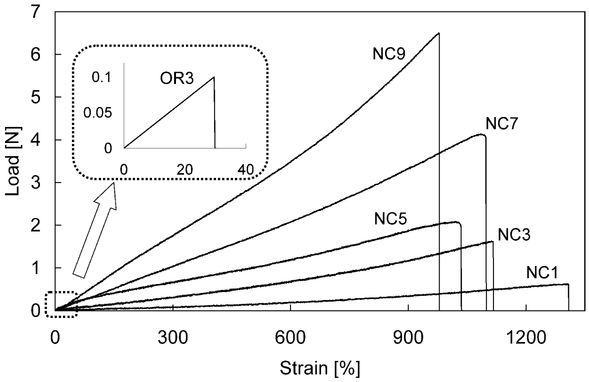

Figure 7. Load−strain curves of NC gels with different clay contents (NC1 to NC9). The approximate data for OR3 gel are also depicted for comparison. All hydrogels had the same polymer/water ratio (=1/10 (w/w)).

carried out a simple elongation test. Approximate estimates of strength and elongation at break were ca. 5 kPa and 30%, respectively, for OR1−5 gels.

Tensile modulus, tensile strength, and elongation at break data for NC gels with different C_{clay} are summarized in Table 1. The most striking result is that the elongations at break attained were close to or greater than 1000% for all NC gels. Elongations at break for NC gels exhibit a slight dependence on the clay content. The elongation at break increased with decreasing C_{clay} in the range of low C_{clay}, whereas NC9 gel with high C_{clay} (ca. 60 wt % against polymer) still exhibited a high elongation near 1000%. On the other hand, the strength and the modulus change more markedly with C_{clay}, as shown in Figure 8. Both of these properties were increased with increasing C_{clay}. Thus, the mechanical properties of NC gels can be varied greatly by changing C_{clay}. Other compositional factors such as polymer, water, and KPS also affect the mechanical properties; these effects will be presented in a subsequent paper.

In the tensile testing described above, it was observed that NC gels exhibited high recovery even after extensive elongation. The permanent elongation measured as the increase in sample length after 500% elongation, was about 3.5% of the total deformation for NC5 gels and decreased with increasing C_{clay}.

Since NC gels show extraordinarily large and reversible extensions, NC gels may be called rubbery polymeric hydrogels. The kinetic theory for rubber elasticity was developed on the basis of the entropy elasticity of flexible polymer chains. In the case of NC gels, polymer chains in the swollen state at ambient temperature should be regarded as flexible polymer chains just like those in the rubbery state of solid polymer above glass transition temperature (T_g), although the actual ambient temperature is much below its T_g (≈142 °C) as a bulk polymer. Subsequently, we will discuss the mechanical properties based on the kinetic theory of rubber elasticity and evaluate the number of effective cross-links and the molecular weight between clay sheets in the NC gels with different C_{clay}.

Table 1. Mechanical Properties of NC and OR Gels and Their Structural Parameters calculated

hydrogel	tensile modulus, kPa	mechanical strength, kPa	properties elongations, %	n,[a] 100 nm^3	F^b at $\alpha = 2$, kPa	N^*,[c] 100 nm^3	$N^*/n^{(4)}$ [d]	$10^4 M_c$, g/mol	T_g[e] of dried gel, °C
NC1	0.84	27	1308	3	0.93	157	52	38	141
NC3	3.8	69	1112	10	3.83	620	62	9.7	141
NC5	7.6	88	1035	16	7.83	1224	77	4.9142	
NC7	15.2	152	998	22	14.4	2026	92	3.0	
NC9	26.1	305	1031	29	25.0	3420	118	1.8	
OR1		ca. 5	ca. 30						145
OR5		ca. 5	ca. 30						152

[a] Number of clay sheets per unit volume (100 nm cube) of NC gels. [b] Stress at elongation of 100%. [c] Number of cross-linking polymer chains per unit volume (100 nm cube) of NC gels. [d] Number of cross-linking polymer chains per clay sheet. [e] T_g of dry linear PNIPA was observed at 142 °C.

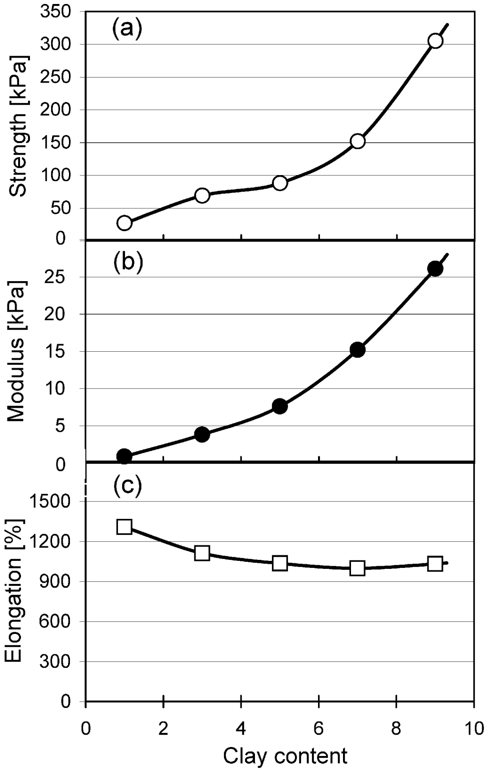

Figure 8. Changes of mechanical properties, such as (a) tensile strength, (b) modulus, and (c) elongation at break, by altering clay contents of NC gels. Initial cross-sectional area (23.75 mm^2) was used for calculating the modulus and strength.

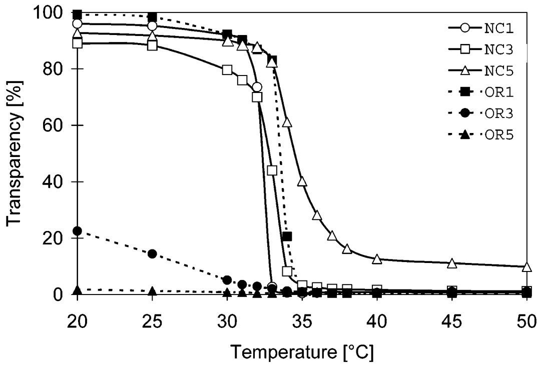

Figure 9. Temperature dependences of the optical transparency for NC and OR gels with different cross-linker contents. A hydrogel (26 mm $\phi \times 35$ mm in length in a glass vessel) synthesized at 20 °C was used for every measurement. Each hydrogel was maintained in a water bath at a specified temperature for 30 min before measurement.

Property Changes at LCST. Here, we investigate the changes in properties associated with the PNIPA coil−globule transition in NC and OR gels and their dependencies on cross-linker content. First, the transparency changes were observed after altering the measuring temperatures. The results are shown in Figure 9. As has been reported for chemically cross-linked PNIPA hydrogels, for OR1 gel, a reversible and clear change in transparency occurred at around 34 °C. The transparency changes in OR gels exhibited a strong dependence on C_{BIS}. By increasing C_{BIS}, the transparency changes at LCST became ambiguous because the transmittance at temperatures below LCST decreased rapidly. Thus, OR gels containing high C_{BIS}, near or above 5 mol %, were opaque (white) throughout the temperature range and did not exhibit any transparency change. This means that OR gels retain their turbidity, arising from the permanent structural inhomogeneity created during preparation, even after being cooled to below LCST. In contrast, all NC gels exhibited reversible transparency. However, in NC gels containing higher C_{clay} than NC5, the transmittance above LCST gradually increased with C_{clay}. Then, the transparency changes of NC gels also became ambiguous. This phenomenon is ascribed to the increasing hydrophilic nature of polymer chains with increasing C_{clay}. Since the clay surfaces are highly hydrophilic, independent of the environmental temperature, the conformational transition to the hydrophobic state may be hindered in polymer chains interposed between closely adjacent clay sheets.

Next, we consider the effects of cross-linker contents on the volume changes at around LCST measured for NC and OR gels and shown in Figure 10. In general, NC gels exhibit larger volume changes than OR gels. For example, NC1−5 gels exhibit about 30−50-fold volume changes, whereas OR gels exhibit volume changes less than 15-fold. The ratio of volumes below LCST: above LCST gradually decreased with increasing cross-linker content in both NC and OR gels. This is mainly due to decreased swelling with increased cross-linking, which occurs similarly in both gels. However, exceptionally, OR gels with low BIS contents, e.g., OR1 gel, did not show the apparent swelling/deswelling behavior under the present experimental conditions. This may be due to the very slow shrinking rate of OR1 gel; OR gels with low BIS contents required much more time to shrink than that used in the experiment.

Thus, it was confirmed that NC gels show well-defined LCST behaviors in terms of transparency and volume change, and that the effects of C_{clay} on LCST behaviors are different from those for OR gels.

Deswelling Kinetics. As mentioned above, the deswelling rate is one of the most important factors and, in particular, high rates are needed in many applications. A general approach to high swelling rate is to

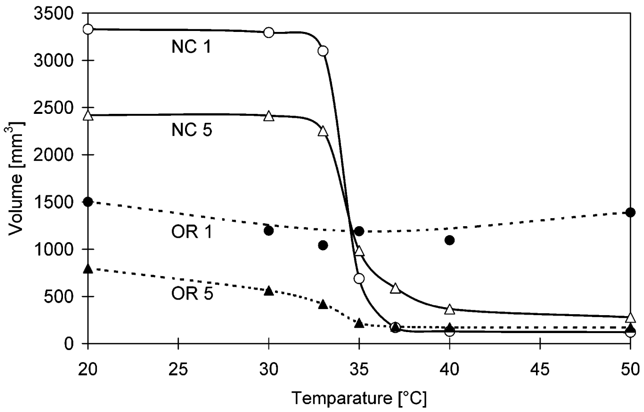

Figure 10. Temperature dependence of the gel volume for NC and OR gels with different cross-linker contents. All original gels had the same water/polymer ratio (=10/1 (w/w)) and the same size (5.5 mm $\phi \times 30$ mm in length). Each gel was first swelled at 20 °C for 48 h and subsequently maintained in a water bath at a specific temperature for 8 h before measurement.

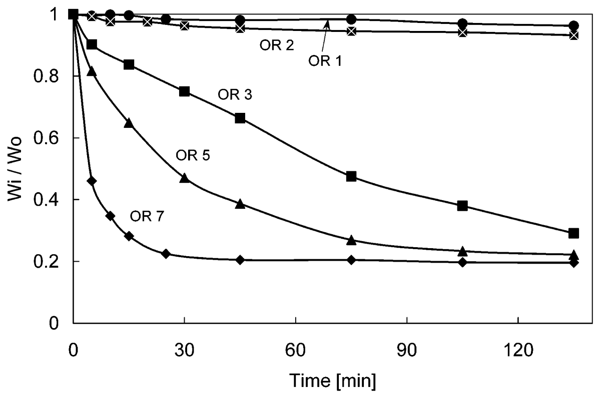

Figure 11. Deswelling kinetics (time dependences of weight) at 40 °C for OR gels with different BIS contents. All original gels had the same water/polymer (=10/1 (w/w)) and sample size (5.5 mm $\phi \times 30$ mm in length).

utilize the size effect. Hydrogels with smaller sizes could exhibit higher deswelling rates because the rate is inversely proportional to the square of the smallest dimension of the gel.[43] In attempts to improve the deswelling rate, even in large-sized samples, it was reported that there was a strong connection between fast shrinking and inhomogeneity caused by increasing C_{BIS}. Deswelling kinetics, where gels are moved from 20 to 40 °C, and the effect of cross-linker contents for OR gels are shown in Figure 11. Here, all initial samples started with the same volume (712 mm^3) and the same water/polymer ratio (10/1 (w/w)). The transparent OR gels with low BIS contents such as OR1 and OR2 gels, which have been most commonly used as conventional PNIPA hydrogels, exhibit insubstantial practical deswelling, taking more than a month to shrink. Also, the deswelling rate increased rapidly with increasing BIS contents, while the OR gels became turbid.

Figure 12 shows the deswelling behaviors measured for NC gels containing different C_{clay} under the same experimental conditions as Figure 11. Contrary to OR gels, NC1 gel containing the lowest clay concentration exhibited the most rapid response. Here, the shrinking was almost complete within 5−8 min, although the water bath temperature (40 °C) was only slightly higher than LCST and the original gel was of rather large size. Furthermore, in contrast to OR gel, the deswelling rate gradually decreased as C_{clay} increased. It should be noted that all NC gels used here were transparent, i.e., structurally homogeneous. Thus, NC gels show totally different deswelling behavior from those of OR gels in terms of cross-linker contents.

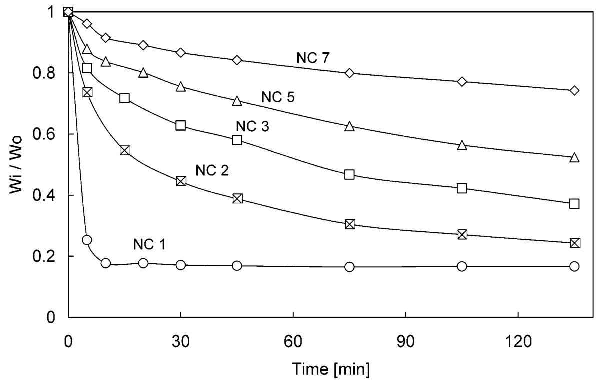

Figure 12. Deswelling kinetics (time dependences of weight) at 40 °C for NC gels with different clay contents. All original gels had the same water/polymer ratio (=10/1 (w/w)) and sample size (5.5 mm $\phi \times 30$ mm in length).

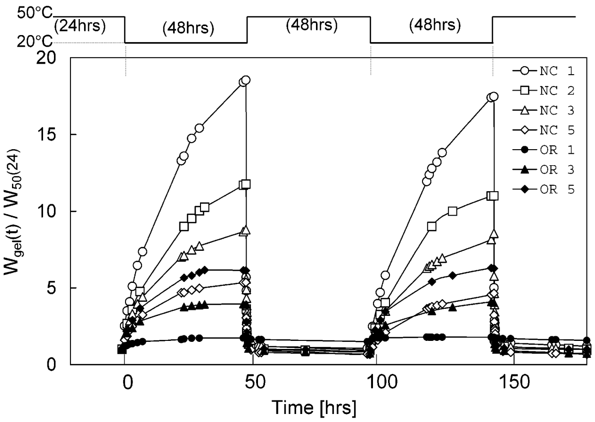

Figure 13. Swelling and deswelling behaviors by alternating temperature changes for NC gels and OR gels with different cross-linker contents. The time dependences of swelling ratio were measured as $W_{\mathrm{gel}}(t)/W_{50}(24)$. Here, $W_{50}(24)$ is the gel weight after the first 24 h retention at 50 °C.

The different characteristics of NC and OR gels in swelling/deswelling behaviors were clearly shown in experiments using alternating temperature changes. Figure 13 shows the time dependencies of the swelling ratio $W_{\mathrm{gel}}(t)/W_{50}(24)$ for NC and OR gels with different cross-linker contents. Here, NC1 gel underwent outstanding swelling and deswelling behavior depending on the retention temperature and time. This is in contrast to OR1 gel, which did not exhibit any apparent change because it could not follow the alternating temperatures. In NC gels, increasing C_{clay} resulted in gradual decreases in volume change. On the contrary, in OR gels, increasing C_{BIS} caused a gradual increase in volume change. These results were to be expected for the individual swelling and deswelling behaviors of NC and OR gels.

Discussion

All results obtained here are consistent with the proposed model structure of NC gels. In the following discussion, we consider the effect of cross-linker content in some detail on a few of the outstanding characteristics of NC gels.

Mechanical Properties. Concerning mechanical properties, excellent improvements in modulus, strength, and elongation have been simultaneously achieved in NC gels. These characteristics are explained by the model structure. NC gels can be greatly extended or freely bent without severing the constituent polymer chains. This is because the polymer chains connecting neighboring clay sheets are long and flexible enough to be deformed to a large extent on macroscopic deformation. Also, the near-complete recovery on release of stress is consistent with extension and contraction of the flexible polymer chains.

On the other hand, OR gels exhibit very weak and brittle mechanical properties, because polymer chains in OR gels are randomly cross-linked by the large number of organic cross-linking units and result in cross-linked networks with a broad distribution of chain lengths. In OR5 gel, the number of BIS is 12 500 per cubic 100 nm, while in NC5 gel there are 16 exfoliated clay sheets per 100 nm cube. Therefore, in OR gels chains were successively broken due to the localization of stress in the shorter chains present at any instant. Needless to say, both recovery after large deformation and the temperature decrease during tensile tests were not observed in OR gels.

Theory of Rubber Elasticity. From the kinetic theory of rubber elasticity, the equation of state of the swollen network, prepared by polymerization of the mixed solution of solvent, monomer, and cross-linking agent, for tensile strains is[44]

$$F = \Phi N^* kT\{\alpha - (1/\alpha)^2\} \tag{1}$$

where F is the force per unit original (undeformed) cross sectional area of the swollen network (F = force/A_0), N^* and N are the number of network chains per unit volume in the swollen and unswollen networks, respectively. When the ratio of volume of the swollen to the unswollen network is s, $N^* = N/s$. k is Boltzman's constant, T is the absolute temperature, and α is the relative extension ($\alpha = L/L_0$). Φ, which is called a front factor, is related to the specifics of the cross-linking process and chains. When $(r_i)^2$ is the mean square distance between network junctions in the swollen network and $(r_f)^2$ is the mean square end-to-end distance of the network chains considered as existing in free space, then $\Phi = \{(r_i)^2/(r_f)^2\}$.

In the present study, it is predicted that Φ is close to unity in NC gels provided the polymer chains take random conformation in the ample space between junctions i.e., between clay sheets. Then, N^* was calculated from (1) by using F at a given elongation. In Table 1, F (at $\alpha = 2$) and calculated values of N^* for all NC gels are listed.

On the other hand, by analogy with the rubber elasticity, N^* is related approximately to the molecular weight between cross-links M_c by

$$N^* = (\rho^* N_{AV}/M_c)\{1 - (2M_c/M_n)\} \tag{2}$$

Here, ρ^* is the density of the polymer in the swollen gel, N_{AV} is Avogadro's number, M_c is the molecular weight of the chain between cross-links, and M_n is the molecular weight of the primary molecular chains. The term $(2M_c/M_n)$ is a traditional correction for chain ends not effectively tied into conventional cross-linked networks and becomes negligible when the number of chain ends is small relative to cross-linked chains. In NC gels, M_c corresponds to the molecular weight of cross-linking χ chain in Figure 1. Since the number of χ chains is considered much larger than that of g chains (elastically ineffective graft chains), which is supported by the fact that mechanically strong hydrogels with effective cross-linking are formed, the term $(2M_c/M_n)$ will be neglected in the present case. On this basis, M_c was calculated from eqs 1 and 2, and values are listed in Table 1. In addition, by assuming the exfoliation of clay with a single layer thickness, the number of clay sheets per 100 nm cubic n, and the number of cross-linked chains per clay sheet N^*/n are calculated; values of both parameters are also listed in Table 1. Thus, it may be estimated, e.g., for NC5 gel, that 16 sheets of clay are dispersed in a 100 nm cube, and several tens of cross-linked chains are grafted onto each clay sheet. Furthermore, the molecular weight of the cross-linking chains is about 50 000.

Deswelling Kinetics. Concerning the deswelling kinetics, NC and OR gels exhibit entirely opposite tendencies with respect to the effect of cross-linker content. In OR1 gel, which is structurally homogeneous, it is difficult to form channels through which water inside the gel can be expelled. This is because the gel first forms a hydrophobic (water-impermeable) skin on the macroscopic gel surface by eliminating near-surface water to the surrounding water phase. Further, the shrinkage is anomalously depressed by very limited water permeation from the gel interior, although it was molecularly de-hydrated, through the collapsed polymer skin. Whereas, in the inhomogeneous OR gels with higher BIS contents, like OR7 gels, water channels can be formed through the occurrence of local phase separation in the inhomogeneous (polymer-rich) network region. Then, the excess water inside the gel is forced out through these channels by compressive forces of collapsing network. Thus, the phase separation in the bulk proceeds rapidly in structurally inhomogeneous OR gels with high C_{BIS}.

In contrast, NC gels with low C_{clay} exhibit high deswelling rates along with structural homogeneity. As mentioned throughout the preceding discussion, PNIPA chains in NC gels are considered to be restricted to only a small extent by cross-linking and are likely to act as free linear polymer chains. As expected, free linear PNIPA chains without restriction have sufficient mobility to allow dehydration and can exhibit the fastest deswelling behavior. Then, in NC gels with lower C_{clay}, phase separation can occur everywhere and the water channels can be formed throughout the gel. Thus, the shrinking proceeds quickly on a macroscopic scale by squeezing out the water from the gel interior. As C_{clay} increased in NC gels, the mobility of PNIPA chains was gradually restricted by the cross-linking. The deswelling rate, therefore, decreased with increasing C_{clay}, although the structural homogeneity is unchanged because the cross-linking occurred homogeneously.

Glass Transition Temperature. Finally, since the existence of flexible polymer chains is identified by measuring the thermal molecular motions in the solid state, it is of interest to consider the change of glass transition temperature of the constituent PNIPA chains in NC and OR gels with different cross-linker contents. The thermograms obtained by DSC measurements for dried (solid) materials of NC1−5 and OR1−5 gels are shown in Figure 14, and T_g are listed in Table 1. Data for dry linear PNIPA are also shown for comparison.

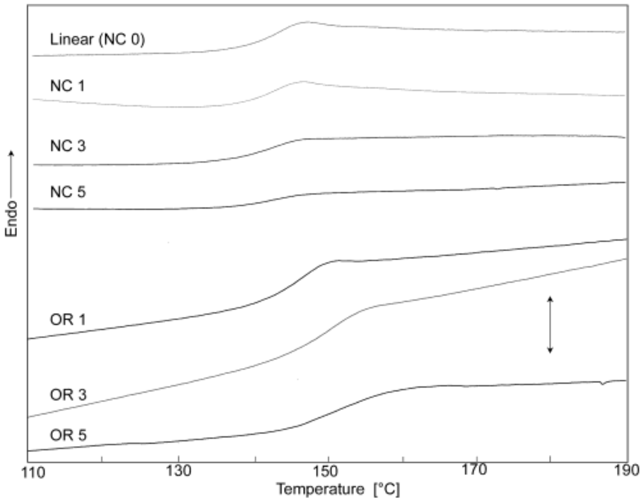

Figure 14. Differential scanning calorimetry thermograms for dried materials of NC and OR gels with different cross-linker contents (NC1−5, OR1−5, and NC0 (linear PNIPA)). The data were obtained in the second run after heating to 250 °C in the first run. The bar indicates 1 W/g.

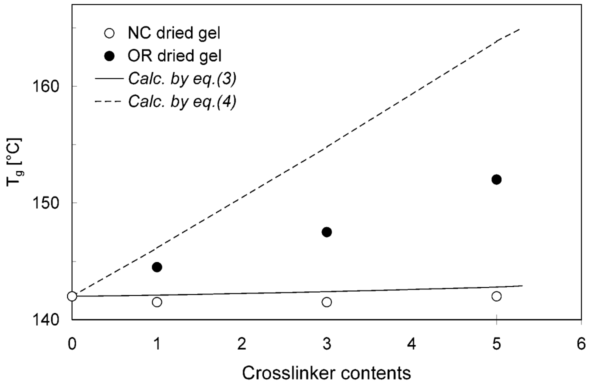

Figure 15. Changes of glass transition temperature of the NC and OR dried gels by altering the cross-linker content. The solid and dotted lines are obtained by calculation using eqs 3 and 4.

The linear PNIPA exhibits T_g of 142 °C. In the case of dried OR gels, it was observed that T_g gradually increased, and that the transition became broader with increasing C_{BIS}. These results indicate that restrictions on PNIPA chains in OR gels increased with increasing C_{BIS}. It is known that cross-linking increases T_g by introducing restrictions on the molecular motions of a chain. A theoretical equation relating the shift in T_g caused by cross-linking has derived by DiMarzio et al.[45] as

$$(T_g - T_{g0})/T_{g0} = KX_c/(1 - X_c) \tag{3}$$

where T_{g0} is the glass transition temperature of the un-cross-linked polymer having the same chemical composition as the cross-linked polymer. X_c is the mole fraction of the monomer units that are coss-linked in the polymer. The temperature is expressed in absolute degrees in this equation. The constant K is predicted to be between 1.0 and 1.2. The increase in T_g for dried OR1−5 gels are calculated using $K = 1.0$ and are shown as a dotted line in Figure 15. Both calculated and experimental results show similar tendencies of increasing T_g, although the gap between calculated and experimental values became large in the high C_{BIS} region. This might be partly ascribed to the copolymer effect of the BIS component.

On the other hand, in dried NC gels, T_g appeared at the same temperature as that for linear polymer, and did not change on varying C_{clay}. For cross-linked polymers in which M_c was known, Nielsen[45] proposed the empirical equation for estimating the shift in T_g as

$$T_g - T_{g0} = 3.9 \times 10^4/M_c \tag{4}$$

For dried NC3 gel, for which M_c was evaluated as 9.7 × 10^4, very little increase in T_g, ca. 0.4 °C, was predicted. Increases in T_g calculated from eq 4 and M_c in Table 1 are shown as a solid line in Figure 15. They are in good agreement with the observed values.

Thus, the existence of flexible polymer chains with a narrow distribution of M_c in the network of NC gels has been fairly substantiated. Since the dawn of network polymer science, the control of cross-linking points (and their distribution) has been an important issue in attempts to improve network properties dramatically. Recently, Okumura et al.[46] developed a polyrotaxane gel with a topological structure of figure-of-eight cross-links and reported that it is expected to be highly extensible because the cross-linking points move to optimum positions during tensile testing. Here, we succeeded in controlling the cross-linking points, so as to have long and relatively uniform M_c, by using a simple and versatile method. Thus, the extraordinary mechanical properties as well as good optical, swelling and deswelling properties were realized simultaneously in the resulting NC gels.

Conclusions

We studied the effects of clay contents on the characteristic properties of PNIPA-NC gels, in comparison with those of BIS contents in conventional PNIPA-OR gels. It was revealed that their properties, such as mechanical properties, transparencies, swelling, and deswelling behaviors, are all changed to a large extent by cross-linker contents in both NC and OR gels. As for mechanical properties of NC gels, which generally exhibit extraordinary mechanical toughness, the tensile modulus and tensile strength increased almost in proportion to C_{clay}, whereas the elongation at break tends to decrease slightly on increasing C_{clay}. On the other hand, in OR gels, which generally exhibit weak properties and brittle fracture, no significant change in mechanical properties with C_{clay} was observed in OR1−5 gels. As for transparency changes related to the phase transition of PNIPA at LCST, for OR gels the change in transparency gradually diminishes with increasing C_{BIS}, because the transmittance at the temperature below LCST decreased steeply on increasing C_{BIS}. Thus, OR gels having high C_{BIS}, over 5 mol %, were constantly opaque and no transparency change was observed. On the contrary, NC gels always exhibited changes in transparency regardless of C_{clay}. Also, NC gels have a tendency to increase their transmittance at temperatures above LCST in the high C_{clay} region. This may be due to the presence of hydrophilic clay surfaces, at which the conformational change of grafted PNIPA chain to that characteristic of its hydrophobic state is partly hindered. As for swelling/deswelling behaviors, volume changes at LCST are similarly inclined to decrease with increasing cross-linker contents in both gels, although swelling ratios below LCST were in general larger in NC gels than those in OR gels. As for deswelling kinetics, the deswelling rate was affected markedly by cross-linker contents in both gels though in opposite directions. In OR gels, deswelling rates increased on increasing C_{BIS} and OR gels with high C_{BIS} showed rapid shrinkage. In contrast, NC gels showed faster deswelling as C_{clay} was lowered. In other words, the more C_{clay} increased, the slower the deswelling rate became. The increases in deswelling rate produced by increasing C_{BIS} in OR gels were attributed to increases in structural inhomogeneity introduced by large numbers of heterogeneous cross-links. Whereas, increases in deswelling rate in NC gels with decreases in C_{clay} are attributed to decreased restriction at lower cross-linking. All these results are self-consistent and explicable on the basis of the proposed model structures for NC and OR gels. By applying the theory of rubber elasticity, N^* and M_c were evaluated for NC gels.

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