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Poly(*N*-isopropylacrylamide) Gel Prepared Using a Hydrophilic Polyrotaxane-Based Movable Cross-Linker

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ABSTRACT: A novel type of thermosensitive polymer gel was fabricated using a hydrophilic polyrotaxane as a movable cross-linker and *N*-isopropylacrylamide (NIPA) as a monomer. An optical transparence, mechanical softness, abnormal swelling capacity, and unprecedentedly fast thermosensitivity are among the salient features of this new polyNIPA gel in comparison with typical polyNIPA gels prepared by bifunctional cross-linker such as *N*,*N*′-methylenebisacrylamide (TN gels) and a previously reported polyNIPA gel using a hydrophobic polyrotaxane as a cross-linker. Whereas TN gels can take more than a day to undergo full deswelling in response to sudden temperature change, our new gel collapses in ∼10 min. The hydrophilicity and movability of the cross-linker contribute to these unprecedented properties of this thermosensitive polyNIPA gel. Moreover, this new type of cross-linker can be applied to any of the conventional gels made by radical polymerization and will likely improve the stimuli responses and mechanical properties of the gels.

Introduction

Thermosensitive poly(*N*-isopropylacrylamide) (polyNIPA) hydrogels that exhibit substantial and abrupt volume changes and hydrophilic and hydrophobic surface properties at ambient temperatures, which are attributable to the coil−globule transition of polyNIPA chains around the lower critical solution temperature (LCST), have received a great deal of interest for manifold applications, including drug delivery systems,[1] biosensors,[2] on−off switches,[3] artificial muscles,[4] biocatalysts,[5] and immobilization of enzymes.[6] Unfortunately, the inherent weak mechanical properties of these hydrogels caused by the underlying inhomogeneity of the polymer network and the extremely slow response due to critical slow down and vitrification during the shrinking process restrict the widespread use of the typical polyNIPA gel (TN gel: a polyNIPA gel prepared by the bifunctional cross-linker such as *N*,*N*′-methylenebisacrylamide (BIS)). There have been numerous attempts to obtain polyNIPA gels with adequate mechanical strength and a rapid shrinking characteristic. The various methods used to enhance the shrinking rate of polyNIPA gels include the preparation of hydrogels with a visually heterogeneous structure[7] or with a macroporous network based on the porosigen technique,[8] the introduction of a small amount of hydrophilic moieties into the gel network,[9] and the introduction of a large amount of freely mobile dangling chains into the gel network.[10] However, these methods may cause a loss of mechanical strength, gradual change in the volume, or a shift in the volume change temperature of the gels. It is highly desirable to obtain hydrogels capable of faster shrinking rates but with good mechanical properties and polyNIPA's characteristic temperature response; however, a method to achieve these goals still does not exist. Recently, we reported[11] the synthesis of a new type of polyNIPA gel using a small amount of a vinyl-modified polyrotaxane (PR) as the cross-linker. This gel exhibits very distinctive features in comparison with the TN gel, in that it is very soft and flexible, mechanically stable, and undergoes homothetic and fast deformation after a temperature jump. The gel demonstrates significant improvements over the TN gel, but because of the hydrophobicity of the cross-linker used; this gel has been reported to be macroscopically heterogeneous in aqueous medium in nature, becoming opaque.

In this study, we developed a water-soluble PR cross-linker and prepared an improved hydrogel in terms of optical property, temperature response, and so on. The equilibrium swelling behavior and shrinking kinetics of the gel were compared with the hydrogel prepared using the previously used hydrophobic PR as the cross-linker. The mechanical strength of the gel is similar to the previous one and is transparent in the swollen state as well as in the collapsed state in aqueous media. Additional features of this gel include an irregular volume change irrespective of the nature of the cross-linker and unprecedentedly rapid deswelling kinetics after sudden temperature changes. We propose a mechanism to correlate the swelling/shrinking behaviors and mechanical properties as a function of the nature of the cross-linkers.

Results and Discussion

The PRs[12−16] used in this study belong to two distinct categories: unmodified PR and hydroxypropylated polyrotaxane (HPR). (See Figure S1of the Supporting Information.) These have been used as starting materials for the preparation of hydrophobic and hydrophilic cross-linkers, respectively. The details of PR and HPR syntheses are reported in literature.[17,18] Because of the presence of strong inter- and intramolecular hydrogen bonds among the hydroxyl groups of α-CDs, PR is insoluble in most of the solvents and particularly insoluble in water. By contrast, the hydroxypropylation of PR weakens the hydrogen bonds between α-CDs and disperses α-CDs on the PEG chain, considerably improving the solubility of HPR, especially in water.[18] Having both isocyanate and vinyl groups

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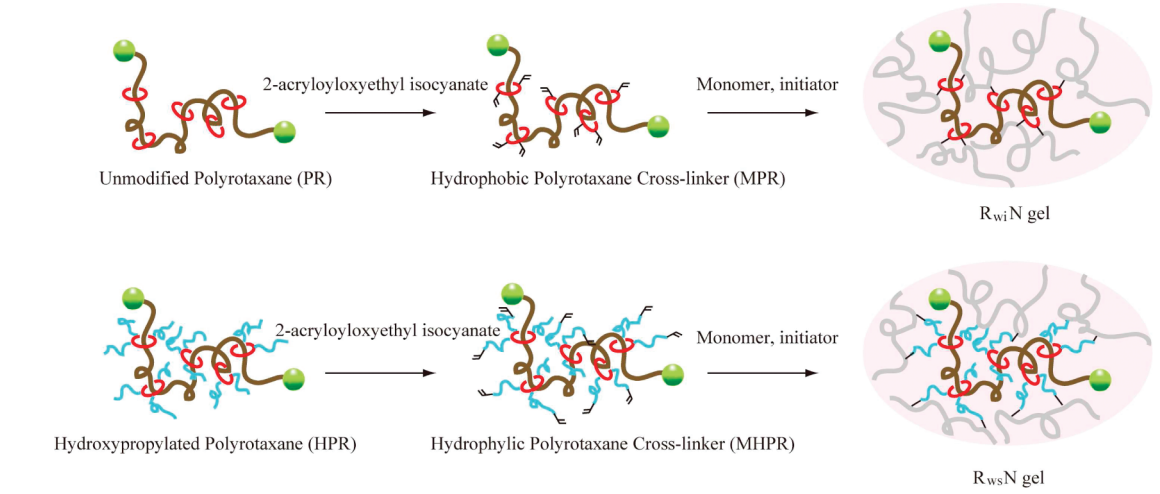
Scheme 1. Schematic Representation of the Preparation of Hydrophobic and Hydrophilic Polyrotaxane Cross-Linkers and Their Applications to the Preparation of RN gels in DMSO



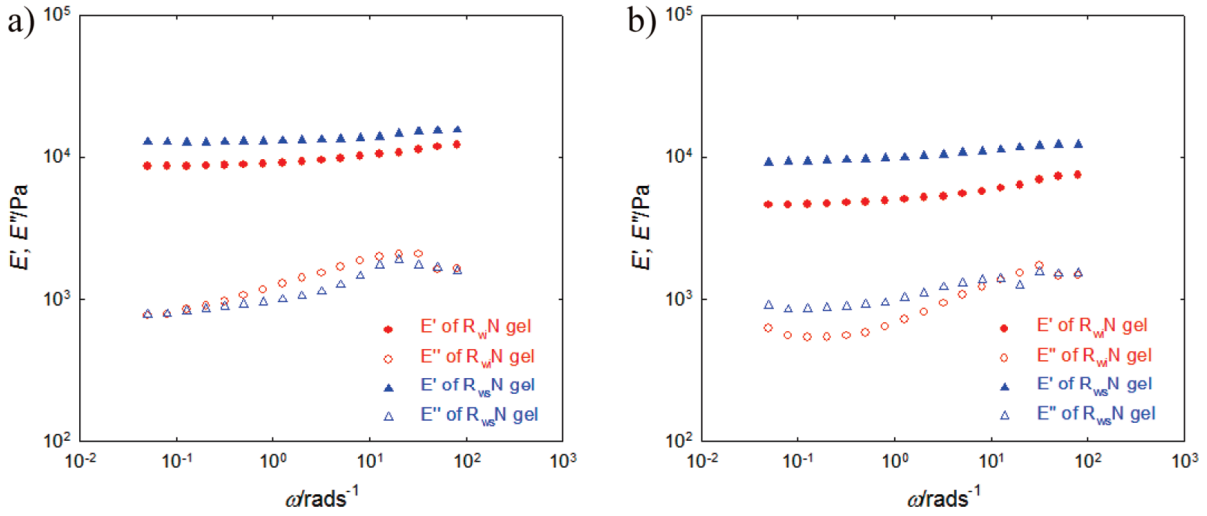


Figure 1. Strain-controlled dynamic frequency sweep test of storage moduli and loss moduli for $R_{wi}N$, and $R_{ws}N$ gels (a) in DMSO and (b) in water at 25 °C. The values of storage moduli, E' are always greater than loss moduli, E'', and the E'' values are not consistent in the frequency ranges; rather, transition peaks appeared at high frequencies for RN gels in either solvent.

in its parent structure, 2-acryloyloxyethyl isocyanate was used to modify PR and HPR. The isocyanate group forms a stable carbamate bond with a hydroxyl group of α-CD or hydroxypropylated α-CD to yield cross-linkers, which we refer to as MPR and MHPR, respectively. The degree of substitution (DS) ($0 \leq DS \leq 18$), that is, the average number of substituted hydroxyl groups per α-CD unit of MPR and MHPR, were determined to be 2.25 and 1.13, respectively, by ^{1}H NMR spectroscopy. (See Figures S4−S6 of the Supporting Information.)

PolyNIPA gels were prepared by conventional free radical polymerization of NIPA in the presence of MPR or MHPR cross-linkers in dimethyl sulfoxide (DMSO) (Scheme 1). These gels are denoted as $R_{wi}N$ and $R_{ws}N$ gels, where $R_{wi}N$ and $R_{ws}N$ stand for rotaxne-NIPA (RN) gels prepared by using the water-insoluble cross-linker (MPR) or water-soluble cross-linker (MHPR), respectively. The values of storage moduli, E', are always greater than loss moduli, E'', in the frequency range for both gels studied in DMSO and water, the findings that substantiate the formation of a stable polymer network inside the RN gels (Figure 1). The E' values are not consistent in the investigated frequency ranges; rather, transition peaks appeared at high frequencies for RN gels in both solvents. At high frequencies, the relaxation of the sliding cross-link points through the template long PEG chains is not favorable because of the decrease in mobility of the constitutive strands of the PR cross-linkers that provides a pronounced E'' peak for RN gels at the high-frequency region. Moreover, relaxation of the sliding cross-link points occurs with ease at low frequencies and consequently give low E'' values. Because in the RN gels, only a small amount of PRs was used as cross-linkers, the effect of solvent on the mechanical behaviors of the RN gels was not so prominent, unlike classical sliding gels.[19] The TN gel gives no transition peak in the viscoelastic regimes at high frequencies; the fixed cross-links do not permit the relaxation of polymer chains by equalizing their experienced tension. It is noteworthy to mention that the decrease in the E'' for TN gels at high frequencies thereby must arise from the micro to macro level damages of the network. Because the E' values for RN gels are smaller than those for TN gel in the whole frequency range (Figure S7 of the Supporting Information), the RN gels are softer and more flexible than the TN gel, which might also indicate the presence of dangling polymer chains in the RN gels network.[20]

Figure 2 shows the transmittance spectra of $R_{wi}N$ and $R_{ws}N$ gels in DMSO and water at 25 °C. The RN gels are highly transparent in DMSO in the visible wavelength region

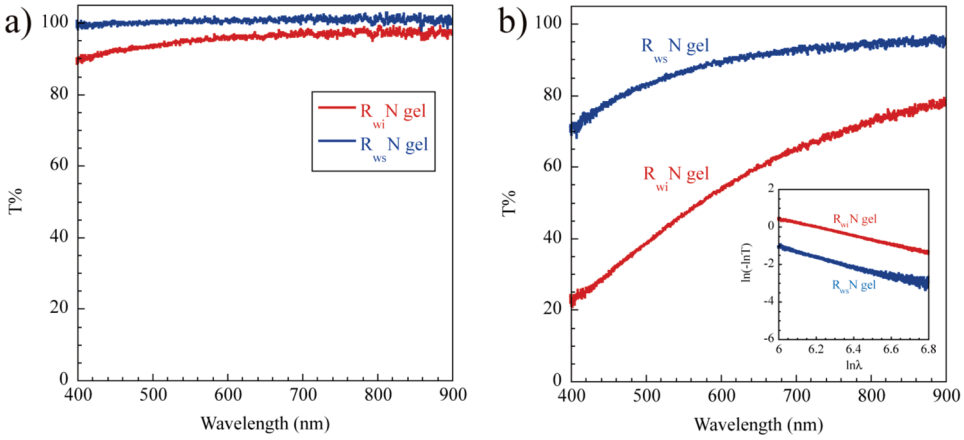


Figure 2. Changes in transmittance spectra of $R_{wi}N$ and $R_{ws}N$ gels in the visible light wavelength range (a) in DMSO and (b) in water at 25 °C. Inset in part b: plots of ln(−ln *T*) versus ln λ. The RN gels are highly transparent in DMSO, but in water, the transparency of the $R_{wi}N$ gel decreases remarkably, whereas the $R_{ws}N$ gel remains transparent.

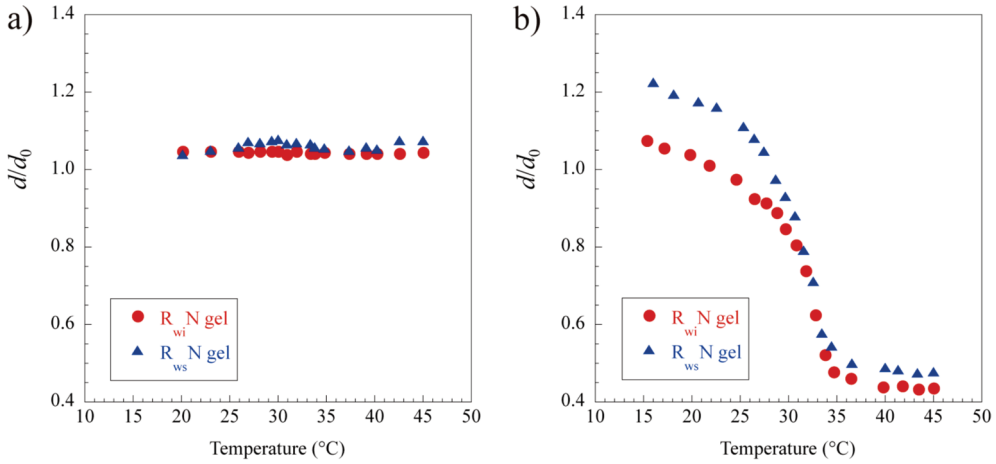


Figure 3. Equilibrium swelling ratio of cylindrical $R_{wi}N$ and $R_{ws}N$ gels (a) in DMSO and (b) in water as a function of temperature. The swelling ratios of the RN gels in DMSO are almost the same at most temperatures, which indicates the formation of similar 3D network structure. In water, increased hydrophilicity of the $R_{ws}N$ gel does not affect the volume change temperature.

(Figure 2a), which is indicative of the formation of visually or macroscopically homogeneous gel networks. When these gels are immersed and equilibrated in water, the transparency of the $R_{wi}N$ gel decreases markedly (Figure 2b), whereas the $R_{ws}N$ gel remains transparent. The water insolubility of MPR must induce local aggregation of the cross-linked polymer networks to form clusters in the highly cross-linked region. The clusters, being larger in size than the wavelength of visible light, can reflect visible light. The $R_{wi}N$ gel remains remarkably opaque in water. The presence of hydroxypropyl groups in MHPR reduces the formation of hydrogen bonds between α-CDs and increases their solubility in water. Therefore, aggregation of cross-linked polymer chains becomes unlikely, and the $R_{ws}N$ gel is transparent in both solvents. When light travels in a medium where the clusters are much smaller than the wavelength of visible light, Rayleigh scattering occurs, which is inversely proportional to the fourth power of the wavelength.[21] In light of this, shorter wavelengths will scatter more than longer wavelengths. Plots of ln(−ln *T*) versus ln λ for $R_{wi}N$ and $R_{ws}N$ gels (inset in Figure 2b) revealed straight lines with slopes of −2.39 and −2.84, respectively, indicating that these samples deviate from Rayleigh scattering. Because the sizes of the aggregated clusters are close to or greater than the wavelengths of visible light, Mie scattering occurs for both gels. Although the RN gels both exhibit Mie scattering, the $R_{ws}N$ gel has relatively smaller clusters.

As shown in Figure 3, the equilibrium swelling ratios d/d_0 of $R_{wi}N$ and $R_{ws}N$ gels in DMSO and water were plotted as a function of temperature. The swelling ratios of these gels in DMSO are almost the same at most temperatures; the gels must have a similar 3D network structure with the same amount of monomer and cross-linker. Analogous to TN gels, RN gels also have a sharp volume change in water around 32.0 °C because of the presence of LCST in the polyNIPA chains at that particular temperature. It is well-known that the subchains in these polymer networks must behave like Gaussian chains under the aforementioned preparation conditions.[22] The static conditions of the subchains in the equilibrium state of the gels can be measured from the lengths of the gels; that is, the linear expansion factor of the polymer chains (α) is equivalent to d/d_0. In the swollen state of the gels, α can be expressed by $\alpha \approx (Bn_0N)^{1/5}$, where *B* is the second virial coefficient describing the solvent quality, n_0 is the average monomer concentration within the network in the preparative state, and *N* is the total number of segments. The second virial coefficient *B* is related to the χ parameter, $B = v_m(^1/_2 - \chi)$, where v_m is the molar volume of the monomer.[23] On the basis of the composition for the pregel solutions and the swelling ratios for both gels swollen in DMSO, the resultant 3D structures of the polymer networks in these gels were expected to be almost identical; however, the $R_{ws}N$ gel has a higher swelling ratio than that of the $R_{wi}N$ gel at temperatures below the LCST in water. In contrast, when the gels are in their collapsed states,

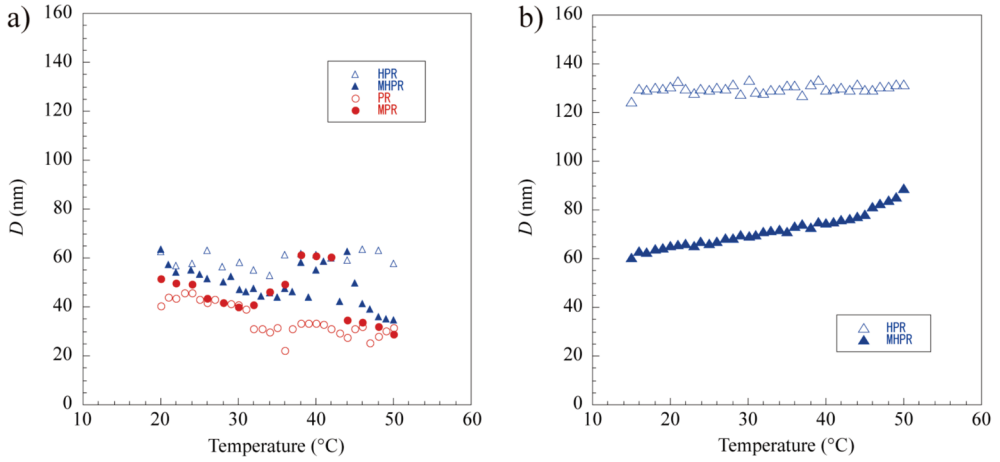


Figure 4. Temperature dependencies of particle sizes of each polyrotaxane (a) in DMSO and (b) in water. The sizes of PR and MPR in water are unmeasurable because of the deep turbidity of their aqueous solutions.

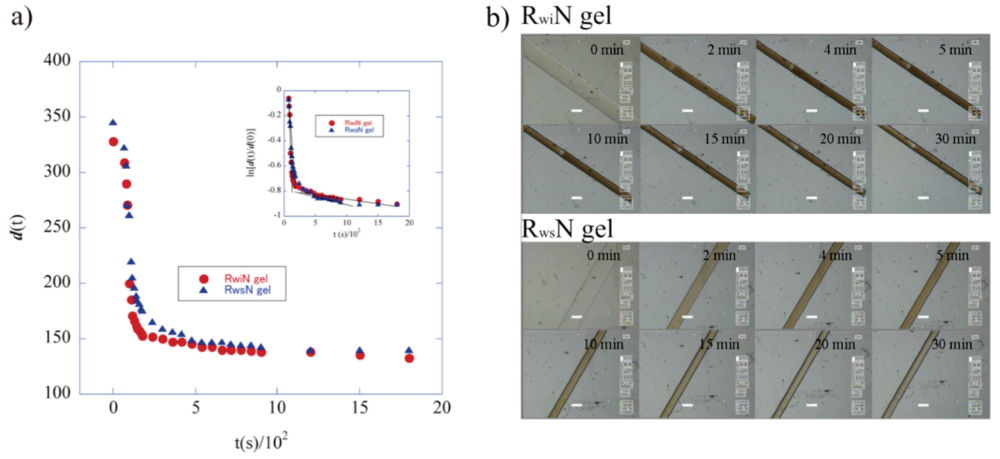


Figure 5. (a) Fast shrinking kinetics of cylindrical $R_{wi}N$ and $R_{ws}N$ hydrogels after a temperature jump from 20 to 40 °C. Inset in part a: plots of $\ln[d(t)/d(0)]$ versus t to calculate the relaxation times in different stages of the RN gels. The relaxation times were determined from the slopes $(-1/\tau)$ of each straight line in different stages. (b) Micrographs of morphological changes of cylindrical RN gels in water after a sudden temperature jump from 20 to 40 °C. Scale bar: 200 μm.

α can be expressed as $\alpha^{-3} \cong (-B/2Cn_0)$, where C is the third virial coefficient and accounts for three-body interactions.[21] Therefore, the swelling degree in the collapsed network depends on the number of monomers comprising a polymer network, whereas the length of a subchain does not affect the swelling ratio. In addition, we experimentally found that the swelling ratio of the $R_{ws}N$ gel is larger than that of the $R_{wi}N$ gel at temperatures above the LCST. With increasing temperatures, the water molecules might be expelled from the $R_{wi}N$ gel networks because of the hydrophobic flocculation of polyNIPA chains; however additional strongly bound water molecules in the hydrophilic moieties of the $R_{ws}N$ gels network cannot be easily emitted to give rise to a higher degree of swelling at high temperatures. Usually, when hydrophilic monomers, such as acrylic acid or acrylic amide,[24] are randomly copolymerized into the polyNIPA gel, an increase in the volume and the volume change temperature is observed. When hydrophilic groups are randomly attached to the polymer networks, water uptake by the gel network increases. To expel these additional physically bound water molecules from the gel networks, more energy is required, and an increase in the volume change temperature of the gel is apparent. By contrast, the copolymerization of hydrophobic monomers with NIPA leads to a smaller volume and a decreased volume change temperature. Interestingly, the swelling behaviors of random copolymer gels and graft or block copolymer gels, which are both composed of NIPA and hydrophilic monomers, are dramatically different.[24,25] The volume change temperatures of graft or block copolymer gels were reported to be similar to those of polyNIPA gels (TN gels) but have higher swelling ratios at all temperatures, which depends on the amount of hydrophilic polymers. The $R_{ws}N$ gel reveals the same swelling behaviors as the graft or block copolymer gels: the coil−globule transition of the polyNIPA chains in the $R_{ws}N$ gel should not be affected by the presence of the hydrophilic PR cross-linker. Because the same thing must go for the $R_{wi}N$ gel, the $R_{wi}N$ gel also has a sharp volume change in water around 32.0 °C. DLS measurements indicate that the sizes of these cross-linkers are almost the same (ca. 50 nm at 25 °C) in DMSO (Figure 4). The size of MHPR in water is slightly larger (ca. 65 nm at 25 °C) than that in DMSO, whereas the size of MPR in water is unmeasurable because of the deep turbidity of the aqueous solution. These results indicate that MHPR can be finely dispersed in water, whereas MPR is strongly flocculated in water. This facilitates a movement of the modified CDs of MHPR in water through the polyethylene glycol chains. The polyNIPA network inside the $R_{ws}N$ hydrogel relaxes because of the increased mobility of MHPR at higher temperatures to maintain the same volume change temperature.

Figure 5a demonstrates the $d(t)$ versus t curves of $R_{wi}N$ and $R_{ws}N$ gels after a temperature jump from 20 to 40 °C. The RN gels have a rapid deswelling rate and shrink isotropically without

creating any deformation on the gel surfaces (Figure 5b). The relaxation time τ was calculated from the plots of $\ln[d(t)/d(0)]$ versus t, assuming that the deswelling rate follows first-order kinetics.[7] Two stages of relaxation are observed for the RN gels during shrinking, although most of the volume shrinkages occur in the first stages. The first stage relaxation times, τ_1, for the $R_{wi}N$ and $R_{ws}N$ gels are (1.26 and 2.11) $\times 10^2$ sec, respectively, whereas the second stage relaxation times, τ_2, for the $R_{wi}N$ and $R_{ws}N$ gels are 1.27×10^4 and 6.10×10^3 sec, respectively. In the first stage, the RN gels were very close to reaching equilibrium shrunken states. In the second stage, the additional volume change for the $R_{wi}N$ gel occurs very slowly, and the gel retains its opacity for a longer time, indicating a macroscopic heterogeneity of the gel. In contrast, the $R_{ws}N$ gel reaches an equilibrium to the transparent shrunken state very quickly. The $R_{ws}N$ gel cannot be vitrescible during the collapse transition because of the presence of hydrophilic portions and the sufficient flexibility of the network, even at higher temperatures, whereas the $R_{wi}N$ gel reaches a nearly vitreous state in the second stage. The second relaxation stage for the $R_{ws}N$ gel may occur because of the final rearrangement of the aggregated nuclei to give a transparent and equilibrium shrunken state. The presence of the hydrophilic cross-linker must help with a smooth rearrangement to reach the final shrunken state. That is why the $R_{ws}N$ gel quickly reaches an equilibrium shrunken state without creating any deformation on the gel surfaces.

When a multifunctional cross-linker MPR or MHPR is used for gelation, the RN gels must not only have a cross-linked polymer network but also contain free and dangling polyNIPA chains attached to the active groups of the α-CDs of the cross-linkers. These dangling one-end free polyNIPA chains have less mechanical constraints. Even cross-linked polyNIPA chains in the $R_{wi}N$ and $R_{ws}N$ gels may exhibit higher degrees of freedom due to the flexibility of the polymer networks. After a temperature jump above the LCST of polyNIPA, the free dangling polyNIPA chains as well as the cross-linked polyNIPA chains of the $R_{ws}N$ gel can quickly collapse to form the shrunken state. The shrinking force developed from the dehydration of polyNIPA chains helps to aggregate the shrunken phase quickly because of the better movability of the cross-link points, even at high temperatures. Hydrophobic aggregation among shrunken phases then commences, forming larger nuclei and water-rich regions that simultaneously combine with one another to form a water channel to expel water quickly from the gel network. The deswelling proceeds via nucleation, but the gel does not enter the unstable spinodal region. The hydrophobic cross-linker MPR used for the synthesis of the $R_{wi}N$ gel exists in a collapsed state in water. Hence, the length of PEG chain for sliding of the macrocycles along the attached polymer chains decreases to some extent at higher temperatures. After the first stage of major collapsing for the $R_{wi}N$ gel, a pinned network structure is formed, and the shrinking speed markedly decreases in the second stage.

Conclusions

In this study, we observed faster shrinking kinetics for macroscopically homogeneous gels by using a multifunctional hydrophilic PR as the cross-linker, which contrast the generalized behavior of macroscopically homogeneous gels, which have slower shrinking kinetics compared with those of macroscopically inhomogeneous gels.[26] Whereas TN gels can take more than a day to undergo full deswelling in response to sudden temperature change (See Figure S8 and S9 of the Supporting Information), our new gel collapses in ~10 min. The hydrophilicity and movability of MHPR must have a variety of roles to enhance the rapid shrinking of the $R_{ws}N$ gel after a sudden temperature jump. This gel also has a very soft and mechanically stable nature, similar to that of the gel prepared by MPR. The softness and mechanical stability of the $R_{ws}N$ gel may also contribute to its use as biomaterials, because the softness of the gel will reduce its mechanical and frictional irritation to surrounding tissues. Moreover, this new type of cross-linker can be applied to any of the conventional hydrogels made by radical polymerization and will likely improve the stimuli responses and mechanical properties of the hydrogels.

Experimental Section

Material. Polyrotaxanes, PR or HPR (Advanced Softmaterials, Tokyo, Japan), were used without further purification. *N*-isopropylacrylamide (NIPA) (Kohjin, Tokyo, Japan) was purified by recrystallization from toluene/*n*-hexane. α,α′-Azoisobutyronitrile (AIBN) (Kanto Chemical, Japan), dibutylenetindilaurate (DBTDL) (Tokyo Kasei Kogyo, Japan), and butyl hydroxyl toluene (Tokyo Kasei Kogyo, Japan) were reagent-grade materials and were used as received, unless otherwise noted. 2-Acryloyloxyethyl isocyanate was purchased from Showa Denko K.K, Japan. Milli-Q ultrapure water was used throughout the experiments.

Preparation of MPR and MHPR. PR and HPR (500 mg), the catalyst DBTDL (1 drop), and butylhydroxy toluene (inhibitor, 0.78 mg) were dissolved in 30 mL of anhydrous DMSO. A solution of 2-acryloyloxyethyl isocyanate (78 mg) was dissolved in 10 mL of DMSO and added dropwise to the mixtures with vigorous stirring in the dark. The mixtures were then continuously stirred overnight at 40 °C to ensure completed reactions. MPR and MHPR were reprecipitated from the reaction mixtures using excess methanol and acetone, respectively, followed by refrigeration. The products were washed several times with methanol and acetone and then freeze-dried.

Preparation of Rotaxane-NIPA Gel. The RN gels were prepared by conventional free radical polymerization of the NIPA monomer with hydrophobic and hydrophilic PR cross-linkers. NIPA (1 M), 2.27 wt % MPR or MHPR, and 8.1 mM AIBN (initiator) were dissolved in anhydrous DMSO. Next, N_2 bubbling was passed through the pregel solutions for 30 min, followed by sonication to remove excess nitrogen from the solution. The pregel solution was infused to glass slides separated by Teflon spacers for the preparation of slab gels. Cylindrical gels were prepared using microcapillaries with an inner diameter of 270 μm. The gelations were carried out at 60 °C for 24 h. The gels were thoroughly washed with DMSO, followed by water for 2 weeks to remove any unreacted monomer or reaction residue.

Transmittance Spectra. The transmittance spectra were obtained using a QE65000 optical-fiber spectrometer (Ocean optics) equipped with a deuterium-halogen (Mikropack) lamp as the light source. The thicknesses of the slab gel samples were ~2 mm.

Equilibrium Swelling Ratio. The cylindrical gel was prepared in a microcapillary tube with a diameter of ca. 270 μm and then used for the measurements of the swelling ratio. The gel sample was immersed in a desired solvent in a glass cell surrounded by an air jacket. The temperature inside the cell was controlled by water flowing through the air jacket from a circulator. The sample was then equilibrated in a desired solvent at a specific temperature for a certain period. The change in volume of the cylindrical gel was monitored under an inverse microscope (Olympus CKX41) equipped with a color measuring unit (Flovel MC-70). The equilibrium swelling ratios, d/d_0, where d_0 is the diameter of the cylindrical gel at the preparative state and d is the diameter of an equilibrated cylindrical gel under specific conditions, was measured at various temperatures.

Setup for Shrinking Kinetics. The cylindrical gels were kept in a desired solvent in a glass cell. Two circulators fixed at two different target temperatures were connected to the glass cell. By changing the path of the solvent, we can quickly switch the temperature inside the cell from one temperature to another.

The temperature inside the cell was stable to ±0.2 °C over a few hours. The time for switching to reach the target temperature was about 70 ± 5 s. Videos of the morphological changes of the investigated gels were recorded using BUFFALO PCast TV capture software on a computer. Pictures were captured from the videos at different time intervals.

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Supporting Information Available: Experimental details of RSA, GPC, and DLS; information about PR and HPR; structures of PR, HPR, MPR, and MHPR; GPC profiles of PR, HPR, MPR and MHPR; ^{1}H NMR spectra of 2-acryloyloxyethyl isocyanate, PR, HPR, MPR, and MHPR in DMSO-d_6; strain-controlled dynamic frequency sweep test of storage moduli and loss moduli for the TN gel in DMSO; and morphological changes of the cylindrical TN gel and its slow shrinking kinetics after a sudden temperature jump. This information is available free of charge via the Internet at http://pubs.acs.org/.

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