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Linear versus Dendritic Molecular Binders for Hydrogel Network Formation with Clay Nanosheets: Studies with ABA Triblock Copolyethers Carrying Guanidinium Ion Pendants

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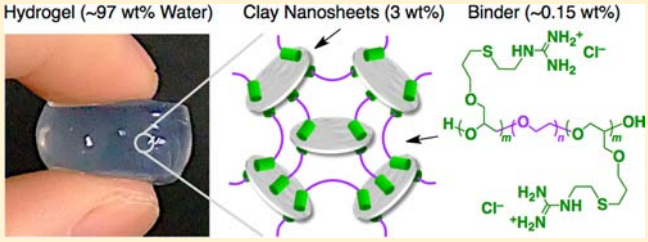
Supporting Information

ABSTRACT: ABA-triblock copolyethers **1a**−**1c** as linear polymeric binders, in combination with clay nanosheets (CNSs), afford high-water-content moldable supramolecular hydrogels with excellent mechanical properties by constructing a well-developed crosslinked network in water. The linear binders carry in their terminal A blocks guanidinium ion (Gu^+) pendants for adhesion to the CNS surface, while their central B block comprises poly(ethylene oxide) (PEO) that serves as a flexible linker for adhered CNSs. Although previously reported dendritic binder **2** requires multistep synthesis and purification, the linear binders can be obtained in sizable quantities from readily available starting materials by controlled polymerization. Together with dendritic reference **2**, the modular nature of compounds **1a**−**1c** with different numbers of Gu^+ pendants and PEO linker lengths allowed for investigating how their structural parameters affect the gel network formation and hydrogel properties. The newly obtained hydrogels are mechanically as tough as that with **2**, although the hydrogelation takes place more slowly. Irrespective of which binder is used, the supramolecular gel network has a shape memory feature upon drying followed by rewetting, and the gelling water can be freely replaced with ionic liquids and organic fluids, affording novel clay-reinforced iono- and organogels, respectively.



1. INTRODUCTION

With increasing demand for human and environment friendly renewable materials, particular attention has been focused on water-based soft materials such as hydrogels.[1] Hydrogels are classified into two categories depending on whether the crosslinked gel network that accommodates water molecules forms covalently[2−4] or noncovalently.[5,6] Covalent hydrogels are mostly brittle and not transparent due to structural heterogeneity.[7] Notable exceptions include double-network hydrogels, which possess extraordinary mechanical properties realized by interlocking two covalently crosslinked polymer networks.[3a,c,d] Nanocomposite hydrogels, whose crosslinked network is formed by hybridization of in situ generated polymer chains with clay nanosheets (CNSs), are also an exception, capable of displaying excellent mechanical properties and optical transparency.[4] However, despite such attractive physical properties, preparation of these hydrogels requires elaborate skills for controlling in situ polymerization. In contrast with covalent hydrogels, noncovalent hydrogels,[5,6] which are often referred to as supramolecular hydrogels, are readily prepared on-site by simply mixing necessary components in water. However, in general, supramolecular hydrogels are mechanically weak and not moldable into self-standing objects.

Quite recently, we reported a new class of supramolecular hydrogels,[8] which we often call 'aqua materials' for convenient differentiation from other supramolecular hydrogels. Aqua materials are characterized by their large mechanical properties, despite a high content of water (95−98 wt %) and an ultralow content of organic components (~0.2 wt %), and can be molded into self-standing objects. Therefore, new applications that have never been considered for conventional supramolecular hydrogels could emerge.[8,9] For preparation, typically CNSs (Laponite XLG, 2.0 wt %), dispersed beforehand in water with a minute amount of sodium polyacrylate (ASAP, 0.05 wt %), are mixed with dendritic molecular binder **2** (0.15 wt %). Binder **2** comprises a long poly(ethylene oxide) (PEO) linker that carries at its both termini water-soluble dendron units decorated at their periphery with multiple guanidinium ion (Gu^+) pendants. Since the CNS surface is full of oxyanions, CNS_{ASAP} (CNSs dispersed with ASAP) and **2** strongly interact via a multivalent salt-bridge formation involving hydrogen-

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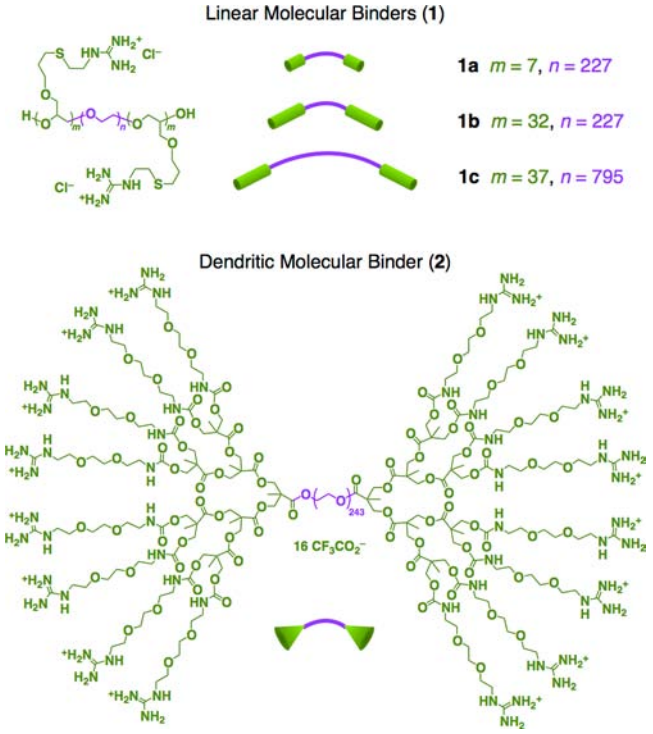
bonding and electrostatic interactions,[10,11] thereby affording a stable and well-developed crosslinked network. Consequently, a mechanically tough and self-reparable supramolecular hydrogel quickly forms. Although this hydrogel has numerous advantages, synthesis of dendritic binder **2** is a challenge, as is commonly recognized for dendritic compounds. This essential problem may hamper practical applications of "aqua materials".

Here we report a family of nondendritic molecular binders for crosslinking CNS_{ASAP} in water to afford supramolecular hydrogels. New binders **1a**−**1c** are water-soluble ABA triblock copolyethers,[12] where the terminal A blocks carry Gu^+ pendants at their side-chain termini, while the central B block, in analogy with dendritic **2**, comprises a flexible PEO linker. Advantageously, binders **1a**−**1c** are readily available and in contrast to **2**, their fundamental structure can be prepared by controlled ring-opening polymerization of allyl glycidyl ether using a PEO-dialkoxide macromolecular initiator.[12] The new linear binders were shown to form supramolecular hydrogels rapidly upon mixing in water with their oxyanionic analogues having sulfate pendants in the terminal A blocks.[12] Although their mechanical properties are similar to other supramolecular hydrogels so far reported, the hydrogels are characterized by a well-defined coacervate structure with a body-centered cubic lattice. In the present paper, we report results of our studies on the hydrogelation by combining linear **1a**−**1c**, together with dendritic reference **2**, with CNSs and discuss about crucial parameters for achieving efficient hydrogelation and excellent hydrogel properties. We also highlight that the hydrogel networks with **1** and **2**, though noncovalently constructed, are strong enough for exchange and removal of incorporated water.



2. RESULTS AND DISCUSSION

2.1. Hydrogelation and Mechanical Properties. Linear binders **1a**−**1c** were synthesized according to the following steps in multigram quantities:[12] (i) anionic ring-opening polymerization of allyl glycidyl ether from a bifunctional PEO macroinitiator with potassium alkoxide termini, (ii) thiol−ene reaction of the side-chain double bonds to introduce amino groups, and (iii) conversion of the amino groups into Gu^+ pendants. The average numbers of the repeating units for the A/B/A blocks and polydispersity indexes (PDI) were 7/227/7 and 1.13 for **1a**, 32/227/32 and 1.14 for **1b**, and 37/795/37 and 1.20 for **1c**.

Under conditions otherwise identical to those using dendritic **2**, linear binders **1a**−**1c**, upon mixing with well-dispersed CNS_{ASAP} in water, brought about hydrogelation (Figure 1a).

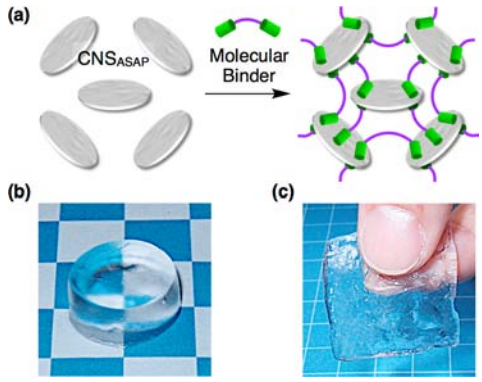


Figure 1. Hydrogelation by mixing CNSs and molecular binders in water. (a) Schematic representation of the mechanism of hydrogelation. (b,c) Pictures of supramolecular hydrogels ($[Gu^+]$ = 0.73 mM); CNS/ASAP/**1a** = 2.9/0.09/0.18 wt %.

Typically, to a stirred aqueous suspension (2.4 mL) of CNSs (60 mg) was added an aqueous solution (0.6 mL) of ASAP (DP = 17 000−22 000, 0.3 wt %) at 20 °C, and to the resultant aqueous dispersion of CNS_{ASAP} was added an aqueous dilute solution (0.15 mL) of **1a** (3.0 wt %) upon vortex stirring. After the addition of **1a**, the mixture was allowed to stand without stirring at 20 °C. In 10 min, the mixture lost its fluidity. While this frozen mixture was allowed to stand further, a certain amount of water (29 wt % with respect to the total amount of water) was expelled due to completion of the network formation. The resultant hydrogel was nearly transparent and capable of self-standing (Figure 1b,c). Similar observations were made when **1b** and **1c** were used as binders (Figure S1). Dispersion of CNSs with ASAP before mixing with binders **1** and **2** is essential. Otherwise, mechanically weak and translucent hydrogels result (Figure S2).

Next, we carried out rheological tests, where all hydrogel samples were allowed to stand at 20 °C for an extended period of time (70 h), in order for their crosslinked gel networks to develop fully. Hydrogel samples with CNS and ASAP contents of 2.9 and 0.09 wt %, respectively, and $[Gu^+]$ = 0.73 mM, prepared by taking into account the amount of water expelled, were employed for rheological tests. The CNS content chosen was moderate for better comparison of the performances of binders. As shown in Figure 2a, the rheological properties with **1a** as binder are similar to those with **2**, where storage (G') and loss moduli (G''), as a function of angular frequency (ω) at a fixed strain (γ) of 0.5%, display a single plateau region. Furthermore, over a wide frequency range (ω = 0.05−100 rad s^{-1}), the G' value remains larger than the G'' value, indicating that the hydrogel with **1a**, just like that with **2**, is elastic. Meanwhile, upon strain amplitude sweep at ω = 6.28 rad s^{-1} (Figure 2b), the G' value is larger than the G'' value when γ is smaller than 4%. However, when γ exceeds 4%, the G' value

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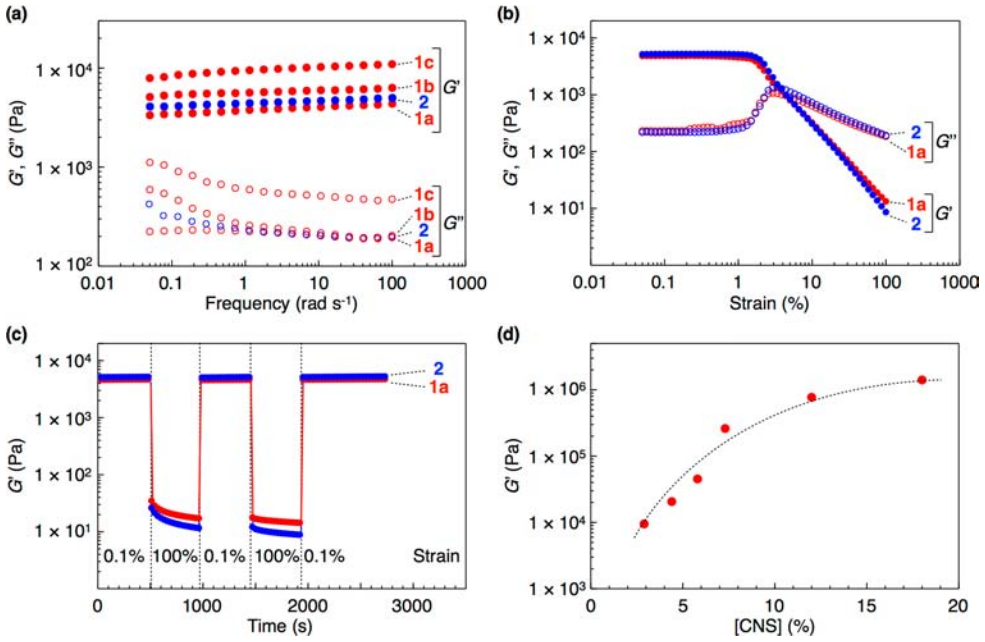

Figure 2. (a–c) G' and G'' values at 25 °C of supramolecular hydrogels ([Gu^+] = 0.73 mM); CNS/ASAP/binder = 2.9/0.09/0.18 wt % (**1a**), 2.9/0.09/0.10 wt % (**1b**), 2.9/0.09/0.15 wt % (**1c**), and 2.9/0.09/0.22 wt % (**2**). (a) Frequency (ω) sweep tests at ω = 0.05–100 rad s^{-1} and strain (γ) = 0.5%, (b) strain sweep tests at γ = 0.05–100% and ω = 6.28 rad s^{-1}, and (c) continuous step strain tests at γ = 0.1 and 100%. (d) G' values at 25 °C of supramolecular hydrogels with CNS/ASAP/**1c** = 100/3/5 (weight ratio) at [CNS] = 2.9–18.0 wt %.

drops more than the G'' value (G''/G': ~0.05 → ~10), indicating a breakdown of the gel network. One may notice that the G'' value increases as γ changes from 1% to 4% and then drops at γ > 4%. This tendency suggests that sliding of crosslinked CNSs precedes this breakdown event.[13] As shown in Figure 2c, such a gel-to-quasi liquid transition is completely reversible,[5b,6d,i,8] where the G' value is recovered rapidly within 20 s as soon as γ is reduced from, e.g., 100% to 0.1%. Thus, not only dendritic **2** as reported[8] but also newly designed linear **1a** allows such a rapid thixotropic response. The recovery process involves regeneration of the gel network. In relation to this, the hydrogel has a self-repairing nature macroscopically. As shown in Figure 3, a disk-shaped hydrogel was cut into two pieces,

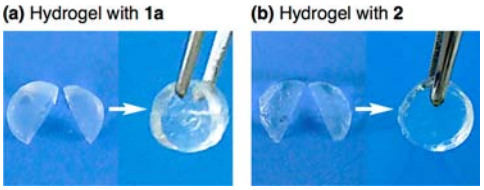

Figure 3. Self-repairing nature of supramolecular hydrogels ([Gu^+] = 0.73 mM); (a) CNS/ASAP/binder =2.9/0.09/0.18 wt % (**1a**) and (b) 2.9/0.09/0.22 wt % (**2**). Pictures before (left) and after (right) adhesion at freshly cut surfaces at 20 °C.

which were immediately held together to allow their freshly cut surfaces to self-heal, where the two pieces started merging and eventually reproduced a disk-shaped single object that was strong enough to hold when suspended or even shaken.[14]

In order to investigate how the number of Gu^+ pendants and PEO linker length affect the mechanical properties of the hydrogels, we performed frequency sweep tests for the hydrogels prepared with **1b** and **1c**. The PEO linker lengths of **1a** and **1b** are the same as one another (DP = 227), but the number of Gu^+ pendants of **1b** in each A block (32) is nearly 4.5 times greater than that of **1a** (7). As shown in Figure 2a, the G' value of the hydrogel prepared with **1b** is obviously larger than that with **1a**, indicating that the multivalency in the interaction between Gu^+ pendants and CNSs affects the stability of the gel network and therefore mechanical properties of the hydrogel. This trend is related to our previous observation that a higher-generation dendritic binder, carrying a larger number of Gu^+ pendants, provides a hydrogel with a greater mechanical strength.[8] However, unexpected was the observation made on the effect of the PEO linker length. While the number of the Gu^+ pendants of **1c** (37) in each A block is approximately the same as for **1b** (32), the PEO linker of **1c** is 3.5 times longer than that of **1b**. We initially thought that a longer linker would provide more flexible joints between CNSs, so that a weaker hydrogel may result. However, contrary to this prediction, the hydrogel prepared with **1c** displayed much larger G' and G'' values than those with **1b** (Figure 2a). This observation suggests that two adhesive parts of a binder, when separated by a shorter linker, may have a higher probability to adhere to the same CNS surface, resulting in a loop structure instead of the desired bridging CNSs motif (Figure 1a). By using **1c** as the best binder among **1a**–**1c** and **2**, we prepared hydrogels with higher CNS contents. As shown in Figure 2d, the mechanical strength of the hydrogel is greater as the CNS content is increased. Noteworthy, at a CNS content of 18 wt % (ASAP/**1c** = 0.5/0.9 wt %), a G' value of 1.5 MPa was achieved. We would like to emphasize that no other supramolecular hydrogel systems have been reported to achieve such a high mechanical strength.

2.2. Kinetics of Hydrogelation. Interestingly, we found that the binder architecture affects the rate of hydrogelation. For example, when dendritic binder **2** (0.15 wt %) was added at 20 °C to an aqueous dispersion of CNS_{ASAP} (CNS/ASAP = 2.0/0.06 wt %), the mixture lost its fluidity in only 2 min (Figure 4a, right). In contrast, when linear binder **1a** (0.13 wt %) was used instead of **2** under conditions otherwise identical

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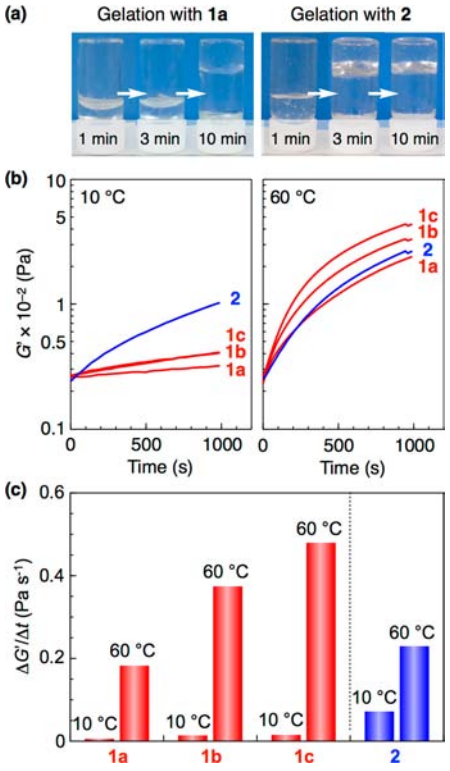

Figure 4. Kinetic aspects of hydrogelation. (a) Pictures of aqueous mixtures ([Gu^+] = 0.50 mM) of CNS, ASAP, and binder with ratios of 2.0/0.06/0.13 wt % (**1a**, left) and 2.0/0.06/0.15 wt % (**2**, right), when allowed to stand for 1, 3, and 10 min at 20 °C. (b) Changes in G' with time at 10 (left) and 60 °C (right) of aqueous mixtures ([Gu^+] = 0.50 mM) of CNS, ASAP, and binder with ratios of 2.0/0.06/0.13 wt % (**1a**), 2.0/0.06/0.06 wt % (**1b**), 2.0/0.06/0.10 wt % (**1c**), and 2.0/0.06/0.15 wt % (**2**). (c) Initial rates of hydrogelation ($\Delta G'/\Delta t$) at 10 and 60 °C of the aqueous mixtures in (b).

to the above, the fluidity of the mixture was lost in 10 min (Figure 4a, left). Accordingly, when the hydrogelation was conducted at 10 °C (Figure 4b, left), the G' values with **1a**−**1c** increased much more slowly than with dendritic **2**, where the initial rate of increase in G' value (Figure 4c) using **1a** ($\Delta G'/\Delta t = 0.6 \times 10^{-2}$ Pa s^{-1}), for example, was 13 times smaller than that with **2** ($\Delta G'/\Delta t = 7.2 \times 10^{-2}$ Pa s^{-1}). As already described, whether the binder is **1a** or **2** hardly affects the ultimate hydrogel toughness attainable (Figure 2a). Furthermore, whether its counterion is Cl^- or $CF_3CO_2^-$ does not essentially influence on the hydrogelation kinetics and mechanical hydrogel properties (Figures S3 and S4). Thus, the considerably large gap in $\Delta G'/\Delta t$ (Figure 4c) mostly reflects the kinetic aspect of the gel network formation. Namely, the dendritic end blocks present Gu^+ pendants with a more preferable fashion than the linear analogues, leading to the dramatic difference in kinetics for gel network formation. In dendritic **2**, the Gu^+ pendants located at its periphery are considered to have the highest availability for binding, hence they are ready for the salt-bridge forming interaction with CNS_{ASAP} (Figure 1a). In contrast, linear binders **1a**−**1c** certainly adopt a random-coil conformation, which would not allow all the Gu^+ pendants to be properly exposed for the salt-bridge formation. Meanwhile, upon heating to 60 °C (Figure 4b, right), the hydrogelation was accelerated irrespective of which binder was used. Noteworthy, the extents of acceleration with linear **1a**−**1c** were roughly 10 times larger than that with dendritic **2** (Figure 4c). Consequently, the apparent hydrogelation rates with **1a**−**1c** became comparable to or even greater than that with **2**. This trend may suggest that the linear binders adopt a larger temperature-dependent conformational change than the dendritic binder.

2.3. Conversion to Iono- and Organogels. Before the development of "aqua materials",[8] there has been a preconceived notion that supramolecular gel networks are dynamic and weak.[5,6] In fact, ordinary supramolecular hydrogels as well as organogels, upon heating, show a gel-to-sol transition. However, the supramolecular hydrogels with **1**, upon heating, did not show any sign of phase transition (Figures S5 and S6). In relation to the stability of the gel network, we found a rather intriguing phenomenon that a hydrogel, once formed, survives even when immersed in a concentrated (1.0 M) aqueous NaCl (Figure S7), although the hydrogelation is significantly interfered by electrolytes (Figure S8). From this observation, we envisioned that ionic liquids might replace the gelling water without deteriorating the supramolecular network. Thus, a disk-shaped hydrogel prepared with **1a** (CNS/ASAP/**1a** = 2.9/0.09/0.18 wt %) was immersed overnight at 20 °C in 1-butyl-3-methylimdazolium tetrafluoroborate ($BMImBF_4$), wherein an optically transparent, tough material containing $BMImBF_4$ resulted with a small volume contraction (Figure 5a,

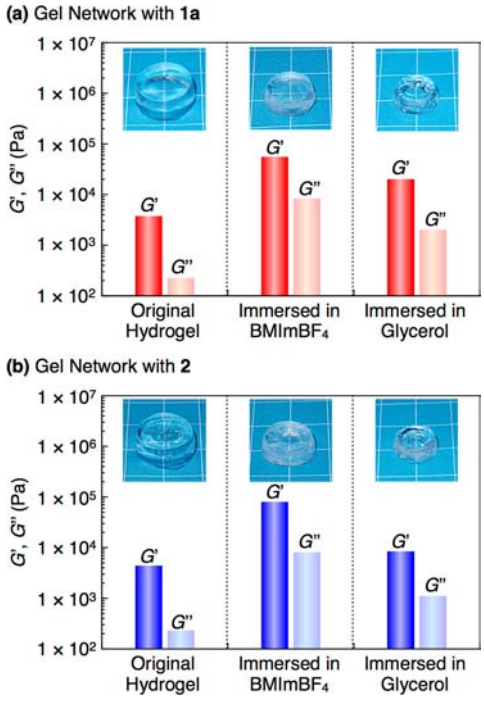

Figure 5. Conversion of supramolecular hydrogels ([Gu^+] = 0.73 mM) with ratios CNS/ASAP/binder of (a) 2.9/0.09/0.18 wt % (**1a**) and (b) 2.9/0.09/0.22 wt % (**2**) into iono- and organogels upon immersion in $BMImBF_4$ and glycerol, respectively. Pictures (insets) and G' and G'' values before and after the immersion overnight at 20 °C.

center). A rheological test on frequency (ω) sweep showed $G' > G''$ over a wide range of ω (0.05−100 rad s^{-1}), typical of gelatinous materials (Figure S9). Noteworthy, the G' and G'' values of this ionogel, respectively, were 15 and 37 times greater than those of the hydrogel precursor. Even upon continuous heating at 200 °C for 6 h, the ionogel did neither show a gel-to-sol phase transition (Figures S10 and S11) nor any weight loss.

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Using the hydrogel prepared with **2** as precursor, a tough ionogel likewise formed (Figure 5b, center). Note that such particular ionogels are not obtainable directly by mixing the binders with CNS_{ASAP} in $BMImBF_4$, since $BMImBF_4$ does not disperse CNSs.

Not only ionic liquids but also organic fluids, such as glycerol, can replace the gelling water, affording an optically transparent organogel (Figure 5a, right). Although a rather remarkable volume contraction took place, the resultant material maintained excellent gel properties such as $G' > G''$ in a frequency sweep test (ω = 0.05−100 rad s^{-1}, Figure S9), and its G' and G'' values were several times greater than those of the hydrogel precursor. Again, no gel-to-sol phase transition took place upon heating (Figures S10 and S11). Needless to say, without the hydrogel precursor, organogels, structurally supported by clay, are unavailable, since no organic fluids are able to disperse CNSs.

2.4. Shape Memory of Supramolecular Gel Network. In relation to the unusually high stability of the supramolecular gel network discussed above, we also found that this network has a shape memory feature even when the hydrogel is converted into a xerogel. For example, a heart-shaped hydrogel (Figure 6a, left) was prepared with **1a** (CNS/ASAP/**1a** = 2.9/0.09/0.18 wt %), and the gelling water was replaced with tetrahydrofuran (THF) for easier evaporation. The resultant organogel was then allowed to stand in air overnight at 20 °C, wherein a translucent, shrunken structure resulted (Figure 6a, center). When soaked in water at 20 °C, this xerogel was rapidly swollen to recover the heart shape and dimensions of the original hydrogel within 1 h (Figure 6a, right). Even though such a drying/rewetting cycle was repeated multiple times, the heart shape was always reproduced. The same held true when dendritic binder **2** was used instead of the linear binders (Figure 6b).

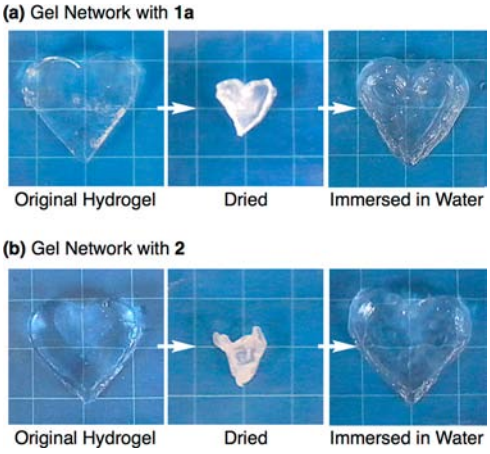

Figure 6. Shape memory profiles of supramolecular hydrogels ([Gu^+] = 0.73 wt %) with ratios CNS/ASAP/binder of (a) 2.9/0.09/0.18 wt % (**1a**) and (b) 2.9/0.09/0.22 wt % (**2**). Pictures before (left) and after (center) air-drying overnight at 20 °C and subsequent rewetting in water for 1 h at 20 °C (right). Prior to drying, the hydrogel samples were converted into organogels by immersion in THF overnight at 20 °C.

3. CONCLUSIONS

We demonstrated that water-soluble linear binders **1a**−**1c**, which comprise adhesive blocks attached to the termini of a flexible PEO linker block, are excellent alternatives to our previously reported dendritic binder **2** for the preparation of highly water-rich and ultralow organic content, moldable hydrogels, called "aqua materials".[8] The hydrogels, prepared by combining **1a**−**1c** with dispersed CNSs, display all of the attractive properties characteristic of the hydrogels with their dendritic analogue **2**, except that gelation takes longer at lower temperatures. This feature is particularly interesting, as it gives insight into the presentation of functional chain ends for dendrimers versus linear chains. In addition, the use of binder **1c** allowed looping due to the shorter PEO central blocks (**1a** and **1b**) as well as dendritic **2** to be minimized, leading to improved mechanical properties. Owing to the unusually stable gel network in ionic liquids and organic fluids, mechanically tough iono- and organogels, which are directly unavailable due to the nondispersibility of CNSs, can be prepared using our hydrogels as precursors. The macroscopic shape memory of the gel network, which is maintained upon solvent exchange and drying, is also noteworthy. With these observations and findings, this work may certainly promote "aqua materials" for many new applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures for hydrogelation and various analytical data of resultant hydrogels. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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