Mechanism of Forming Organic/Inorganic Network Structures during In-situ Free-Radical Polymerization in PNIPA−Clay Nanocomposite Hydrogels

Kazutoshi Haraguchi,* Huan-Jun Li, Kaori Matsuda, Toru Takehisa, and Eric Elliott

Material Chemistry Laboratory, Kawamura Institute of Chemical Research,
631 Sakado, Sakura, Chiba 285-0078, Japan

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ABSTRACT: The process of forming the unique organic/inorganic network structure of nanocomposite hydrogels (NC gels) was studied through changes in viscosity, optical transparency, X-ray diffraction, and mechanical properties. It was concluded that, during the preparation of the initial reaction solutions, a specific solution structure was formed from monomer (NIPA) and clay, where NIPA prevents gel formation of clay itself, and initiator (KPS) is located near the clay surface through ionic interactions. In subsequent in-situ free-radical polymerization, it was observed that the viscosity increased markedly during NC gel syntheses and in a manner similar to that in OR gel syntheses. Also, NC gels with different polymer contents exhibit characteristic two-step changes in the stress−strain curves, which correspond to the primary network formation and subsequent increase of cross-link density. These are because the polymerization proceeds on the clay particles which are relatively immobile, and clay platelets act as effective multifunctional cross-linking agents (plane cross-link). Then, it was proposed that clay−brush particles, consisting of exfoliated clay platelets with numbers of polymer chains grafted to their surfaces, were formed in the very early stage of polymerization, at around 7% of monomer conversion. Novel decreases in transparency were observed corresponding to the formation of clay−brush particles, but transparency recovered on further polymerization. Clay−brush particle formation was confirmed by XRD measurements on dried NC gels prepared using small amounts of monomer. Thus, a mechanism for forming the unique organic/inorganic network structure, including the formation of clay−brush particles in the synthetic pathway, is proposed. Furthermore, it was found that NC gels with excellent mechanical properties and structural homogeneity could not be prepared using other methods such as mixing clay and polymer solutions or by in-situ polymerization in the presence of the other inorganic nanoparticles instead of clay. These results indicate that the formation of organic/inorganic network structures in NC gels is highly specific and only realized by in-situ free-radical polymerization in the presence of clay.

Introduction

Polymer hydrogels are soft materials retaining substantial amounts of water (e.g., 90 wt %) within three-dimensional polymeric networks. Because of the environmental sensitivity of the gel volume (swelling/contraction)[1−4] and surface property (hydrophilic/hydrophobic)[5] resulting from their phase transition at their lower critical solution temperature (32 °C), poly(*N*-isopropylacrylamide) (PNIPA) hydrogels were considered to be the most promising materials as advanced hydrogels. Although PNIPA hydrogels were studied extensively, from both academic[1−9] and technological[10−17] viewpoints over the past two decades, all PNIPA hydrogels used were chemically cross-linked. Conventional PNIPA hydrogels, prepared using organic cross-linkers (hereinafter, abbreviated to OR gels), had some serious disadvantages arising from the random arrangement of large numbers of cross-links. The main disadvantage was their lack of mechanical toughness; i.e., the gels were very weak and brittle. Thus, in general, OR gels were too weak to withstand the high levels of stress and strain needed for various applications. Also, swelling/deswelling properties, such as the degree of swelling at equilibrium and the swelling/deswelling rates, were insufficient for applications such as drug delivery systems and soft actuators. Furthermore, the transparency (structural homogeneity) of OR gels was often lost by changing their composition and the polymerization conditions.

Recently, we developed a new type of hydrogel (nanocomposite hydrogel: designated NC gels), consisting of PNIPA and inorganic clay.[18,19] The novel NC gels were prepared by in-situ free-radical polymerization of *N*-isopropylacrylamide (NIPA) in the presence of exfoliated clay, without using any organic cross-linker. It was found that NC gels simultaneously solved all of the problems associated with OR gels. That is, NC gels exhibit extraordinary mechanical properties with high strengths and elongations at break in excess of 1000%. NC gels exhibit high transparency, even at high clay contents, and also high degrees of swelling, as well as high deswelling and swelling rates. These remarkable improvements in mechanical, optical, and swelling/deswelling properties of NC gels were ascribed to their characteristic network structure, since NC and OR gels had the same composition except for the nature of the cross-linking agent. On the basis of the results of mechanical and swelling/deswelling properties of NC gels, we proposed the existence of a unique organic/inorganic network structure,[20] which consists of exfoliated clay uniformly dispersed in an aqueous medium with a number of flexible polymer chains linking them together. The network structure was confirmed by transmission electron microscopy (TEM), thermogravimetry (TG), X-ray diffraction (XRD), and differential

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* To whom correspondence should be addressed: e-mail hara@kicr.or.jp; Tel +81-43-498-0062; Fax +81-43-498-2202.

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scanning calorimetry (DSC) measurements for dried NC gels[18−20] and dynamic light scattering (DLS) and small-angle neutron scattering (SANS) measurements on NC gels.[21] As also shown in the present paper, the outstanding characteristics of NC gels only emerge as a result of in-situ free-radical polymerization of NIPA and were not realized by the other procedures for preparation, such as mixing clay and PNIPA solutions. Therefore, it is important to investigate the process of forming the organic/inorganic network structure during the course of NC gel synthesis. In the present paper, we reveal that NC gels are only obtained by using exfoliated clay as inorganic nanoparticles. Also, we describe the changes in viscosity, optical transmittance, mechanical properties, and X-ray diffraction patterns during the preparation of initial reaction solution and during the course of in-situ free-radical polymerization and discuss the mechanism of formation of the unique organic/inorganic network structures of NC gels.

Experimental Section

Raw Materials and Synthesis of Hydrogel. *N*-Isopropylacrylamide (NIPA) monomer (Kohjin Co., Japan) was purified by recrystallization from a toluene/*n*-hexane mixture, followed by drying under vacuum. *N*,*N*-Dimethylacrylamide (DMAA) monomer (Kohjin Co., Japan) was purified by filtering through activated alumina. As an inorganic clay, synthetic hectorite “Laponite XLG” (Rockwood Ltd.: $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$), was used after washing and freeze-drying. Potassium persulfate (KPS) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were used as initiator and catalyst, respectively. The water used for all experiments was ultrapure water supplied by a Puric-Mx system (Organo Co., Japan). Oxygen in the pure water was removed by bubbling N_2 gas for more than 3 h prior to use, and throughout all experiments, oxygen was excluded from the system. Other reagents were used without further purification. The synthetic procedure is almost the same as that reported previously.[20] For example, to prepare N-NC2-M1 gel, a transparent aqueous solution consisting of water (28.5 mL), inorganic clay (0.457 g), and NIPA (3.39 g), was prepared. Next, the catalyst (TEMED, 24 μL) and, finally, an aqueous solution of initiator [KPS (0.03 g) in H_2O (1.5 mL)] were added to the former solution at ice-water temperature while stirring. Then, free-radical polymerization was allowed to proceed in a water bath at 20 °C for 20 h. The sample code defines the kind of monomer (N- and D- for NIPA and DMAA, respectively) and the concentrations of clay and monomer relative to water; e.g., N-NC*n*-M*m* indicates an NC gel prepared using $n \times 10^{-2}$ moles of clay (for $n = 2$; 15.24 g) and *m* moles of NIPA (for $m = 1$; 113.2 g) in 1 L of water. The monomer concentration, *m*, was varied in the wide range, $1/32 \leq m \leq 1$ for N-NC gels and $1/32 \leq m \leq 5$ for D-NC gels, while the clay concentration, *n,* was varied between 2 and 5. OR gel (N-OR1-M1 gel) was prepared using 1 mol % (0.042 g) of *N*,*N*′-methylenbis(acrylamide) (BIS), instead of clay, relative to NIPA. Linear polymer PNIPA (LR-Mm) was prepared similarly, but using no cross-linking agent.

For the preparation of hydrogels by simple mixing of components, the same amount (20 g) of aqueous clay and linear polymer (PNIPA) solutions with concentrations of $C_{clay} = 10 \times 10^{-2}$ mol/L and $C_{NIPA} = 2$ mol/L, respectively, were mixed to prepare hydrogels with the same composition as N-NC5-M1 gel. For the preparation of hydrogels by mixing, and subsequently concentrating, more dilute aqueous solutions (30 g each) of $C_{clay} = 0.5 \times 10^{-2}$ mol/L and $C_{NIPA} = 0.1$ mol/L were used. The mixed solutions were centrifuged at 16 000 rpm for 30 min.

For the polymerization of NIPA in the presence of the other inorganic nanoparticles, the same aqueous NIPA solutions, except that the clay was replaced by the same amounts of silica (colloidal silica: Snowtex-20; 10−20 nm in diameter, Nissan Chem. Ind., Japan) and titania (colloidal titania, Nano-Tech-TiO_2, 43 nm in diameter, C.I. Kasei, Japan) were prepared and then polymerized in a manner similar to the NC gel.

Viscosity Measurements during the Preparation of Reaction Mixtures and the Polymerization Process. A series of viscosity measurements were performed during two stages of NC gel preparation. One was the change in viscosity during the preparation of initial reaction solutions, and the other was the change in viscosity during the subsequent polymerization. Viscosities were measured using a vibration digital viscometer, VM-100A (Yamaichi Electronics, Japan). The temperature of the surrounding water bath was controlled by circulating water at 20 ± 0.1 °C during all measurements. The sensor (Rotor L) was fixed at the center of reaction solution (50 mL) contained in a glass vessel (35 mm in diameter and 60 mm length). To avoid oxygen contamination, the top of the solution was sealed with paraffin, in addition to the usual cap, and the system was purged with nitrogen.

Optical Transmittance Measurements during Polymerization. Changes in optical transmittance during polymerization were measured using a UV/vis spectrophotometer with temperature control unit (V-530 and EHC477T, JASCO Co., Japan). The reaction solution was contained in a quartz cell (10 × 10 × 30 mm length) with cap and held in sample holder which was regulated electrically at 20 ± 0.1 °C. The sample was maintained in a nitrogen atmosphere. Transmittances at 600 nm were recorded continuously during the polymerization. The reaction solutions for NC gels, OR gels, LR, and others (containing silica particles) were measured and compared. In one case, for an NC gel, the reaction solution was transferred into liquid nitrogen at minimum optical transmittance, and the reaction was quenched. The monomer conversion was measured by subsequent dissolution in water containing a polymerization inhibitor, centrifugation, and drying.

Mechanical Properties of NC Gels. Tensile mechanical properties were measured using a Shimadzu Autograph AGS-H for various N- and D-NC gels with different *m* and for silica and titania contained LR. The test conditions were as follows: temperature, 25 °C; a sample size, 5.5 mm in diameter; 70 mm in length; gauge length, 35 mm; crosshead speed, 100 mm/min. The tensile strength and modulus were calculated on the basis of the initial cross section.

X-ray Diffraction and FTIR Measurements of Dried NC Gels. X-ray diffraction (XRD) and Fourier transfer infrared (FTIR) spectroscopy measurements were carried out using dried NC gels of various compositions or clay itself; samples were dried under atmospheric conditions (25 °C) for 3 days and then at 80 °C under vacuum for 24 h. XRD profiles of milled dried samples and clay were measured using an X-ray diffractometer (RX-7, Rigaku-Denki, Japan) with Cu Kα radiation, $2\theta > 1.5°$. FTIR spectra were obtained using an FTIR spectrometer (FT/IR-550 JASCO, Japan) with KBr pellets containing dried NC gels or linear polymer.

Results and Discussion

1. Viscosity Changes during the Preparation of Initial Reaction Solutions.

The inorganic clay (Synthetic Hectorite: XLG) with a lamellar crystal structure was swollen when dispersed in water and gradually cleaved into discrete disklike particles (Figure 1a,b). Monolayer XLG clay particles are anisotropic platelets 30 nm in diameter and 1 nm thick.[20,22,23] The resulting aqueous clay suspension, composed of exfoliated clay particles, was homogeneous and transparent. As shown in Figure 2, the viscosity of aqueous clay suspensions naturally depend on the clay concentration, but also the viscosity shows remarkable time dependence. Above a critical clay concentration (C_{crit}), the suspension viscosity gradually increased with retention time and finally became a gel. This is because the clay platelets, of which the surfaces and edges are negatively and positively charged, respectively, tend to form a so-called house-

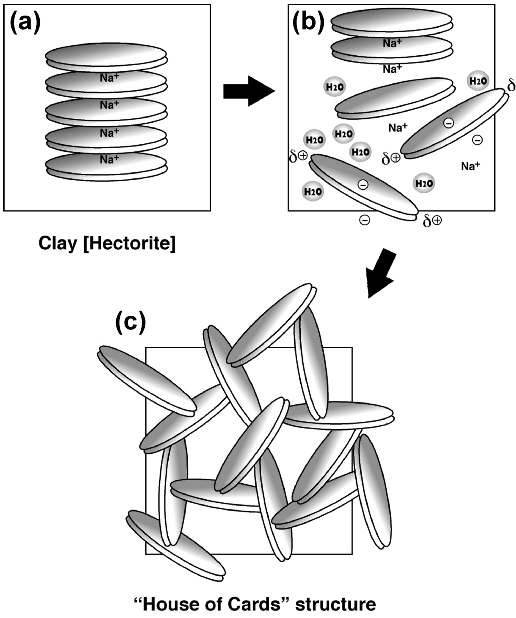

Figure 1. Schematic representation of the preparation of clay aqueous suspension and the formation of the house-of-cards structure: (a) clay, (b) dispersion (exfoliation) of clay platelets in water, and (c) house-of-cards structure.

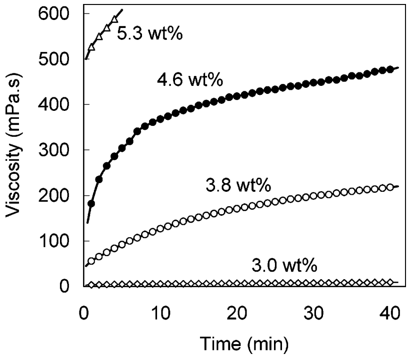

Figure 2. Variations in viscosity with retention time for aqueous clay suspensions of different concentrations (3.0−5.3 wt %).

of-cards structure (Figure 1c) through ionic interactions.[24,25] In the present study, C_{crit} for Laponite XLG was observed to be about 1 wt %, on standing for 4 weeks at 25 °C after sample preparation.

Figure 3a shows the effects of adding salts on the viscosity of an aqueous clay suspension ($C_{\mathrm{clay}} = 3.0$ wt %). The viscosity increased with increasing ionic strength of salt, and the transition from sol to gel was accelerated. It was observed that the increase in viscosity was almost proportional to the cation valency (KCl < $CaCl_2$ < $AlCl_3$) as well as to the salt concentration. When the same amount of KPS (3.7 mmol/L) as used in the reaction solution for NC gel synthesis was added, the viscosity of the clay suspension increased rapidly. The increase in viscosity caused by adding KPS, which has a divalent anion, was consistent with that caused by adding the same amount of divalent salt ($CaCl_2$) or double the amount of monovalent salt (e.g., KCl: 7.4 mmol/L). On the other hand, with further increase in salt concentration, the solutions became turbid and flocculation was observed. In XRD measurements, after centrifugation and drying of the floc, an X-ray diffraction peak was observed at $d = 1.9$ nm, which is ascribed to clay/KPS intercalation. Thus, it was concluded that KPS strongly interacts with clay platelets through ionic interactions and that KPS molecules are closely associated with the clay surface in aqueous suspensions.

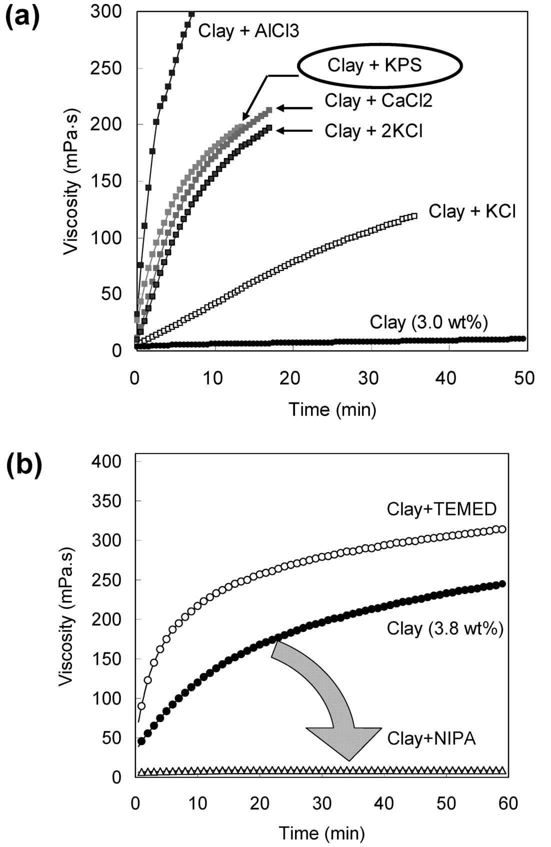

Figure 3. (a) Effects of addition of various salts on the viscosity of clay aqueous suspension with $C_{\mathrm{clay}} = 3.0$ wt %. The concentration of salt was 3.7 mmol/L, unless otherwise noted. (b) Effects of adding NIPA and TEMED on the viscosity of an aqueous clay suspension with $C_{\mathrm{clay}} = 3.8$ wt %. The same concentrations of NIPA and TEMED with those in a typical reaction solution are used: $C_{\mathrm{NIPA}} = 1$ mol/L, $C_{\mathrm{TEMED}} = 800\ \mu$L/L.

In contrast, the effect of NIPA monomer on the suspension viscosity is very different and the reverse of that for addition of KPS. As shown in Figure 3b, the increase in viscosity of an aqueous clay suspension with retention time was markedly depressed by the addition of NIPA. For a solution containing $C_{\mathrm{clay}} = 3.8$ wt % and NIPA of 1 mol/L, which were the same concentrations as used in the synthesis of an N-NC5-M1 gel, it was observed that the solution was very stable, and the sol−gel transition did not occur for more than 1 month, while the same clay suspension without NIPA became a gel within a few hours. This indicates that nonionic NIPA monomers effectively surround each clay platelet with a mild interaction between ionic clay and dipolar NIPA molecules and that the surrounding NIPA molecules prevent the clay platelets from forming the house-of-cards structure, because of the decrease in the electric double layer of the clay. Furthermore, in dried NC gels, it was observed by TEM that XLG was mainly exfoliated as monolayer platelets,[19,20] although the average thickness of discrete clay particles in the XLG/pure water suspension was reported to be 2−4 nm (i.e., consisting of 2−4 sheets).[23,26] These results indicate that the addition of NIPA to the clay suspension may also enhance the molecular dispersion of clay platelets in the solution. Concerning the other constituent of reaction solutions, the increase in viscosity was accelerated

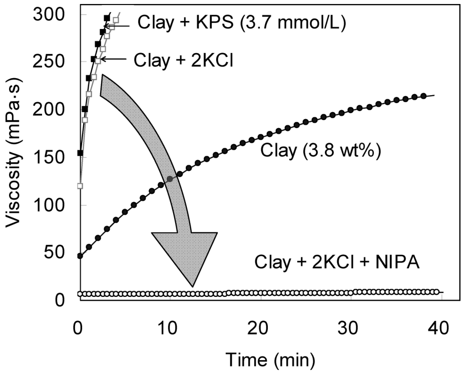

Figure 4. Changes in viscosity of aqueous solutions containing clay, KPS (KCl), and NIPA.

slightly by adding catalyst (TEMED) (Figure 3b). This result indicates that interactions between TEMED and clay are weaker than with KPS but stronger than with NIPA and that TEMED is located near the clay surface due to interactions between the anionic clay surface and the first amine.

Thus, it was revealed that addition of NIPA and KPS produce opposing effects on the changes in viscosity of aqueous clay suspensions. When both NIPA and KPS or all three components (NIPA, KPS, and TEMED) were added to the aqueous clay suspension, it was found that the viscosity of resulting solution was very stable or increased slightly with retention time, as shown in Figure 4. Here, KPS (3.7 mmol/L) was replaced by KCl (7.4 mmol/L) in order to prevent polymerization. These results suggest that the effect of NIPA in depressing the viscosity change predominates over the accelerating effects of KPS (KCl) and TEMED.

From the results described above, we propose a model structure for the initial reaction solution for the synthesis of NC gels is as depicted in Figure 5a,b. The solutions were prepared in an ice bath, at about 1 °C, and then, by increasing the solution temperature to 20 °C, free-radical polymerization in the redox system was initiated on the surface of clay (Figure 5c). The conclusion that initiation only occurs on the clay surface was supported by the fact that no free polymer was extracted from resulting NC gels during swelling processes; that is, all polymer chains were attached to clay platelets through ionic or polar interactions. From this conclusion, we estimate the formation of "clay−brush particles", as depicted in Figure 5d in early stages of NC gel syntheses, which are composed of exfoliated clay platelets and numbers of grafted chains.

2. Viscosity Changes during the Course of Polymerization. The changes in solution viscosity during polymerizations to form NC gels, OR gels, and linear polymer were measured utilizing a vibration digital viscometer, in which very small (several micrometers) vibrations were used as stimuli. Therefore, viscosity changes can be monitored while maintaining static conditions, without disturbing the polymerization mixture. Figure 6 shows the changes in solution viscosity during the syntheses of an NC gel (N-NC4-M1), an OR gel (N-OR3-M1), and linear polymer (LR-M1, LR-M0.5, LR-M0.3). In the case of linear polymer, the viscosity gradually increased until it reached a plateau after about 40 min and then remained constant. The final viscosity of LR solutions depended on the polymer concentration, as shown in Figure 6. LR-M1 was a highly viscous gel-like material, although LR-M0.5 and LR-M0.3 were solutions. The significant increases in viscosity during LR-M1 syntheses were attributed to the formation of entanglements between linear polymer chains.

In the case of OR gel, although the onset of viscosity increase occurred after almost the same time as with LR, the increase in viscosity was much steeper than that for linear polymer due to the effects of chemical cross-linking and subsequent gel formation. On the other hand, in the case of NC gel formation, it is interesting that the changes in viscosity were almost identical to those for OR gel synthesis, although no organic cross-linker was added in the reaction solution. Here, it should be noted that the presence of inorganic particles did not always result in such large increases in viscosity. For example, in the in-situ polymerization using silica and titania nanoparticles, both which have a few tens of nanometers in diameter, the abrupt viscosity change was not observed. Instead, the viscosities gradually increased in a manner similar to that for linear polymer. This indicates that the simple uniform dispersion of inorganic nanoparticles of the same content with NC gel did not give rise to a steep increase in viscosity. Therefore, the steep increase in viscosity observed for NC gel synthesis should be ascribed to the formation of a specific superstructure consisting of clay and polymer chains. This may correspond to the formation of clay−brush particles which was expected from the former section. During the early stages of polymerization, clay−brush particles effectively increase the viscosity of the mixture because of their lack of mobility. Then, those clay−brush particles subsequently lead to the unique organic/inorganic network structure consisting of PNIPA and clay.

It is noteworthy that NC gels can ultimately form network structures using very small numbers of clay platelets, 15 per 100 nm cube for NC4 gel, compared with a large number of BIS molecules, 5400 in the same volume, for an OR1 gel. This result indicates that clay particles act as effective multifunctional cross-linking agents and create networks by forming cross-links between the faces of clay platelets (plane cross-link). Also, these facts indicate that the presence of exfoliated clay particles in the reaction solution (Figure 5b) and the formation of clay−brush particles (Figure 5d) are essential to the formation of the unique organic/inorganic networks (Figure 5e) of NC gels. In the case of the other inorganic nanoparticles such as silica and titania, particles were just dispersed in the polymer/water matrix and did not form effective networks. The mechanical properties of such silica- or titania-containing PNIPA gel-like materials were very low and similar to that of PNIPA (LR) itself, as shown in a later section.

3. Optical Transparency Changes during NC Gel Synthesis. As mentioned above and reported in the previous papers,[18−20] the initial reaction solutions for NC gel syntheses were always uniform and highly transparent, and the resulting NC gels were uniform and exhibited high transparency. However, in the present study, it was found that the optical transparency of the reaction solution changed markedly during polymerization in NC gel syntheses. Here, we describe the characteristics of the optical transparency changes and discuss the results in relation to the formation of clay−brush particles. Figure 7 shows the time dependence of transmittance during the in-situ polymerization at 20 °C for an NC gel (N-NC2-M1 gel). A unique and

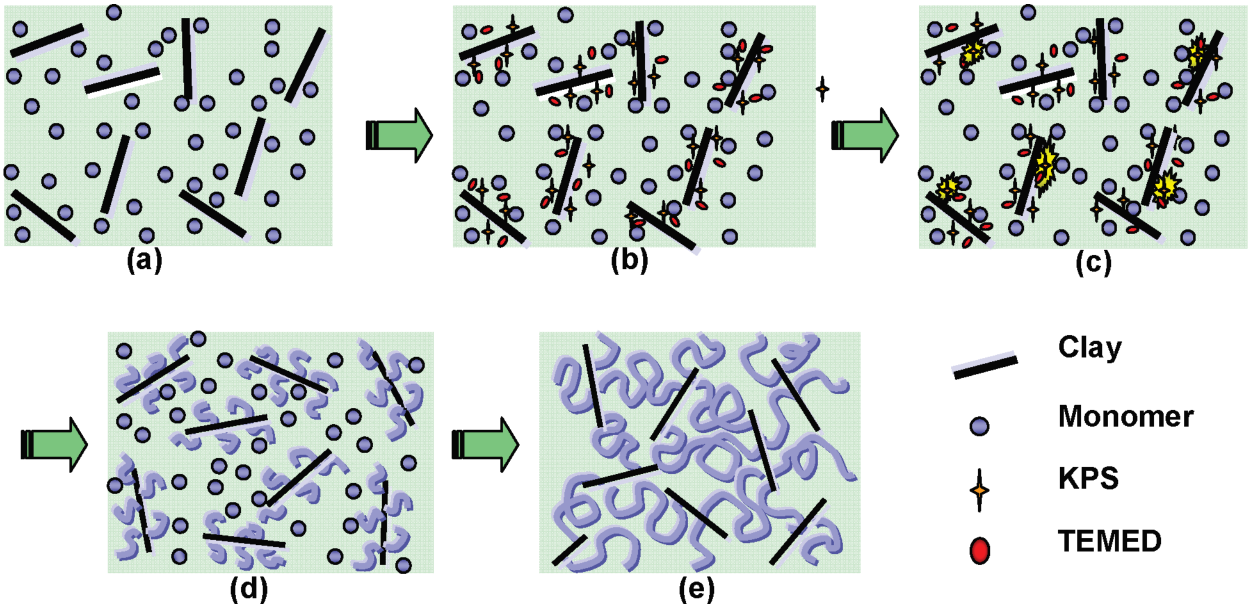

Figure 5. Schematic representations of the model structures for the reaction solution and the mechanism of forming organic/inorganic network structure in an NC gel. (a) Aqueous solution consisting of clay and NIPA. Here, the formation of house-of-cards structure does not form. (b) Reaction solution consisting of clay, NIPA, KPS, and TEMED. (c) Radical formation near the clay surface in the reaction solution. (d) Formation of clay−brush particles. (e) Formation of organic/inorganic networks. In the models, only a small number of monomer (polymer), KPS, and TEMED are depicted for simplicity.

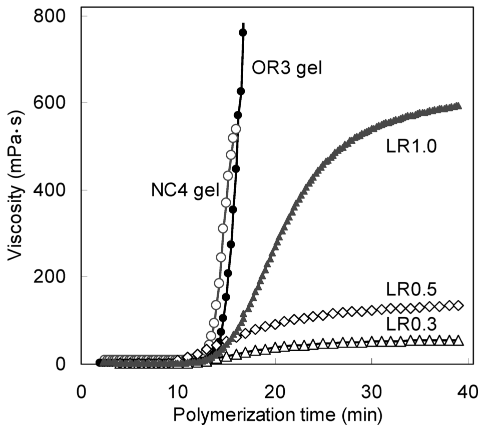

Figure 6. Viscosity changes during the polymerization of NC gel (N-NC4-M1 gel), OR gel (N-OR3-M1 gel), and linear polymers (LR: N-LR-M0.3, -M0.5, -M1).

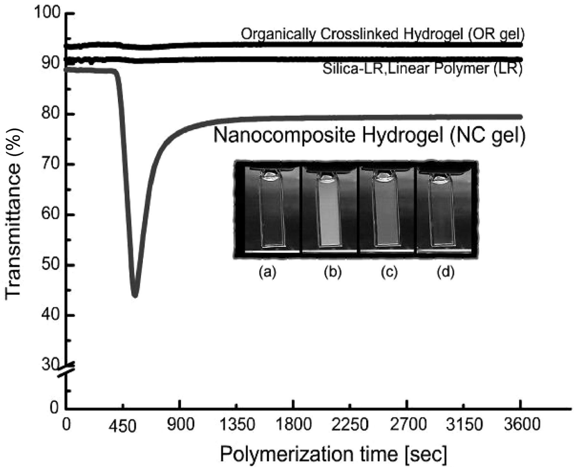

Figure 7. Changes of optical transparency during the polymerization of NC gel (N-NC2-M1 gel), OR gel (N-OR1-M1 gel), linear polymer (LR:N-LR-M1), and silica-containing LR. Silica-contained LR shows no transparency change similarly to LR. Photos a−d were obtained during the polymerization of NC gel.

distinct change in transparency was observed during the early stages of polymerization. The transmittance of the reaction solution, which was high (T = 90%) at the beginning, abruptly decreased about 7−10 min after starting the polymerization. During the decrease in transparency, it was observed that turbidity (whiteness) appeared uniformly throughout the sample as shown in photos a and b in Figure 7, and no heterogeneous macroscopic phase separation or precipitation was observed. After reaching a minimum (T = 44%), the transmittance rapidly reverted to high transparency (T = 80%), and the turbidity disappeared smoothly over a short time, as seen in photos b−d. Contrary to this, no transparency change was observed during the course of polymerizations of either OR gels or linear polymer (LR) with the same water and polymer concentrations (Figure 7). In the case of OR gels, although three-dimensional networks were formed, no decrease in transparency was detected throughout the polymerization. Therefore, it was concluded that the newly observed transparency change in Figure 7 was characteristic of NC gel synthesis, that is, relating to the formation of clay−brush particles and the subsequent organic/inorganic network. A number of brush particles, or their aggregates, formed during the early stages of polymerization, may cause the reflection of visible light because the formation of a number of grafted chains on the clay surfaces would cause a change in density locally and that an aggregate of such particles over several tens of nanometers across would scatter light. As polymerization progresses, the transparency was reestablished since the grafted polymer chain become longer and the density difference between clay−brush particles and matrix tends to disappear. Thus, high transparency is recovered on further polymerization. It was found that the unique transparency change was generally observed during NC gel syntheses, regardless of the identity of the monomer, e.g., not only NIPA but also the other monomers such as DMAA, *N*,*N*-diethylacrylamide

(DEAA), *N*-acryloylmorphorine (ACMO), some polymers of which (DMAA, ACMO) do not exhibit coil−globular transitions, showed the same effect. However, although all NC gels exhibited transparency changes, the precise pattern of these changes depended greatly on the monomer, solution composition, polymerization temperature, etc. The detailed data and overall analyses of these transparency changes will be reported in a subsequent paper.

Furthermore, Figure 7 shows the lack of any change in transparency during the polymerization of NIPA reaction solution containing silica particles instead of clay. The results were the same as those for linear polymer and OR gels. No transparency change was observed in the presence of silica nanoparticles. This is consistent with the fact that the brush particles are only formed during NC gel formation using clay. Silica nanoparticles did not result in the characteristic NC gel. These results are also consistent with the results of viscosity measurements (section 2) and mechanical properties for PNIPA solutions containing silica (section 6).

To evaluate the approximate monomer conversions at the point of minimum transparency in Figure 7, the sample was transferred into liquid nitrogen, and polymerization was quenched by freezing. The solid component was separated by subsequent dissolution into water containing a polymerization inhibitor, centrifugation, and drying. It was found that the monomer conversion at minimum transparency for this system (N-NC2-M1 gel) was 7.0%. This result shows that the transparency change occurred during the early stages of polymerization, and the clay−brush particles at this point consisted of polymer and clay with a polymer/clay weight ratio of 0.0791/0.381 (= 0.2/1).

4. Effects of Polymer Content in NC Gels on the Stress−Strain Curves. For NC gel syntheses, we normally used a fixed monomer concentration (*m*) of 1 mol/L in the initial reaction solution. Since the monomer conversion was almost quantitative, the polymer content in the resulting NC gel was directly proportional to *m*. In previous papers,[19,20] we reported that both modulus and strength in the stress−strain curves increased with increasing *m*, while the elongation at break remained large, e.g., about 1500% for D-NC gels regardless of *m* from 1 to more than 5. This indicates that the number of cross-linking chains in the network structure increased with increasing polymer content.

Here, we studied effects of lower monomer concentrations in the reaction solution on the stress−strain curves of NC gels and discussed them in relation to the network formation process. Figure 8a shows the stress−strain curves for D-NC2.5 gels prepared using a wide range of values of *m*, including those less than 1 (mol/L). When *m* was less than 1/16, it was difficult to measure the stress−strain curves for NC gels because samples were too weak and brittle. With increasing *m* from 1/16 to 1/2, the elongation at break increased from 50% (*m* = 1/16) to 1500% (*m* = 1/2), while the strength and the modulus remained low. Next, with increasing *m* from 1/2 to 5, the strength and the modulus increased almost proportionally to *m*, while the elongation at break remained at about 1500%.

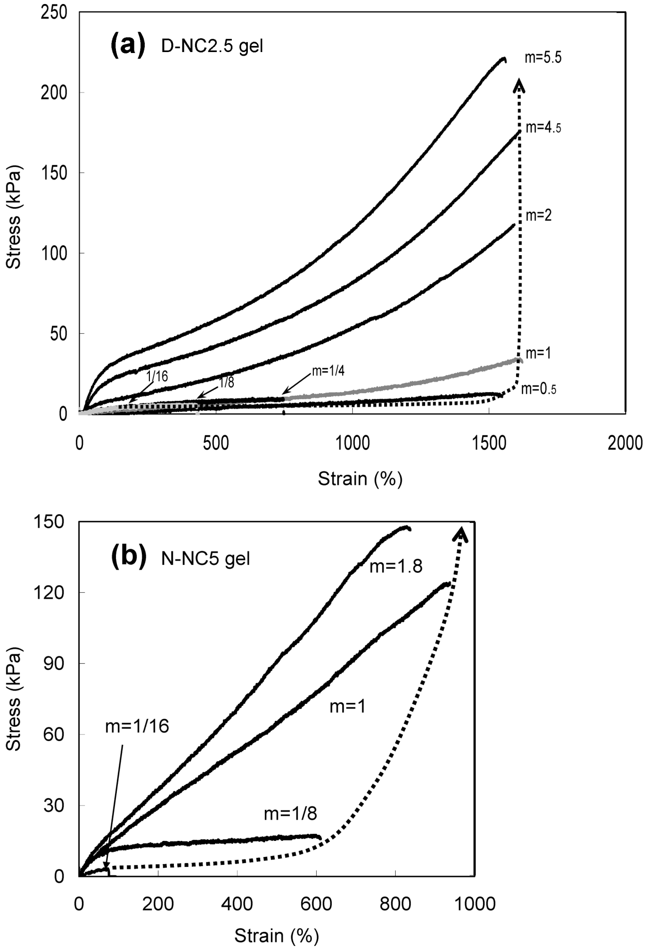

Figure 8. Effects of polymer content (*m*) on the stress−strain curves of NC gel: (a) D-NC2.5 gels with various polymer contents (*m* = 1/16−5.5); (b) N-NC5 gels with various polymer contents (*m* = 1/16−1.8).

Thus, as shown by the dotted line in Figure 8a, the elongation at break increased at first with increasing *m*, and then in the next stage, the strength and the modulus increased with further increasing *m*. These characteristic changes in stress−strain curves on changing *m* were also observed for N-NC gels (N-NC5 gel) (Figure 8b), although the dependence on *m* changed slightly in detail. Here, in the case of N-NC gels, *m* cannot exceed 2 because of the limited solubility of monomer in water. In Figure 8a,b, it was considered that the first stage, where the elongation at break increased, corresponds to the process of primary network structure formation, and the second stage, where the modulus and strength increased, corresponds to the increase in number of cross-linking chains, i.e., increase of network density.

These results strongly suggest the following mechanism for formation of the organic/inorganic network. That is, the basic architecture of NC gel network was first formed with increasing *m* for small *m* (e.g., *m* ∼ 1/2 for D-NC2.5 gels, *m* ∼ 1/8 ∼ for N-NC5 gels), and then, in the subsequent step, the number of cross-linking chains (the cross-link density) increased with further increase in *m*. Also, in the very early stage of network formation, i.e., NC gels with very low *m* (*m* ∼ 1/16), only clay−brush particles were formed, and three-dimensional networks throughout the sample did not form. Therefore, the NC gels produced with very low *m* were very weak and brittle. The results that NC gels with low *m* mainly consist of clay−brush particles were consistent with the facts that the transparencies of those NC gels were low. For example, transmittances were about 40% for D-NC2.5 gels with *m* = 1/8 because they

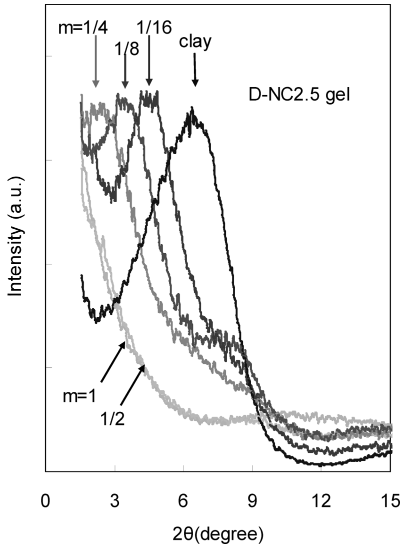

Figure 9. X-ray diffraction profiles for D-NC2.5 gels with different polymer contents.

include assemblies (or aggregates) of grafted particles. Also, this conclusion of the formation of clay−brush particles was confirmed by the XRD measurements on dried NC gels with low *m*, as shown in the next section.

5. XRD Measurements for Dried NC Gels with Low Polymer Contents. We previously reported that in the NC gels the clay is extensively exfoliated, and the clay platelets are dispersed uniformly throughout the sample.[18−20] That conclusion was based on the high transparencies of NC gels, direct TEM observations on a thin layer of dried NC gels, and X-ray diffraction (XRD) measurements for dried NC gel powders. In XRD profiles, no distinct diffraction peak was observed in 2θ range from 1.5° to 7° for dried D-NC gels, which means that there is no regular stacking of clay or of clay/polymer intercalation in the dried NC gel and so, by analogy, in the NC gel. Here, we studied NC gels prepared using small amounts of monomer. Because of the deficiency of monomer, network formation during the course of polymerization could be prevented at various early stages, depending on the amount of monomer used. From the mechanical properties and optical transparencies, it was estimated that those NC gels contained clay−brush particles. XRD profiles were measured for the dried NC gels with low *m*.

Figure 9 shows XRD profiles for dried D-NC2.5-M*m* gels with $m = 1$ to 1/16. The XRD profile for clay itself is also shown in Figure 9 as a control. No diffraction peak was observed for the dried D-NC2.5-M1/2 gel, in the 2θ range between 1.5° and 7°, similar to the D-NC2.5-M1 gel (standard), but only a monotonic change in diffraction intensity due to the atomic diffraction factor. In contrast, all other dried NC gels, with lower *m*, exhibited a clear diffraction peak in the same 2θ range. The position of the diffraction peak maximum gradually shifted from $2\theta = 2.38°$ to 4.54° with decreasing *m* from 1/4 to 1/16. This means that NC gels with low *m* contain regular clay−polymer−clay stacks in the dry state. The average spacing between clay sheets in dried D-NC2.5-M*m* gels increased from $d = 1.95$ nm ($m = 1/16$) to 3.71 nm ($m = 1/4$) with increasing polymer content (*m*) compared with $d = 1.37$ nm for pure clay−clay stacks (without polymer). Therefore, it was concluded that intercalated stacking composed of polymer and clay formed in the dried NC gels with $m \leq 1/4$, which may correspond to the clay−brush particles formed in the early stages of polymerization in NC gel synthesis. Also, the clear diffraction peaks due to the presence of clay−polymer−clay stacks and the similar shifts of peaks by altering *m* were observed for N-NC5 gels with low *m* ($m = 1/4$, 1/8, and 1/16), similarly to those of D-NC gels. Thus, clay−brush particles, which formed and disappeared during the NC gel synthesis, were generally observed in NC gels with low *m*. This is because network formation was stopped in early stages owing to the deficiency of monomer. From the weight ratio of polymer/clay (= 0.2) measured at the minimum transparency point, the clay−brush particle at that point corresponds to an NC gel with $m = 1/14$.

6. Attempts To Prepare NC Gels by Other Methods. NC gels are readily prepared by in-situ free-radical polymerization in aqueous media. Here, we checked whether NC gels can also be prepared by other methods. The first trial was a simple mixing of the corresponding aqueous solutions of clay and polymer (PNIPA). The second one was the mixing of more diluted solutions of clay and polymer and subsequent concentration by centrifugation. From the results, it was concluded that it was difficult to prepare NC gel by either of these methods.

By simple mixing of the corresponding aqueous solutions of clay and polymer for a typical N-NC5-M1 gel, a uniform blend of these two solutions was not achieved, but only heterogeneous turbid viscous mixtures (gel-like materials) were obtained. This is because both aqueous solutions had high viscosities and were almost in a gel state. The resulting blends were very brittle and, the mechanical properties could not be measured.

By mixing the diluted solutions of low viscosity (PNIPA solution with $C_{\mathrm{NIPA}} = 0.1$ mol/L (3.6 mPa·s) and clay solution with $C_{\mathrm{clay}} = 0.5 \times 10^{-2}$ mol/L (1.5 mPa·s)), the mixed solution became turbid due to the formation of aggregates of exfoliated clay and PNIPA chains. The turbid solution was centrifuged, and a gel-like material (hereinafter referred to as mix-centrifuged gel) settled out at the bottom. The mix-centrifuged gel contained 96.4 wt % of water relative to solids. This corresponded to a hydrogel swollen about 4-fold of NC5-M1 gel (87 wt % water). The mix-centrifuged gel was turbid and was difficult to measure the mechanical properties because of their weakness. The mix-centrifuged gel was further dried to obtain a similar water content to NC5-M1 gel. However, the resulting gel was turbid and quite brittle. The approximate elongation at break for this sample was 100%. We also measured the swelling behavior of the mix-centrifuged gel in water at 20 °C. Then, it was observed that the swelling ratio ($W_{\mathrm{gel}}/W_{\mathrm{dry}}$) initially increased with swelling time from 28 to 80 over a few tens of hours, and then the swelling ratio gradually decreased to 40 or less with a further increase in swelling time. This indicates that the mix-centrifuged gel was swollen, but at the same time some of the polymer and/or the clay were dissolved in the surrounding water and lost from the gel. This phenomenon was never observed during the swelling of NC gels.

Thus, from these results, it was concluded that NC gels with excellent optical and mechanical properties could not be obtained by mixing aqueous solutions of clay and polymer, regardless of their concentrations. In other words, NC gels are specifically prepared only by in-situ free-radical polymerization in the presence of exfoliated clay. Even in the case of mixing of two diluted

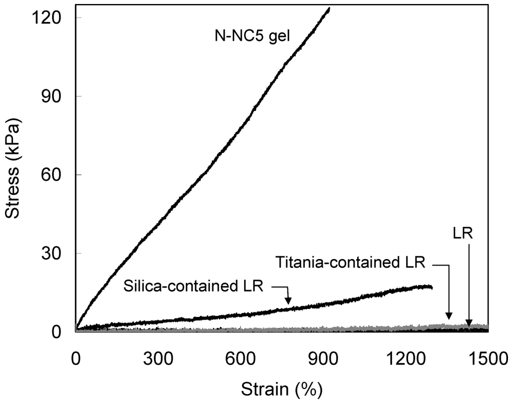

Figure 10. Stress−strain curves for N-NC5-M1 gel, LR (N-LR-M1), and silica- or titania-contained LRs. Silica and titania were contained in the same weight with clay in N-NC5-M1 gels.

aqueous solutions, since the mixing and subsequent concentration can only cause random interactions between clay and polymer, and so, a uniform dispersion of exfoliated clay within a polymer matrix, and controlled cross-linking between neighboring clay platelets cannot be achieved in the mix-centrifuged gel.

Here, we note observations relevant to the origin of cross-links in NC gels, i.e., to interactions between clay and polymer. In comparisons of FTIR spectra of linear PNIPA and dried N−NC2.5-M1 gel, no distinctive differences were observed in absorptions of PNIPA, only the existence of clay in the gel could be confirmed (1073, 1005, 652, and 443 cm^{-1}). Even for the FTIR of dried N-NC and D-NC gels with low m, in which the ratio of polymer interacting with clay should be high, it was difficult to prove the existence of specific clay−polymer interactions, such as strong hydrogen bonding between clay (Si−O or SiOH) and polymer (amide: CONH) or ionic interaction through KPS. This is probably because PNIPA itself possess quite strong hydrogen bonding in the dried state, which prevents hydrogen bonding with clay from being clearly observed in the dried NC gel. However, as evidenced by the formation of aggregates of PNIPA and clay in mixed solutions, hydrogen bonding between PNIPA and clay may be important as an effective interaction for network formation in NC gels. Also, as shown in this paper, KPS also plays an important role in early stages of network formation. Thus, at present, we consider that interactions at cross-linking points in NC gels are the result of hydrogen bonding between PNIPA and clay and/or ionic interactions involving KPS fragments. We will investigate and discuss this aspect further, based on the results of swelling properties of NC gels in various solvents, in a future paper.

Finally, in Figure 10, the mechanical properties of PNIPA (gel-like materials) containing other inorganic nanoparticles, which were prepared by in-situ free radical polymerization of NIPA in the presence of silica or titania nanoparticles instead of clay, are shown. Figure 10 clearly shows that NC gels with superb mechanical properties are only obtained from clay dispersions. The other inorganic nanoparticles (silica and titania) could not result in NC gel formation. In the case of silica, the modulus and strength were only a little higher than that of LR, which may be due to the reinforcing effect by interaction with PNIPA. On the other hand, the stress−strain curves hardly changed from that of LR in the case of titania, which indicates that titania nanoparticles were just uniformly dispersed in the matrix. Thus, it was concluded that nanoparticles other than clay did not act as effective reinforcing agents by forming organic/inorganic network structure in aqueous media.

Conclusion

The process of forming the unique organic/inorganic network structure, which is the chief determining factor for the superior properties of NC gels, was studied. The structure and stability of the initial reaction solutions, consisting of clay, monomer (NIPA), initiator (KPS), catalyst (TEMED), and water, were clarified in terms of changes in viscosity. In particular, it was revealed that NIPA plays an important role in preventing gel formation of clay itself and that KPS and TEMED are located near the clay surface through ionic interactions in the reaction solution. In subsequent in-situ free-radical polymerization, it was observed that the viscosity increased markedly during NC gel syntheses and in a manner similar to that in OR gel syntheses. Also, NC gels with different polymer contents exhibit characteristic two step changes in the stress−strain curves, which correspond to formation of a primary network and subsequent increase of cross-link density. Then, it was proposed that unique clay−brush particles, which consist of exfoliated clay platelets with numbers of polymer chains grafted on the clay surface, are formed in very early stages of polymerization, at around 7% of monomer conversion. The unusual decrease in transparency was observed to correspond to the formation of assemblies of clay−brush particles which have high density due to the high polymer concentration on them. The transparency was reestablished on further polymerization. The formation of clay−brush particles was also confirmed by XRD measurements on dried NC gels prepared by using insufficient monomer to form gels. Thus, a mechanism for forming the unique organic/inorganic network structure, including the formation clay−brush particles in the synthetic pathway, is proposed, where clay platelets act as effective multifunctional cross-linking agents in the form of plane cross-linking agents. On the other hand, it was confirmed that NC gels with excellent mechanical and optical properties could not be prepared using other procedures such as simple mixing of clay and polymer solutions or by mixing diluted solutions and subsequent concentration. Further, it was found that the use of the other inorganic nanoparticles instead of clay, such as silica and titania, could not result in the formation of NC gels with superior mechanical properties. These indicate that the formation of the organic/inorganic network structure of NC gels is peculiar to specified systems and is only realized in the free-radical polymerization in the presence of inorganic clay.

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