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ARTICLE

Synthesis and Characteristics of Nanocomposite Gels Prepared by In Situ Photopolymerization in an Aqueous System

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ABSTRACT: Nanocomposite (NC) gels consisting of poly(*N*-isopropylacrylamide) (PNIPA) and inorganic clay were prepared by photoinitiated free-radical polymerization in the presence of exfoliated inorganic clay in an aqueous solution. To obtain NC gels with superior properties, very low concentrations (e.g., 0.1 to 0.4 wt % relative to a monomer) of a hydrophobic photoinitiator were used. The resulting photopolymerized NC gels (photo-NC gels) were uniform and transparent, irrespective of their clay and polymer contents. In contrast with chemically cross-linked hydrogels (photo-OR gels), which are mechanically fragile, photo-NC gels exhibit excellent mechanical properties with large elongations at break of ~1000% and high tensile strength, that is, up to 50 times that of photo-OR gels. In addition, the modulus and the tensile strength could be controlled over a wide range by altering the clay content. From the analytical results and mechanical and swelling properties, it was concluded that photo-NC gels are composed of an organic (PNIPA)/inorganic (clay) network structure similar to that of NC gels prepared by redox-initiated free-radical polymerization and that the network structure is fabricated through the formation of clay-brush particles. Photo-NC gels exhibit a number of outstanding characteristics. They can exist in various forms including thin films and large monoliths with a wide range of thicknesses ($10^{-3}-10^{2}$ mm) and can form thin coatings on a substrate. In addition, they can be patterned using photolithography, their sliding frictional behavior can be controlled by the thermosensitivity, cell harvesting can be achieved without enzymatic treatment, and microchannels can be fabricated with a controllable flow system.

Introduction

Because of the successful fabrication of a unique organic (polymer)/inorganic (clay) network structure, nanocomposite hydrogels (NC gels)[1−4] have attracted great interest because they overcome most of the disadvantages, such as mechanical weakness, structural heterogeneity, and insufficient sensitivity to stimuli, associated with conventional chemically cross-linked hydrogels (OR gels). For example, NC gels consisting of poly(*N*-isopropylacrylamide) (PNIPA) and clay (hectorite) exhibit extraordinary optical, mechanical, and swelling/deswelling properties,[1,2] and many of their properties, for example, tensile and compressive properties,[2,4−6] coil-to-globule transition,[4,7] swelling/deswelling behaviors,[2,7] optical anisotropy,[5,8], and so on, can be controlled over a wide range by altering their network compositions. Furthermore, it has been found that NC gels are endowed with properties that make them suitable for a number of new applications related to biomedicine,[9,10] optics,[8] sensing,[11] and surface properties.[12]

Thus far, NC gels have been prepared by in situ free-radical polymerization initiated by aqueous redox systems.[1−4] In practice, the initial reaction solution, consisting of a monomer, initiator, accelerator, exfoliated clay, and water, was injected into a closed vessel of arbitrary shape, and free-radical polymerization was allowed to occur in the hydrophilic state at temperatures below the transition temperature of PNIPA, which is referred to as the lower critical solution temperature (LCST ≅ 32 °C). By the use of this process, NC gels were obtained in various forms such as a film, sheet, rod, hollow tube, and monolith with thicknesses of $10^{-1}-10^{4}$ mm.[13,14] Furthermore, because of their high mechanical toughness, NC gels with uneven-structured surfaces, such as bellows or cacti, could be readily prepared by the use of seamless tubular templates of corresponding shapes.[14] Furthermore, microstructures (fine patterns on a 10-μm scale) could be fabricated on the surfaces of NC gels by direct replica molding.[15] Therefore, NC gels are expected to be promising soft and wet materials for various applications because of their superior properties and a number of new functions as well as their ready accessibility.

Despite these impressive technological attributes of NC gels, further investigation of the scientific significance and applicability of one particular subject is required. That subject relates to “photopolymerized NC gels” which are prepared by photoinitiated free-radical polymerization. In general, photopolymerization has been carried out in nonaqueous systems for vinyl monomers such as acrylate and methacrylate monomers by using photoinitiators (PIs) at concentrations of a few mole percent (i.e., several weight percents) relative to the monomer. Thus far, photoinitiated polymerization in aqueous systems has not been extensively studied except for emulsified dispersion polymerization or graft polymerization on the surface of a substrate.[16,17] As for PNIPA, photopolymerization has been mostly used to fabricate some specific morphologies, such as temperature-sensitive coatings[16−19] or membranes[20,21] by forming grafted PNIPA on substrates, and microgels. Here specific photosensitizers immobilized onto the substrate surface were used as PIs.

With regard to photopolymerized NC gels, there have been a few attempts to synthesize NC gels consisting of PNIPA and inorganic nanoparticles (silica or clay). However, these attempts were not successful in achieving superior properties that were

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characteristic of NC gels. In the PNIPA/silica system,[22] the resulting photopolymerized hydrogels showed very poor mechanical properties, similar to those of conventional OR gels. In the PNIPA/clay system,[23] the gelation mechanism was studied only by dynamic and static light scattering, and there has been no investigation of the mechanical, structural, and functional properties of the resulting NC gels. In both cases, a water-soluble PI at a concentration of 3−8 wt % relative to monomer was used in accordance with conventional photopolymerization. However, as shown later in this article, these preparative conditions are not suitable for achieving excellent properties in photopolymerized NC gels. In this article, we report the first successful synthesis of NC gels with superior mechanical, optical, and thermoresponsive properties by photoinitiated polymerization, and we demonstrate the outstanding characteristics of the resulting photopolymerized NC gels (referred to as photo-NC gels).

Experimental Section

Raw Materials. *N*-isopropylacrylamide (NIPA), provided by Kohjin Co., Japan, was purified by recrystallization from a toluene/*n*-hexane mixture (2/1 w/w) and dried under vacuum at 40 °C. *N*,*N*-dimethylacrylamide (DMAA), provided by Kohjin Co., was purified by filtering through activated alumina. Two types of PIs, that is, a water-soluble PI, 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (Irgacure 2959 (Irg. 2959)), and a hydrophobic PI, 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184 (Irg. 184)), were obtained from Ciba Specialty Chemicals, Switzerland. Other reagents were purchased from Wako Pure Chemical Industries, Japan, and used without further purification. The water used for all experiments was ultrapure water supplied by a Puric-Mx system (Organo Co., Japan). Dissolved oxygen in pure water was removed by bubbling nitrogen gas for > 3 h prior to use, and oxygen was excluded from the system throughout the synthesis. As the inorganic clay, the synthetic hectorite “Laponite XLG” (Rockwood, Ltd., U.K.; $[Mg_{5.34}Li_{0.66}Si_8O_{20}(OH)_4]Na_{0.66}$: layer size = 30 nm in diameter × 1 nm in thickness;[24,25] cation exchange capacity = 104 m equiv/100 g) was used after washing and freeze-drying.

Preparation of Photo-NC and Photo-OR Gels and their Nomenclatures. Uniform aqueous solutions containing clay (Laponite XLG), monomer (NIPA), and PI were prepared. The concentrations of NIPA (C_{NIPA}) and clay (C_{clay}) were varied between 0.05−1 M and $3-15 \times 10^{-2}$ mol·L^{-1}, respectively. The concentration of PI relative to monomer (C_{PI}) was varied in a range of 0.05−5 wt %. As a typical example, to prepare the photo-NC5 gel using Irg.184 (0.1 wt %), a transparent aqueous solution consisting of water (20 mL), inorganic clay (0.762 g) and NIPA (2.26 g) was prepared. Next, PI (Irg.184) at a concentration of 2.26×10^{-3} g was added as a methanol solution (150 μL) to the former solution at ice-water temperature with stirring. The aqueous reaction mixture was then irradiated with UV light (365 nm) for 3 min at ice−water temperature. The resulting gel was purified in water through the swelling/deswelling process. Photo-NC gel was identified as being photo-NC*n* gel by the concentration C_{clay} (= $n \times 10^{-2}$ mol·L^{-1}). Photo-NC gels were synthesized in various kinds of vessels as well as by coating on the substrate and filling in microchannels. By using a similar procedure, DMAA-based photo-NC5 gel (abbreviation: photo-D-NC5 gel) was prepared. Photo-OR gels were prepared using the same procedure except for the use of an organic crosslinker, (*N*,*N*′-methylenebis-(acrylamide)) (BIS), instead of clay at a concentration of 1 mol % relative to NIPA. PNIPA (abbreviation: photo-PNIPA) was similarly prepared but using no cross-linking agent. In addition, a normal NC5 gel was prepared by thermal redox-initiated polymerization using the same procedure as that reported previously,[2,5], that is, by free-radical redox-initiated polymerization at 20 °C (< LCST) using a thermal initiator (potassium peroxodisulfate: KPS) and an accelerator (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine: TEMED).

Measurements. *Transmission Electron Microscopy* (*TEM*). Ultrathin films (ca. 70 nm thick) of dried photo-NC5 gels were prepared using an ultramicrotome (Reichert Ultracut S) and examined by TEM using a JEM-2200FS instrument (Nihon Denshi Co.) operating at 200 kV.

X-ray Diffraction (*XRD*). XRD profiles were obtained using milled, dried samples with Cu−Kα X-ray using a Rigaku-Denki RX-7 diffractometer.

Differential Scanning Calorimetry (*DSC*). DSC measurements were performed using a DSC-7 apparatus (Perkin-Elmer) with a nitrogen gas atmosphere and milled dried NC gels: 30−250 °C, 1 °C min^{-1}.

Tensile Mechanical Properties. Tensile measurements were performed on as-prepared photo-NC*n* gels, photo-OR1 gel, and normal NC5 gel of the same size (5.5 mm diameter × 70 mm long) using a Shimadzu Autograph AGS-H under the following conditions: 25 °C ; gauge length, 30 mm; crosshead speed, 100 mm min^{-1}. The initial cross section (23.75 mm^2) was used to calculate the tensile strength (TS) and the initial tensile moduli (E_i). E_i was calculated from the increase in load detected between elongations of 5 and 15%.

Swelling and Deswelling Ratios. We performed swelling and deswelling experiments by immersing the as-prepared photo-NC*n* gels (initial size: 5.5 mm ϕ × 30 mm in length) in a large excess of water at 20 and 50 °C, respectively, for ∼140 h, changing the water several times. Throughout the experiments, we measured the weight of the gel at specific times after removing excess water from the surface. Swelling and deswelling ratios were represented by the ratio of the weight of the hydrogel to the corresponding as-prepared gel ($W_{\mathrm{gel}}/W_{\mathrm{o}}$).

Viscosities. Viscosities were measured for clay, clay-PI, and clay-KPS aqueous suspensions using a vibration-type digital viscometer, VM-100A (Yamaichi Electronics, Japan), at 20 °C.

Transparencies. Transmittances were measured at 600 nm using a UV/vis spectrophotometer (V-530, Jasco Co., Japan) for photo-NC*n* gels, photo-OR gels, and photo-PNIPA in a cubic polystyrene cuvette (10 × 10 × 30 mm length) at 20 °C.

Sliding Frictional Behavior. The apparatus used for sliding frictional tests was the same as that previously reported.[26] A glass plate (pyrex glass: 15 mm width × 20 mm length × 3 mm in thick) with a straight smoothly rounded front edge was used as the sliding plate. The sliding plate was placed at one end of the photo-NC gel sheet with a size of 100 × 200 mm^2 and was pulled by using a tensile-testing machine that consisted of a free rotor and a drawing wire. The frictional force was recorded as a function of sliding distance with accuracies of ±0.005 N and ±0.01 mm. The sliding speed was fixed at 0.5 mm/s, and a constant load of 0.265 N (9 g/cm^2) was placed on the sliding plate. The photo-NC3 gel sheet was partially heated to 50 °C.

Cell Harvests. A polystyrene dish coated with a 5 μm layer of photo-NC5 gel (in dried state) was used in the cell harvesting experiments. Normal human dermal fibroblast (NHDF) was seeded on the surface at a density of 1.0×10^4 cells/cm^2 and was incubated in 5% CO_2/95% air at 37 °C by replacing the medium every 2 days. After culturing to confluence for 5 days, the medium was replaced by a cold medium (cooled to 5 °C in advance) and held in an incubator at 20 °C. Cell cultivation and subsequent detachment were documented by photomicrography, using a phase-contrast optical microscope (OLYMPUS CkX41).

Microfluidic Measurements. Laboratory-made microchannels (width and height of the channel: 100 μm) were used for the microfluidic measurements; two sections (length: 15 mm) of the microchannels were filled with photo-NC5 gel and were alternately heated to 50 °C and cooled to 20 °C. The water flux was 10 mL/min·mm^2.

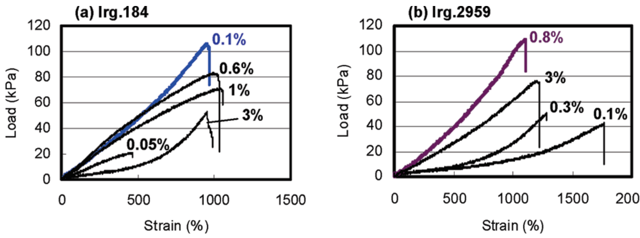
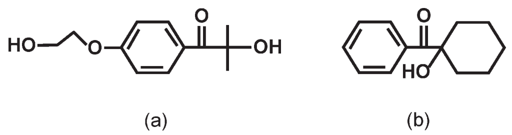


Figure 1. Stress−strain curves of photo-NC5 gels prepared with different C_{PI} values: (a) hydrophobic PI (Irg. 184) and (b) water-soluble PI (Irg. 2959).

Scheme 1. Structure of Photoinitiator Used[a]



[a] (a) Water-soluble PI (Irgacure 2959): 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone and (b) hydrophobic PI (Irgacure 184): 1-hydroxy-cyclohexyl-phenyl-ketone.

Results and Discussion

Syntheses and Properties of Photo-NC Gels. For the synthesis of photo-NC gels, the monomer (NIPA) was photopolymerized in water in the presence of PI and exfoliated clay platelets (Laponite XLG) by irradiation with UV light (365 nm) for 3 min at ice-water temperature. The concentrations of NIPA (C_{NIPA}) and clay (C_{clay}) were fixed at 1 M and 5×10^{-2} mol·L^{-1}, respectively, unless otherwise noted. In the preparation of photo-NC gels, the most important factor was the PI. We employed two types of PI: (1) a water-soluble PI (Irg. 2959: Scheme 1a) that is normally used in aqueous systems and (2) a hydrophobic PI (Irg. 184: Scheme 1b) that has never been used in aqueous systems. Although Irg. 184 is essentially hydrophobic and soluble only up to 1×10^{-2} wt % in water, its solubility increased to 9×10^{-2} wt % (against water) in the aqueous reaction solution consisting of clay (5×10^{-2} mol·L^{-1}) and NIPA (1 M). In other words, up to 0.8 wt % of Irg. 184 relative to the monomer NIPA (C_{PI} = 0.8 wt %) dissolved in the reaction solution. In comparison, up to 0.9 wt % of hydrophilic Irg. 2959 dissolved in water and a greater amount in the reaction solution; the solubility corresponded to $C_{PI} \geq 8$ wt % in the reaction solution.

The resulting photo-NC5 gels showed different features depending on the PI and its C_{PI}. The changes in the tensile stress−strain curve of photo-NC5 gels prepared using different PIs of varying concentrations are shown in Figure 1a (Irg. 184) and Figure 1b (Irg. 2959), and the effects of C_{PI} on the tensile strength are summarized in Figure 2. When a C_{PI} of 3−5 wt % was used at a similar concentration to that in conventional photopolymerization, the resulting photo-NC5 gels had many disadvantages (insets in Figure 2) such as (1) a heterogeneous morphology (e.g., 5 wt % of Irg. 184); (2) the formation of linear PNIPA (e.g., 3−5 wt % of Irg. 2959 and 1−5 wt % of Irg. 184) that was not incorporated into the organic/inorganic network and was released during subsequent swelling/deswelling processes; (3) yellowish coloring of the gels as revealed by the lightfast test (for most C_{PI} values of Irg. 2959); and (4) relatively low tensile strength (TS = 15−75 kPa).

As shown in Figure 2, it was found that these problems could be solved by using low C_{PI} over a very limited range, such as 0.1−0.4 wt % for Irg. 184 and 0.8 to 1 wt % for Irg. 2959, although the yellowish coloring did not completely disappear with Irg. 2959 regardless of C_{PI}. Therefore, it was concluded that to synthesize photo-NC gels with superior properties, molecularly dispersed and preferably hydrophobic PI (Irg. 184) should be used at very low concentrations (0.1 to 0.4 wt %) compared with that for conventional photopolymerization (3−8 wt %).[22,23] Furthermore, to ensure the molecular dispersion of very small amounts of hydrophobic PI (Irg. 184: solid) in aqueous reaction solutions, a PI-methanol solution can be added, although it is advisible to use as little methanol as possible so as to prevent its interference in the formation of the PNIPA/clay network. In the procedures described hereafter, Irg. 184 (C_{PI} = 0.1 wt %) was used as a methanol solution (50 μL per 10 mL reaction mixture).

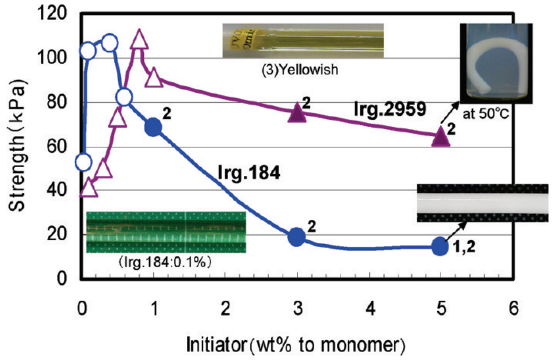


Figure 2. Changes in tensile strength of photo-NC5 gels with changing C_{PI}. The closed symbols with suffixes 1 and 2 indicate the heterogeneous gel and release of linear PNIPA by the swelling/deswelling process, respectively. In the photo of suffix 2, the water becomes turbid because of linear PNIPA released from the gel at 50 °C. Suffix 3 indicates the yellowish coloring of the gels as revealed by the lightfast test.

In addition, photo-NC gels were prepared using a different monomer, *N*,*N*-dimethylacrylamide (DMAA), and clay using the same preparative conditions (Irg. 184: C_{PI} = 0.1 wt %). The results are summarized in Table 1. The resulting photo-D-NC5 gel was transparent and exhibited excellent mechanical properties such as high TS of 114 kPa and high ε_b of 1500%. It is interesting to note that photo-NC gels with 5.5 mm φ × 70 mm length can be prepared by irradiation of UV light for < 3 min, for example, 10 s at 20 °C for both PNIPA-based photo-NC5 gels and photo-D-NC5 gels, as shown in Table 1.

Effects of Clay Concentration on Properties of Photo-NC Gels. Figure 3 shows the tensile stress−strain curves of the photo-NC*n* gels prepared using Irg. 184 (C_{PI} = 0.1 wt %) for different values of C_{clay} (n = 3−15). All of the photo-NC*n* gels obtained were uniform and transparent regardless of the value of C_{clay} and exhibited extraordinarily high mechanical toughness compared with the photo-OR gel, which is mechanically fragile (shown in the inset of Figure 3). Photo-NC*n* gels essentially showed the same mechanical characteristics as normal NC*n* gels[2,5] prepared by thermal redox-initiated free-radical polymerization. That is, E_i and TS increased markedly with increasing C_{clay}, whereas a large ε_b was retained at around 1000%. However, the values of E_i and TS in Figure 3 are mostly somewhat lower (by a factor of 0.75 to 0.9) than those of corresponding normal NC*n* gels. The stress−strain curve of a normal NC5 gel prepared by KPS-initiated free-radical polymerization is also shown in Figure 3 for comparison. These results indicate that the effective cross-link density of the PNIPA/clay network in photo-NC*n* gels is slightly lower than that in normal NC*n* gels.

Table 1. Tensile Mechanical Properties of Two Types of Photo-NC5 Gels, Consisting of PNIPA/Clay and PDMAA/Clay, Prepared Using Different UV Irradiation Time and the Temperature: 180 and 60 s at Ice Water Temperature and 10s at 20 °C

	Photo-NC5 gel (PNIPA)[a]			Photo-D-NC5 gel (PDMAA)[b]		
	180 s	60 s	10 s	180 s	60 s	10 s
strength (kPa)	106	95	110	114	100	125
elongation (%)	966	800	1000	1500	1350	1360

[a] PNIPA: Poly(*N*-isopropylacrylamide). [b] PDMAA: Poly(*N*,*N*-dimethylacrylamide).

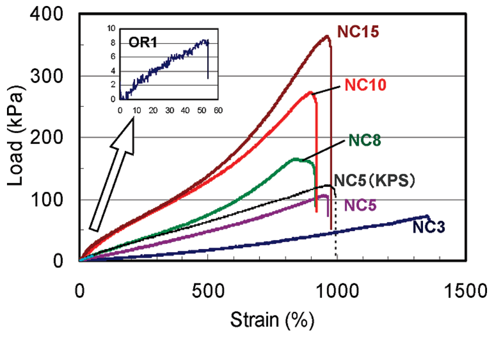


Figure 3. Stress–strain curves of photo-NC*n* gels with different C_{clay} (n = 3–15). The curve for the normal NC5 gel prepared by redox polymerization is shown by the dotted line. For comparison, data on the photo-OR gel are also shown in the inset.

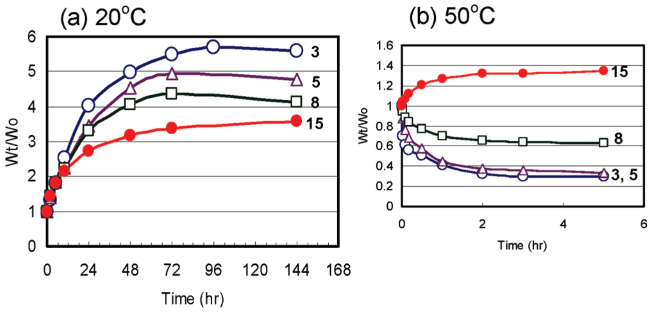


Figure 4. Swelling/deswelling behaviors of photo-NC*n* gels with different C_{clay} values (n = 3, 5, 8, 15) at (a) 20 and (b) 50 °C.

Figure 4a,b shows the swelling and deswelling behaviors of photo-NC*n* gels (n = 3, 5, 8, 15) in water at 20 and 50 °C, respectively. All photo-NC*n* gels underwent swelling at 20 °C, and the degree of equilibrium swelling was almost inversely proportional to the value of C_{clay}. In contrast, photo-NC3 gels exhibited a rapid and large deswelling in water at 50 °C (> LCST). However, the degree of equilibrium deswelling gradually decreased with increasing C_{clay}, and consequently, the photo-NC15 gel exhibited swelling even at 50 °C. This abnormal swelling/deswelling behavior that depended strongly on C_{clay} was consistent with that of the NC*n* gels prepared by redox-initiated polymerization; these abnormal behaviors were attributed to the clay platelets acting as effective cross-linking agents and to the high clay concentration severely restricting the transition of PNIPA chains to their hydrophobic state.

Network Structure and Formation Mechanism of Photo-NC gels. With respect to the network structure, it was concluded, from the mechanical and swelling properties of photo-NC gels and analytical data (TEM, DSC, and XRD) for the dried gels (Supporting Information), that an organic (PNIPA)/inorganic (clay) network structure is also formed in photo-NC gels, analogous to the structure of normal NC gels.[2,3] The TEM observation and XRD profile of the photo-NC gels revealed the exfoliation of clay and its uniform dispersion in the gel. A DSC thermogram showed that the glass-transition temperature of PNIPA in a photo-NC gel was the same as that of linear PNIPA; this indicated that the PNIPA chains were flexible and adopted random-coil conformations. The mechanism of the formation of the PNIPA/clay network structure during in situ photopolymerization was surmised and is shown in Figure 5a. Hydrophobic PI (Irg. 184) was molecularly dispersed in the aqueous reaction solution and was concentrated near the clay platelets (Figure 5a (i)). The interaction between clay platelets and PI (Irg. 184) was confirmed by the viscosity change of the aqueous clay suspension upon the addition of Irg. 184 (Figure 5b). This change was similar to that caused by the thermal initiator (potassium peroxodisulfate: KPS),[24] although the increase was smaller than that caused by ionic KPS. It has been reported that during the preparation of normal NC gels, a unique transparency change, attributed to

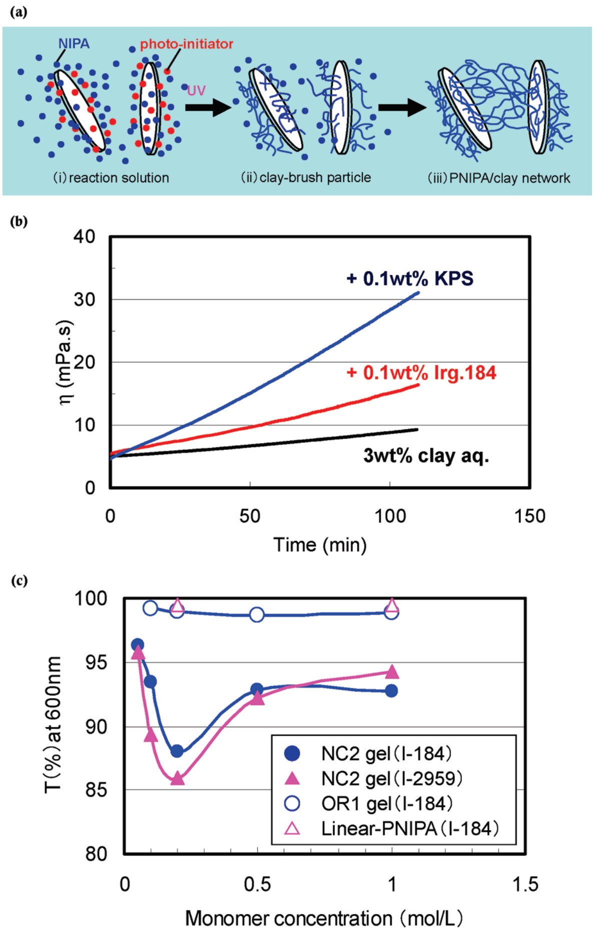


Figure 5. (a) Schematic representations of model structures for (i) reaction solution, (ii) clay-brush particles, and (iii) PNIPA/clay network structure in photo-NC gels. (b) Effect of additions of PI (Irg. 184: C_{PI} = 0.1 wt %) and KPS (C_{KPS} = 0.1 wt %) on viscosity of clay aqueous suspension with C_{clay} = 3 wt %. (c) Changes in optical transparency with changing C_{NIPA} in photo-NC2 gels prepared using Irg. 184 and Irg. 2959, photo-OR gel, and photo-PNIPA.

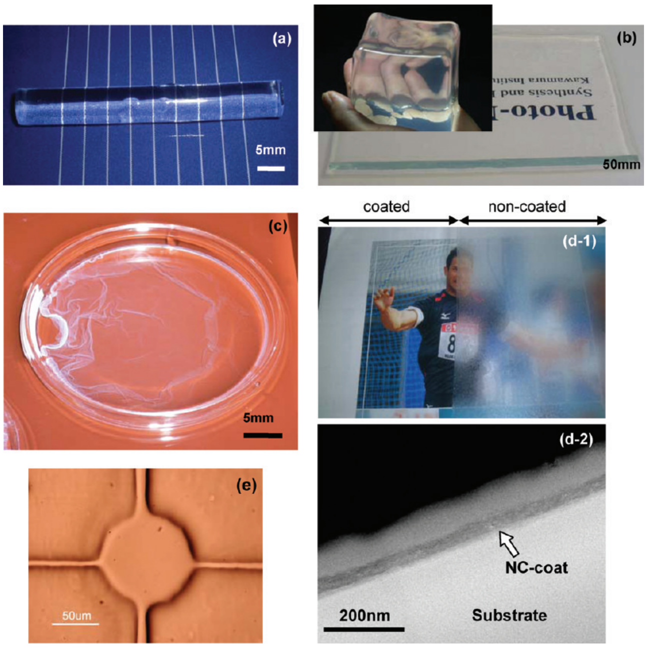


Figure 6. Photo-NC5 gels with various shapes: (a) rod, (b) sheet and monolith, (c) thin film, and (d-1) coating of photo-NC5 gel on the left half of glass plate. (d-2) shows the TEM image of coated photo-NC5 gel (dried). (e) Patterned photo-NC5 gel prepared using photomask.

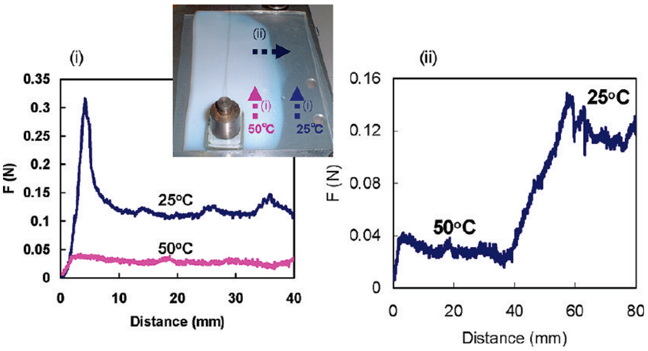
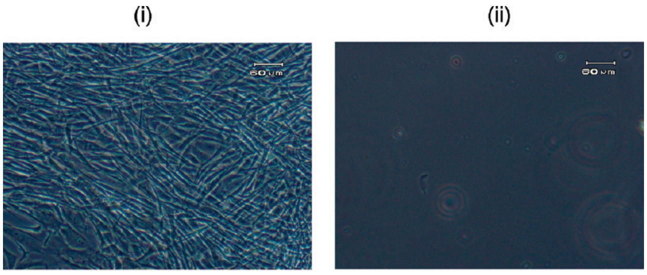


Figure 7. Thermosensitive sliding frictional behaviors (frictional force vs sliding distance) of photo-NC3 gel films. The force profiles were measured on the gel surface heated to 25 (transparent) and 50 °C (whitened) along the arrows (i) and (ii).



On ice for 5 minutes（fibroblast detached）

Figure 8. Phase-contrast photomicrographs of NHDF cultures (i) on photo-NC5 gel coating on polystyrene dish and (ii) after detaching cell sheet by decreasing temperature to 10 °C for 5 min.

the formation of clay-brush particles, was observed in the early stages of in situ polymerization.[24] However, this was not observed in the present case, probably because the rate of photopolymerization was much faster than that of redox-initiated polymerization using KPS. We examined the transparency of photo-NC2 gels prepared with different C_{NIPA}. A transparency change was observed in which the transmittance dropped at $C_{\mathrm{NIPA}} = 0.2$ M, after which high transparency was observed again (Figure 5c). Conversely, absolutely no transparency change was observed in either photo-OR gels or photo-PNIPA, regardless of C_{NIPA} (Figure 5c). These observations strongly suggest that the PNIPA/clay network in photo-NC gels is formed by a mechanism similar to that for normal NC gels, as shown in Figure 5a. For photo-NC gels prepared with Irg. 2959, the same mechanism was also surmised because of the similar result shown in Figure 5c. It is readily expected that some PI molecules would be dispersed in the surrounding aqueous medium when C_{PI} is high. In that case, linear PNIPA chains that are not incorporated in the network would be formed, and consequently, free PNIPA would be released during the subsequent swelling/deswelling process. This is consistent with the experimental results shown in Figure 2 (2).

Characteristics of Photo-NC Gels. *a. Various Forms.* This extension to the forms of gels is a very interesting development that can be expected from photo-NC gels. Various forms of gels, including thin films and coatings, with a wide range of thicknesses (e.g., $10^{-3}-10^{2}$ mm) could be prepared by irradiation with UV light. Figure 6 shows examples of photo-NC5 gels with different forms such as (a) rod, (b) sheet and monolith, (c) thin film, and (d) thin coating (dried) on a glass plate. In case (c), the thickness of the thin film could be controlled over the range of $1-100$ μm in the swollen state. Figure 6(d-2) shows a TEM image of (d) dried nanocoating (50 nm thickness). From Figure 6(d-1), it can be observed that the coated surface shows good antifogging characteristics by preventing the condensation on the surface under conditions of high humidity. Another possible development by the use of photo-NC gels is the preparation of patterned NC gels by irradiation of UV light through photomasks and the subsequent washing of the residual unreacted part with water. An example is shown in Figure 6e.

b. Thermosensitive Sliding Frictional Behavior. Because photo-NC gels, composed of PNIPA/clay networks, exhibit well-defined thermosensitive transitions, it is expected that the surface properties would change significantly if the temperature crossed the transition temperature (LCST). Figure 7 shows changes in the sliding frictional force on the surface of a photo-NC3 gel sheet caused by heating parts of the sheet to 50 °C (> LCST). Here, because it was known that a small amount of free water would greatly affect the sliding frictional behavior,[26] any water released on the surface heated at 50 °C, due to the transition, was removed by lightly pressing tissue paper on the surface before undertaking the measurements. It was observed that the sliding frictional force greatly decreased because of the phase transition.

c. Cell Harvesting on Photo-NC-gel-coated Polystyrene Dish. Figure 8 shows a phase-contrast photomicrograph of NHDF culture on the surface of a polystyrene dish coated with photo-NC5 gel. It was observed that NHDF was attached and cultured to be confluent (Figure 8i) and that the cell sheet was subsequently detached without requiring treatment by tripsin but simply by decreasing the temperature to 10 °C for 5 min (Figure 8ii). Similar cell cultivation and subsequent cell detachment was also observed for other cells such as human hepatoma cells and normal human umbilical vein endothelial cells. Although the same behaviors were also observed for normal NC5 gel films,[10] the coating of photo-NC gels on a polystyrene dish should be more useful and applicable for actual biomedical research.

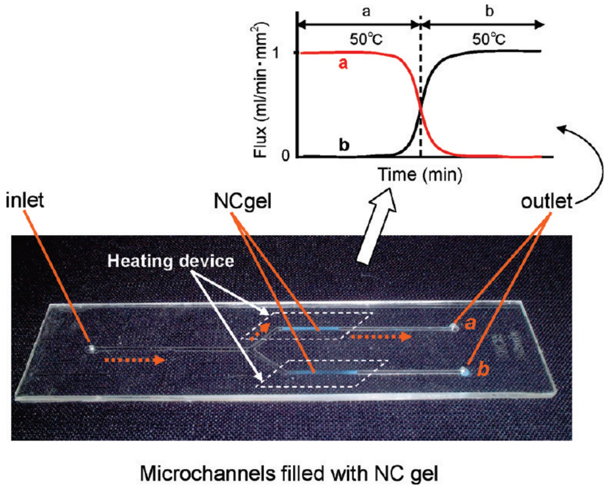


Figure 9. Microchannels partially filled with photo-NC5 gels. The inset shows water flow caused by alternately changing the temperature (20 and 50 °C) in photo-NC5 gel zones.

d. Microchannel Flow System. Figure 9 shows the fabrication of microchannels partially filled with photo-NC5 gel. The flow of water through the channels (from an inlet on the left to outlets on the right) can be controlled by heating either of the photo-NC5 gel zones. When the photo-NC5 gel sets at room temperature (< LCST), the channels are closed. The channels open when the photo-NC5 gel is heated because the gel shrinks. Therefore, the flow and pathways of the microchannel system were controlled by heating or cooling the photo-NC gel zones in the channels.

Conclusions

We have shown that photo-NC gels with superior mechanical, optical, and thermosensitive properties can be synthesized by free-radical polymerization initiated by a PI and irradiated with UV light under optimized conditions. The selection and dispersion of the PI, preferably hydrophobic PI with a very low concentration in a very limited range, are the most important factors to be considered for the photopolymerization of NC gels in an aqueous system. Uniform, transparent photo-NC gels of various forms and with a wide range of sizes were obtained. The organic (polymer)/inorganic (clay) network structure and the mechanism of formation were thought to be similar to those of normal NC gels prepared by thermal redox-initiated free-radical polymerization. The resulting photo-NC gels exhibited very desirable mechanical properties, for example, ultrahigh elongation at break and high tensile strength compared with the mechanically fragile photo-OR gels, and these properties could be varied over a wide range by altering the clay content. Furthermore, a number of outstanding characteristics were observed, including the antifogging property of the coating, thermosensitive sliding frictional behavior, flow control in microfluidic channels, formation of patterned NC gels by UV light, and cell harvesting without enzymatic treatment. New applications of polymer hydrogels in many advanced research fields will be made possible by UV-curable NC gels.

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Supporting Information Available: Transmission electron micrograph of thin film of dried photo-NC5 gel, differential scanning calorimetry thermogram for dried photo-NC5 gel, and X-ray diffraction XRD profiles for milled dried photo-NC5 gel. This material is available free of charge via the Internet at http://pubs.acs.org.

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