Ultrahigh Deformability and Transparence of Hectorite Clay Nanocomposite Hydrogels with Nimble pH Response

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ABSTRACT: Nimble pH response nanocomposite hydrogels (NC gel) with ultrahigh tensibility and high transparency were synthesized via in situ copolymerization of acrylamide and sodium acrylate (SA) in the aqueous suspension of hectorite clay Laponite RDS with a minute amount of *N*,*N*′-methylenebisacrylamide (BIS). The stability of the Laponite suspension containing ionic monomers and the tensile properties of the NC gels were investigated. The addition of ionic monomer SA was found to reduce the ζ potential and stability of the suspension. The tensile strength and elongation at break of these ionic NC gels obviously decreased when SA was greater than 10 mol % in the monomers. Interestingly, the addition of a minute amount of BIS ($\leq$0.05 mol %) enhanced the homogeneity of the ionic NC gels and thus improved their transparency (transmittance >90%), tensile strength (>100 kPa), and elongation (>2000%). The relaxation modulus of the ionic NC gels was fit with $G(t) = G_e[1 + (t/\lambda_0)^{-n}]$, where G_e was the equilibrium modulus and λ_0 was a material-dependent time constant. The relaxation exponent, n, for the ionic NC gels was 0.10 to 0.18, which is similar to that of the lightly cross-linked nature rubber. This moderate relaxation observed was considered to be the origin of the ultrahigh tensibility of the ionic NC gels. Fortunately, the nimble pH response still remained in the present NC gels containing carboxyl groups. The oscillatory swelling−shrinking circles switched by pH at 7.4 and 3.0 were observed from the present NC gels.

1. Introduction

Polymer hydrogels have been intensively studied for their unique properties and potential applications. Recently, Haraguchi et al. reported a novel polymer−clay nanocomposite hydrogel (NC gel), which was in situ polymerized with *N*-isopropylacrylamide (NIPAm) monomer in aqueous suspension of hectorite clay Laponite.[1] The NC gel exhibited excellent properties, such as extraordinary tensibility (elongation at break ~1300%, 50 times larger than that of chemically cross-linked hydrogels, OR gel), high transparency, and so on.[2] The Laponite platelets worked as a multifunctional cross-linker, and the polymer chains were attached to the surface of clay platelets in the NC gels.[3−12] Unlike the OR gel, the NC gel has uniform network structure and low effective network chain density, which is probably the origin of its ultrahigh tensibility.[13,14]

However, all of the NC gels reported up to now are based on the monomers of acrylamide derivatives, which do not respond to stimuli other than temperature.[15,16] Thermal response was reported on the PNIPAm/Laponite NC gel.[2,17] Laponite, carrying strong negative charges on the surface and weak positive charges on the rim, can form a clear and colorless colloidal suspension in water, which is stabilized by the repulsive electrostatic interaction.[18,19] However, aggregation and gelation occur when the concentration or ionic strength of the Laponite suspension becomes too high.[20,21] Consequently, it is difficult to fabricate responsive NC gels with ionic monomers (e.g., acrylic acid, AA) by the in situ copolymerization because of increasing ionic strength. Recently, Song et al. reported a temperature- and pH-sensitive NC gel with a semi-interpenetrating organic/inorganic network, which was prepared by radical polymerization of NIPAm in the suspension of the gel-forming grade Laponite XLG containing linear PAA;[22] however, the synthesized semi-IPN NC gel was not transparent (transmittance ~25%), and the elongation was less than 800%. Mujumdar et al. tried to prepare pH-sensitive NC gel by in situ copolymerization of NIPAm and ionizible monomers, such as methacrylic acid (MAA) and sodium methacrylate.[23] Nevertheless, this technique failed to produce transparent ionic NC gel because of flocculation of the Laponite XLG platelets. Although the NC gel of MAA and NIPAm was synthesized by Laponite XLG modified with sodium pyrophosphate decahydrate, the transmittance of the gel was lower than 70%.

Haraguchi et al. found that the addition of nonionic monomer NIPAm to the clay suspension delayed the formation of the house-of-cards structure because the NIPA monomer effectively surrounded each clay platelet.[3] In contrast, the addition of a small amount of ionic monomer AA to the clay suspension led to a steep decrease in transmittance and an increase in viscosity due to the hydrogen bonding between COOH and Si−OH on the clay surface.[22] The sol-forming grade clay of Laponite RDS, produced by incorporating inorganic polyphosphate to the gel-forming grade clay Laponite RD, may delay or prevent gel formation because of the absence of positive charges at the platelet rim.[24]

In the present work, a nimbly pH-sensitive NC gel with excellent tensibility and high transparency was synthesized via the in situ copolymerization of acrylamide and sodium acrylate in the suspension of the sol-forming grade clay Laponite RDS with a minute amount of co-cross-linker, *N*,*N*′-methylenebisacrylamide (BIS). The mechanical properties, transparency, and pH sensitivity were investigated with varying gel composition.

2. Experimental Section

Materials. Acrylamide (AM) and potassium peroxydisulfate (KPS) were purified by recrystallization from deionized water and were dried under vacuum at room temperature. We prepared sodium acrylate (SA, 1 M) solution by neutralizing acrylic acid (AA, 2M) aqueous solution with 2 M NaOH aqueous solution. *N*,*N*,*N*′,*N*′-tetramethyl-ethylenediamine (TEMED, Sinopharm Group Chemical Reagent) and BIS were used as received. Synthetic hectorite clay of sol-forming grade Laponite RDS $\{Na^+_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{0.7-}\}$, modified from gel-forming grade Laponite RD with

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Table 1. Composition of Some Ionic NC Gels[a]

code	Laponite RDS (g)	AM (mol)	SA × 10^2 (mol)	BIS (0.1 M) (μL)	KPS (20 mg/mL) (mL)	water (mL)
S6SA4.8-BIS0.03	0.6	0.013	0.066	41.5	0.5	9.46
S6SA11-BIS0.03	0.6	0.012	0.150	40.5	0.5	9.46

[a] Total volume of the suspension was 10 mL.

pyrophosphate ions ($P_2O_7^{4-}$), was kindly provided by Rockwood and was used after being dried at 100 °C for 4 h. Milli-Q ultrapure water was used in all experiments, and argon gas was bubbled into the water for more than 1 h prior to use.

Synthesis of Nanocomposite Hydrogels. The NC gel was synthesized through the in situ radical copolymerization of AM and SA in aqueous suspension of Laponite RDS with minute BIS as co-cross-linker. First, we prepared Laponite suspension by dispersing the white power in Milli-Q ultrapure water at the desired concentration under stirring for at least 4 h. Then, the monomer AM, catalyst TEMED, aqueous solution of initiator KPS (20 mg/mL), and subsequently, aqueous solution of the co-cross-linker BIS (0.1 M) were added to the Laponite suspension under stirring. Finally, the SA solution (1 M) was added to the reaction mixture. In all cases, the total monomer concentration was fixed at 10% w/v, and the mole percent of SA in all monomers was varied from 4.8 to 11 mol %. The initiator was 1 wt % of the total monomers. The radical polymerization was allowed to proceed at 30 °C for 72 h. The NC gel was formed in three shapes in glass vessels: a disk of 25 mm diameter × 1.5 mm thickness for rheology measurement, a rod of 6.0 mm diameter × 80 mm length for tensile measurement, and a strip of 1.0 mm diameter × 5 mm length for swelling measurement. For comparison, we also prepared the NC gel without the co-cross-linker BIS by following the same procedure, except for the addition of BIS.

The NC gel samples in this work are referred to as the S*m*SA*n*-BIS*p*, where S and SA stand for the Laponite RDS and monomer, respectively, and *m*, *n*, and *p* stand for the clay-to-water percent in % w/v and the mole percent of SA and BIS in all monomers, respectively. Some examples are demonstrated in Table 1. S6SA11-BIS0.03 means that a NC gel contains 6% w/v of Laponite RDS, 10% w/v (fixed) of all monomers with 11 mol % of SA and 0.03 mol % of BIS in all monomers. The term BIS was eliminated when *p* was zero. The traditional copolymer hydrogel samples of AM and SA cross-linked with BIS are referred to as the OR*q*, where *q* stands for the BIS concentration in mol % against all monomers, and the SA in all monomers (the total monomer concentration was 10% w/v) was fixed at 11 mol %.

Mechanical Measurements. Tensile strength was measured on the as-synthesized NC gel samples of 6.0 mm diameter × 80 mm length with a Zwick Roell testing system at 30 °C. The sample length between jaws was 20 mm, and the crosshead speed was 100 mm/min. The tensile strain was taken as the length change relative to the initial length of the specimen, and the tensile stress was evaluated on the area of the initial cross section.

Dynamic moduli were measured on the as-synthesized NC gel samples to estimate the network chain density with a strain-controlled rheometer ARES-RFS using parallel plates of diameter of 25 mm. The gel sample stuck the fixture well without slippage. Silicone oil was laid on the edge of the fixture plates to prevent solvent evaporation. First, the dynamic strain sweep was carried out at angular frequency of 1 rad/s to determine the linear viscoelasticity region. Then, the frequency sweep was performed over the frequency range of 0.001 to 100 rad/s. The stress relaxation was measured at a constant shear strain of 0.5%. All rheology measurements were carried out at 30 ± 0.1 °C controlled by a Peltier plate.

Swelling Experiments. We performed swelling experiments at room temperature by immersing the as-prepared NC gels (initial size of 1.0 mm diameter × 5.0 mm length) in pure water and in buffers of different pH values from 3 to 10 at constant ionic strength of $I = 0.01$ M. We followed the approach to swelling equilibrium by monitoring the diameter of the sample using a microscope with a microruler. The diameter ceased to change when equilibrium was reached. The swelling ratio was defined as the gel volume, V, at swelling equilibrium related to its original volume, V_0, of the as-prepared gel (not the dried gel). Assuming isotropic swelling, the swelling ratio V/V_0 was calculated from $V/V_0 = (d/d_0)$,[3] where, d and d_0 denoted the corresponding diameters of the gel sample.

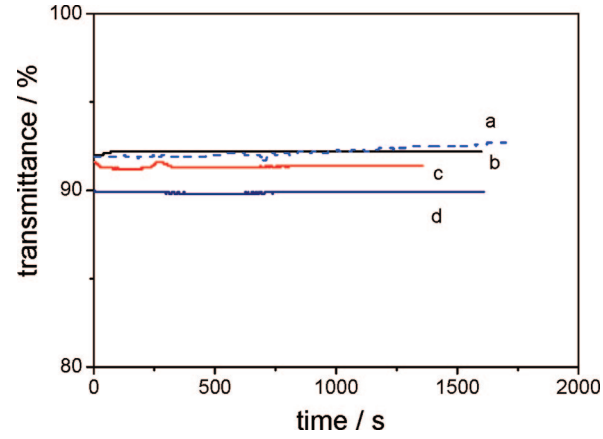

Figure 1. Transmittance of Laponite RDS aqueous suspensions of 6% w/v with different SA concentrations: (a) without any monomers; (b) AM 10% w/v; (c) (SA + AM) 10% w/v with 0.07 M SA; and (d) (SA + AM) 10% w/v with 0.15 M SA.

Characterization. Transparency of the suspension was detected with a UV/vis spectrophotometer (Hitachi U-3010) at 600 nm and 25 °C to test the suspension stability. The viscosity of the suspension was measured with a stress-controlled rheometer AR-G2 using parallel plates of diameter of 60 mm at 10 and 25 °C. A water seal was used at the up fixture plate to prevent water evaporation. The ζ potential of the suspension was determined with a Zetasizer Nano-ZS90 apparatus (Malvern Instruments) at 25 °C. The suspension was filtered through a Millipore filter of 0.45 μm pore size before the measurement. A ζ potential value was the average of at least three successive measurements.

The Fourier transform infrared (FTIR) spectrum was recorded on a Bruker Vector 33 FTIR spectrometer for dried and milled hydrogel sample and Laponite powder by the conventional KBr pellet method at room temperature.

3. Results and Discussion

Stability of Laponite Suspension with Ionic Monomer. In the present work, anionic monomer SA was added to the aqueous Laponite RDS suspension containing monomer AM. The pH value of suspension at 25 °C was about 10.0 and decreased slightly (to 9.8) with increasing SA concentration. (See the Supporting Information.) The suspension stability was investigated with transmittance, viscosity, and ζ potential. Figure 1 shows the transmittance during 30 min for the Laponite RDS aqueous suspensions of 6% w/v with different compositions of monomers AM and SA. All of the suspensions were transparent without precipitation during the observation. The result implies that the addition of ionic monomer SA does not cause precipitation in the Laponite suspension. In contrast, adding ionic monomer AA of only 0.5 wt % induced a steep decrease in transparence for the Laponite XLG suspension with NIPAm.[22]

The viscosity of 6% w/v of the Laponite RDS suspensions with different monomer compositions is plotted in Figure 2 against shear rate. Compared with the viscosity of 10^{-3} Pa·s for pure water at 25 °C, the viscosity of the Laponite RDS suspension is quite low without shear rate dependence, suggesting no physically jointed structure formed in the suspension. The viscosity increases with increasing concentration of ionic monomer SA because of the hydrogen bonding and electrostatic interaction. The addition of more SA induces the instability of the suspension, showing a viscosity increase with measuring

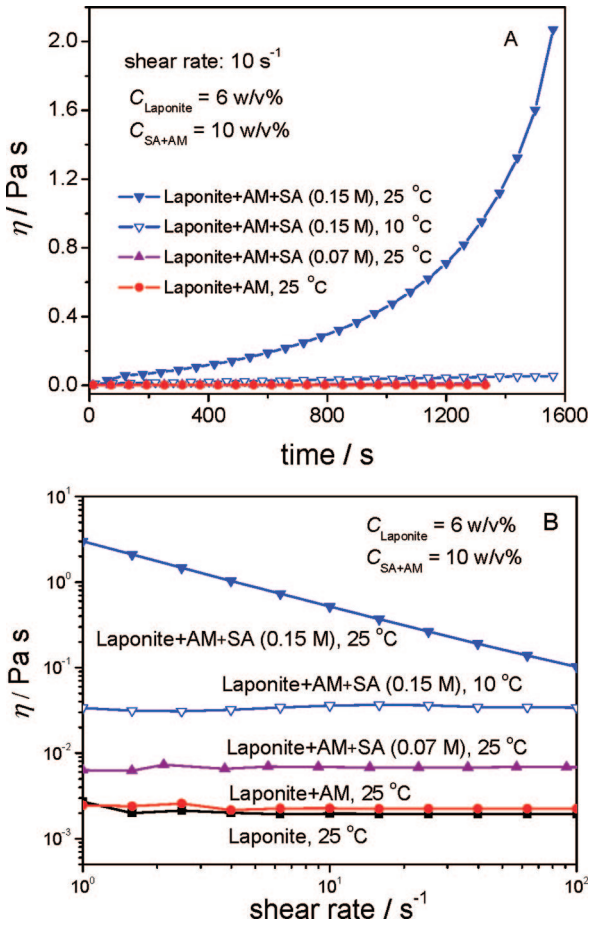

Figure 2. (A) Time dependence and (B) shear rate dependence of viscosity for the Laponite suspensions just after preparation with indicated SA concentrations. C_{Laponite} and $C_{(\text{SA+AM})}$ were fixed at 6 and 10% w/v, respectively.

time (Figure 2A) and shear thinning (Figure 2B) for 0.15 M SA (11 mol % to all monomers) at 25 °C. These facts suggest that aggregates are formed in the suspension because of the increase in ionic strength and decrease in electrostatic repulsion among the Laponite platelets. Therefore, the time window, within which the homogeneous ionic NC gel can be produced via in situ polymerization, becomes narrow with increasing concentration of ionic monomer SA. Nevertheless, the viscosity of the Laponite suspension containing 0.15 M SA at 10 °C was found to be stable, even for more than 25 min (Figure 2A), without shear rate dependence (Figure 2B), indicating no aggregation at this temperature. It was also reported that the aggregation in the Laponite suspension slowed down with decreasing temperature.[25]

The stability of the Laponite RDS suspension containing monomers AM and SA was also examined with ζ potential, and the results are shown in Figure 3. The absolute value of the ζ potential decreases with increasing SA concentration, leading to instability of the suspension accompanying the addition of SA. This suggests that the sodium cation from the monomer SA would bind to the Laponite platelet to reduce its surface charge. The clay suspension is stabilized by the electrostatic repulsion among the clay platelets. The addition of ionic monomer SA reduces the stability of the clay suspension because of the weakening repulsive interaction and the increasing ionic strength of the suspension. Therefore, the ζ potential represents the stability change in the clay suspension more effectively than transmittance and viscosity.

The FTIR spectrum of the NC gels is depicted in Figure 4 together with that of Laponite RDS. The absorption bands at

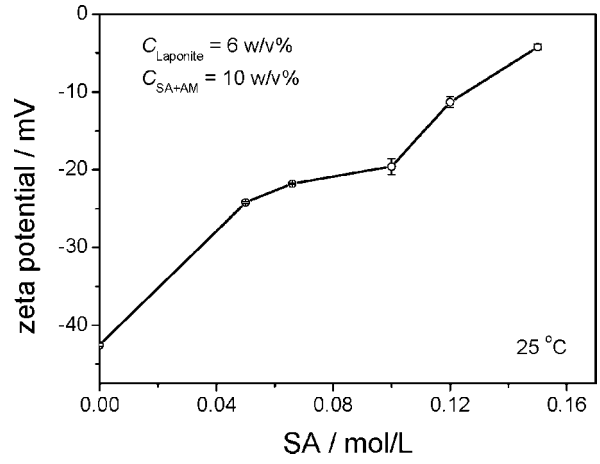

Figure 3. ζ potential of the Laponite suspension as a function of SA concentration. C_{Laponite} and $C_{(\text{SA+AM})}$ were fixed at 6 and 10% w/v, respectively. The ζ potential was measured immediately after suspension preparation.

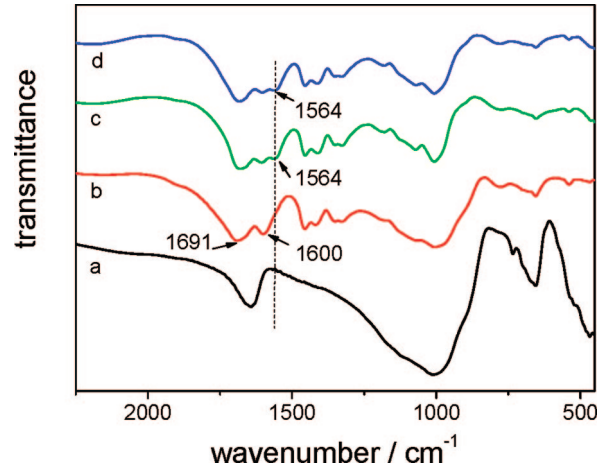

Figure 4. FTIR spectrum of (a) Laponite RDS, (b) S6SA0, (c) S6SA11, and (d) S6SA11-BIS0.03 dried gels.

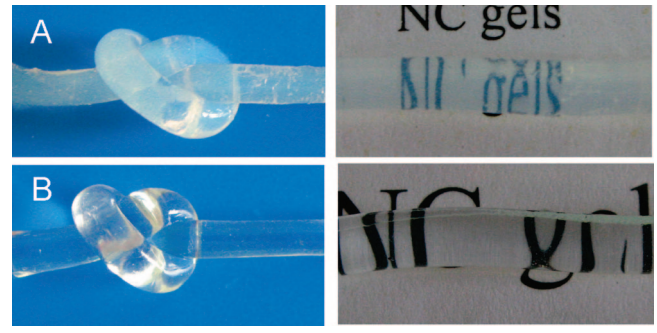

Figure 5. Appearance of the NC gels: (A) S6SA11 and (B) S6SA11-BIS0.03.

1691 and 1600 cm^{-1} are attributed to the amide groups in the AM unit, which appear in all three of the gel samples. A new band at 1564 cm^{-1} for the ionic NC gel of S6SA11 and S6SA11-BIS0.03 belongs to the carboxyl groups in the SA units.

Ultrahigh Tensibility. Figure 5 shows the appearance of the ionic NC gels S6SA11 (A) and S6SA11-BIS0.03 (B). The NC gel S6SA11 without co-cross-linker BIS, is translucent, whereas the NC gel S6SA11-BIS0.03 with a bit of BIS is very transparent. It is more surprising that these NC gels containing ionic units are still tough enough to withstand torsion and tensile deformation even with a knot.

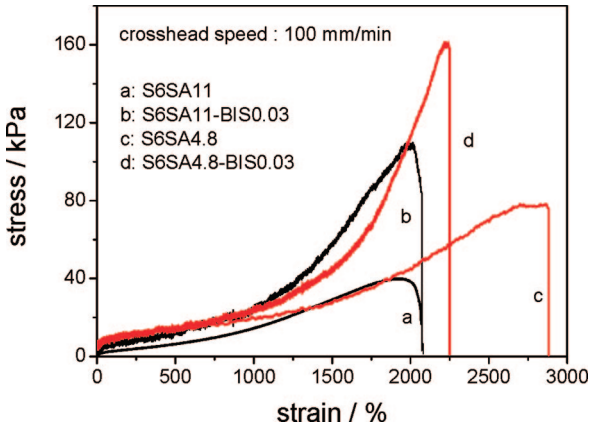

Figure 6. Stress−strain curves for the indicated NC gels at 30 °C.

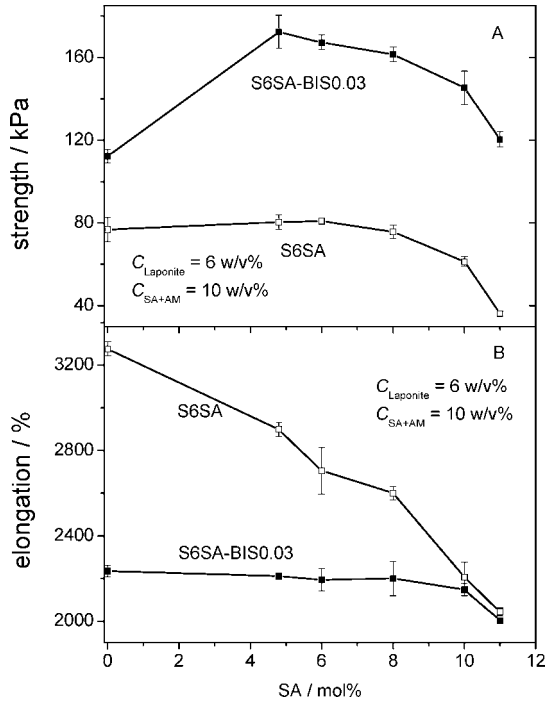

Figure 7. Ionic unit SA concentration dependence of (A) the tensile strength and (B) elongation at break for S6SA and S6SA-BIS0.03 NC gels at constant total monomer concentration of 10% w/v.

Figure 6 demonstrates the stress−strain curves for some as-prepared NC gels containing different amounts of ionic monomer SA with or without co-cross-linker BIS as examples. The OR gels without Laponite are brittle and cannot be elongated. These curves are similar to those of the NC gels without SA.[13] The SA concentration dependence of the tensile strength and elongation at break is shown in Figure 7 for the as-prepared NC gels of 6% w/v of Laponite RDS at constant total monomer concentration of 10% w/v with or without BIS. When the SA concentration was higher than 0.15 M (11 mol % in all monomers), the viscosity of the reaction suspension became too high to obtain homogeneous NC gels. Therefore, the SA concentration of this work was restricted to within 0.15 M. The tensile strength of the NC gels with 0.03 mol % of BIS is obviously higher than that of the NC gels without BIS; however, the elongation for the former is lower than that for the latter because of the additional cross-linking effect of BIS. It appears that incorporating a bit of BIS increases the homogeneity of the NC gel, which is known from the increased transparency in Figure 5B. Therefore, the addition of a minute amount of co-

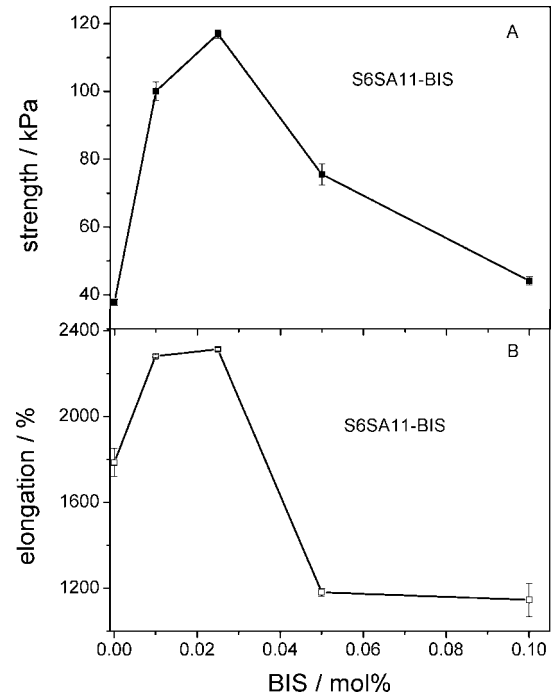

Figure 8. Tensile strength and elongation at break of S6SA11-BIS gels as a function of BIS mole fraction in all monomers.

cross-linker BIS improves the strength of the ionic NC gels by increasing their homogeneity.

It is interesting that there is a maximum in the tensile strength but a monotonic decrease in the elongation for the ionic NC gels with increasing SA concentration. The addition of ionic monomer SA to the reaction suspension causes instability and aggregation of the Laponite platelets because of the reduction of the ζ potential, which results in translucent and heterogeneous NC gels. This heterogeneous structure is the origin of the decrease in strength and elongation with increasing SA content. The existence of a few BIS molecules appears to maintain the Laponite suspension stability, consequently leading to homogeneous NC gels. Haraguchi et al. found that the addition of BIS and NIPAm to 4 wt % of Laponite XLG suspension depressed the viscosity increment, and this depressing effect was stronger for BIS than NIPAm.[26] They considered that the clay platelets were surrounded more effectively by BIS than by NIPAm. Therefore, BIS is helpful for preparing homogeneous ionic NC gels. For comparison, we also synthesized the OR0.03 gel cross-linked with 0.03 mol % of BIS, and its tensile strength was only 25 kPa. These facts indicate that the addition of 0.03 mol % of BIS plays only a supplementary cross-linking role and cannot replace the cross-linking effect of the Laponite platelets in the NC gels.

Figure 8 depicts the influence of the co-cross-linker BIS concentration on the tensile strength and elongation at break for the ionic NC gels. The ionic NC gels with a bit of BIS in the reaction suspension manifest higher strength and higher elongation. However, excessive BIS induces a decrease in strength and elongation. As discussed above, a small amount of BIS in the reaction suspension enhances the homogeneity of the ionic NC gels, leading to an improvement in their mechanical and optical properties. Superfluous BIS in the NC gel produces high cross-linking density and very long relaxation time, which cause the NC gels to be brittle like the OR gels without Laponite.

Relaxation and Effective Network Chain Density. To understand the effect of BIS on strength of the ionic NC gels, we evaluated the effective network chain density and relaxation in these gels. First, we tested the shear strain, γ, dependence of

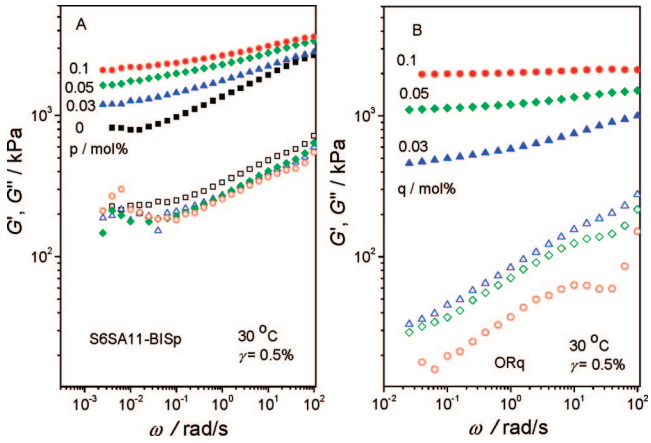

Figure 9. Angular frequency, ω, dependence of storage modulus G' (solid symbol) and loss modulus G'' (open symbol) at 30 °C for the gels (A) S6SA11-BISp and (B) ORq with indicated mole percent of p and q.

the complex modulus, G^*, at 30 °C and 1 rad/s to determine the linear viscoelasticity region. The absolute value of G^* was independent of γ over the range from 0.1 to 10% for all of the samples. Therefore, the viscoelastic measurements were carried out at $\gamma = 0.5\%$ to ensure availability of the linear viscoelasticity and enough sensitivity.

Figure 9A depicts angular frequency, ω, dependence of the storage modulus, G', and loss modulus, G'', for the S6SA11-BIS gels with a comparison of different BIS contents. For comparison, the similar results for the OR gels are included in Figure 9B. At high frequencies, G' of the S6SA11-BIS gels is higher than that of the corresponding OR gels containing the same amount of BIS, whereas at low frequencies, G' for the former is almost the same as the latter. This means that the relaxation occurs at low frequencies for the network chains in the NC gels, unlike the plateau behavior of the OR gels. For the gels containing 0.03 mol % of BIS, the ionic NC gel shows G' to be much higher than that of the OR0.03 gel in the plateau region. The above facts imply that the addition of Laponite platelets increases the modulus of the ionic gels to fast deformation, which can be relaxed to some extent during slow deformation. For the ionic NC gels with BIS lower than 0.05 mol %, the Laponite contributes more to the cross-linking than BIS.

Therefore, the relaxation modulus $G(t)$ is significant for understanding the relaxation behavior in the ionic NC gels. We have reported that the network chain relaxation for the NC gels of polyacrylamide without charged monomers is moderate, which contributes to the ultrahigh tensibility of the NC gels because the network chains bridging neighboring Laponite platelets adjust their orientation and distribution.[13] In the present case, the addition of chemical cross-linker BIS postpones the network chain relaxation in the ionic NC gels of S6SA11-BIS (Figure 10). In contrast, for the OR0.1 gel without Laponite, almost no relaxation can be observed during the experimental time interval.

We fit the relaxation data according to eq 1[27,28] and estimated the exponent n.

$$G(t) = G_e[1 + (t/\lambda_0)^{-n}] \quad (1)$$

Here G_e is the equilibrium modulus and λ_0 is a material-dependent time constant. For the NC gels shown in Figure 10, the n value decreases from 0.18 to 0.10 with increasing BIS content in the gel. Moreover, the relaxation exponent, n, for the S6SA11-BIS gels with co-cross-linker BIS is obviously smaller than that for the S6SA11 gel without BIS ($p = 0$). These

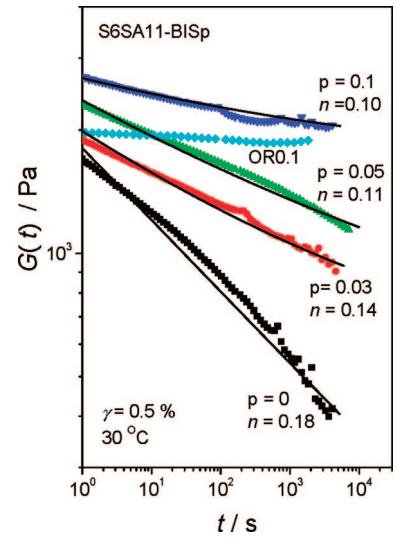

Figure 10. Relaxation modulus $G(t)$ of S6SA11-BISp NC gels with indicated p compared with OR0.1 gel at 30 °C. The solid lines are the numerical fit by eq 1 with indicated n.

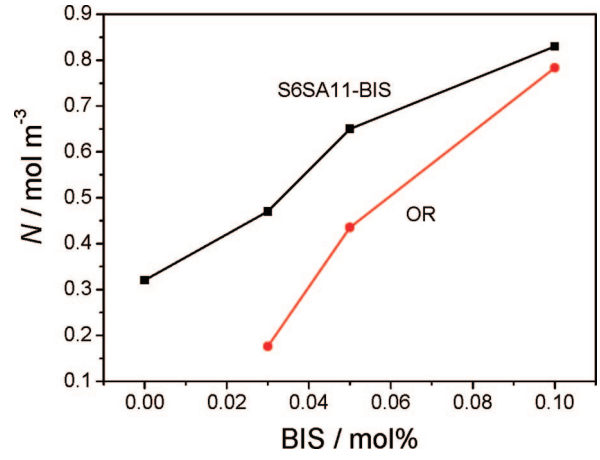

Figure 11. Effective network chain density, N, calculated from equilibrium shear modulus varying with BIS concentration for the S6SA11-BIS gels (■) and OR gels (●).

facts suggest that the addition of BIS would cumber the network chain relaxation in the ionic NC gels. Nevertheless, as long as the BIS content is not higher than 0.05 mol %, the network chains will still keep the moderate relaxation, and the n value is similar to that of the slightly cross-linked natural rubber ($n = 0.12$ to 0.17). When the BIS content is 0.1 mol %, the network chain relaxation is restricted with the relaxation exponent, n, of 0.10. The relaxation behavior demonstrates again that a minute amount of BIS (≤0.05 mol %) benefits the formation of a more elastic network. When the BIS content is greater than 0.05 mol %, the strength of the ionic NC gels steeply decreases (Figure 8) because of the restriction to the network chain mobility.

We estimated the effective network chain density, N, on the basis of the equilibrium shear modulus,[13] G_e, as $G_e = NRT$, and the results are plotted in Figure 11 against the BIS concentration in all monomers. As expected, the effective network chain density, N, increases with increasing BIS concentration. N for the ionic NC gel S6SA11-BIS is higher than that of the OR gels because of the cross-linking effect of the Laponite platelets. At high BIS concentration, the BIS dominates the cross-linking in the NC gels, and the contribution of the Laponite to the cross-linking is gradually weakened.

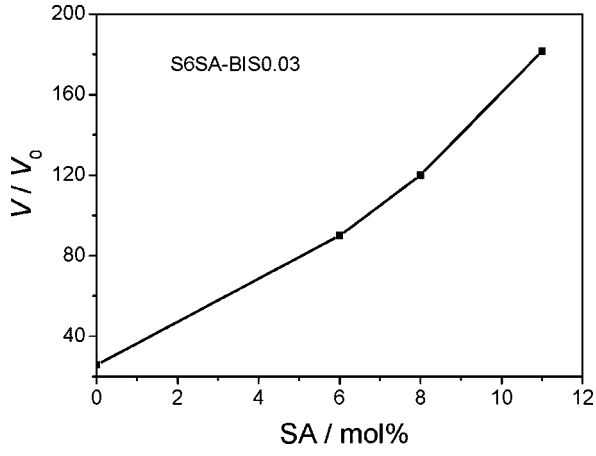

Figure 12. Equilibrium swelling ratio V/V_0 of the S6SA-BIS0.03 gels in pure water at room temperature varying with SA concentration.

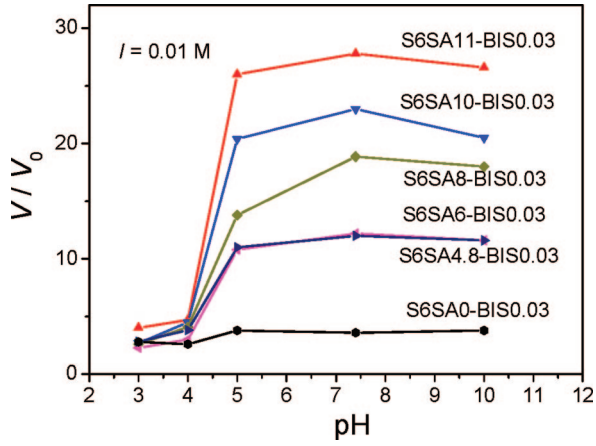

Figure 13. Equilibrium swelling ratio V/V_0 for the S6SA-BIS0.03 gels in buffers ($I = 0.01$ M) at room temperature.

Swelling Behavior and Nimble pH Response. We determined the equilibrium swelling ratio V/V_0 of the S6SA and S6SA-BIS0.03 gels in pure water. The swelling for the S6SA gels without BIS was so high that the gels become invisible in water under the microscope after swelling. Therefore, the swelling ratio of the S6SA gels without BIS cannot be determined with the microscope, and only the V/V_0 data for the ionic NC gels with BIS are plotted against the SA concentration in Figure 12. As expected from the well-known swelling behavior of polyelectrolyte hydrogels, V/V_0 increases almost linearly with increasing SA concentration owing to the increase in concentration of mobile counterions and electrostatic repulsion in the gels, which raise the osmotic pressure in the ionic NC gels. The above swelling behavior also indicates that the ionic monomer SA has been copolymerized in the NC gels.

To reveal the pH response of the ionic NC gels, the swelling equilibrium was conducted in buffers of different pH at fixed ionic strength, I, of 0.01 M and at room temperature. Figure 13 represents the equilibrium swelling ratio, V/V_0, for the S6SA-BIS0.03 gels containing various amounts of SA as a function of pH. The swelling ratio abruptly increases at pH 4 to 5 for the NC gels containing ionic SA units, which is consistent with the swelling behavior of poly(acrylic acid) gels because the carboxyl acid groups in the NC gels ionize at pH higher than 4.3. The higher the SA content in the NC gel, the higher the swelling ratio becomes. This fact confirms again that the present NC gels are polyelectrolyte hydrogels containing ionizible SA

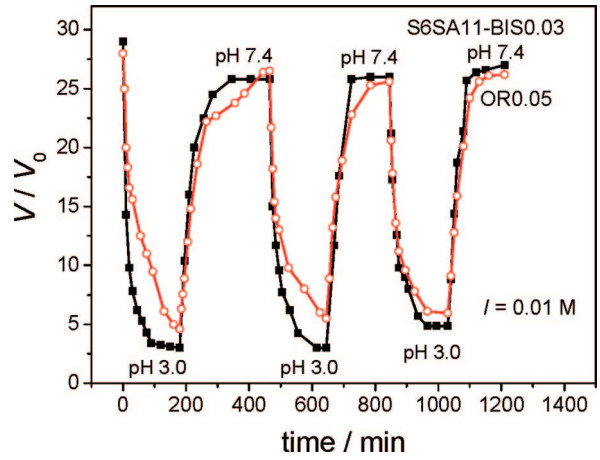

Figure 14. Oscillatory swelling−shrinking behavior of the S6SA11-BIS0.03 gel and OR0.05 gel containing 11 mol % of SA upon pH switching between 7.4 and 3.0.

units, except for S6SA0-BIS0.03. The gel S6SA0-BIS0.03 swells a little regardless of pH change because it contains no ionic SA unit.

The nimble pH response of the NC gels containing ionizible SA units can be further demonstrated with oscillatory swelling−shrinking behavior. Figure 14 illustrates the oscillatory swelling−shrinking behavior of the S6SA11-BIS0.03 gel switched by pH between 7.4 and 3.0. The OR0.05 gel containing the same amount of AM and SA cross-linked with 0.05 mol % of BIS instead of Laponite is taken to be a reference. At pH 7.4, both hydrogels swell because of ionization of the carboxyl groups, whereas at pH 3.0, they shrink because of association of the carboxyl groups. Similar oscillatory swelling−shrinking behavior for both gels means that the ionic NC gels respond to the repeat pH change as well as the carboxylate hydrogels merely cross-linked with BIS, but the former has ultrahigh tensibility of over 2000%.

4. Conclusions

Novel pH-sensitive NC gel with excellent tensibility (elongation >2000%) and high transparency (>90%) was synthesized by in situ copolymerization of AM and SA (up to 11.0 mol %) in aqueous Laponite RDS suspension with a bit of co-cross-linker BIS. The addition of ionic monomer SA to the Laponite suspension reduced the ζ potential and stability of the suspension. The tensile strength and elongation at break of these ionic NC gels obviously decreased when SA was greater than 10 mol % in the monomers. Interestingly, the addition of a minute amount of BIS (≤0.05 mol %) enhanced the homogeneity of the ionic NC gels and thus improved their transparency, tensile strength, and elongation. Moderate relaxation like that of the nature rubber was observed from the ionic NC gels and considered to be the origin of the ultrahigh tensibility. Fortunately, the nimble pH response still remained in the present NC gels containing SA units.

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Supporting Information Available: SA concentration dependence of pH for the Laponite suspensions. This material is available free of charge via the Internet at http://pubs.acs.org.

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