A Novel Hydrogel Showing Super-Rapid Shrinking but Slow Swelling Behavior

Xinjiang Chen[†,‡] and Kaoru Tsujii*[,†,§]

Nanotechnology Research Center, Research Institute for Electronic Science, Hokkaido University, N-21, W-10, Kita-ku, Sapporo 001-0021, Japan; Graduate School of Science, Hokkaido University, N-10, W-8, Kita-ku, Sapporo 060-0810, Japan; and JST, CREST

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Phase transition phenomena in polymer gels have attracted much attention from the viewpoints of their scientific interest and technological significance. Thermoresponsive poly(*N*-isopropylacrylamide) (PNIPA) gel shows a volume phase transition at about 34 °C[1,2] (which is close to physiological temperature) and has a wide range of applications in biotechnology and medical fields.[3−5] Below the phase transition temperature, the hydrogel is in a swollen, hydrated, and hydrophilic state; above the phase transition temperature, on the other hand, the gel is in a dehydrated and collapsed one. The rate of the phase transition of PNIPA gel is quite slow resulting from the skin formation on the surface of the gel.[6] In order to obtain more rapid volume change around the phase transition temperature, several strategies have been adopted. By comb-type grafting,[7] PNIPA gel showed a rapid deswelling behavior due to the dehydrated grafted chains creating hydrophobic cores, which enhanced the hydrophobic aggregation of the networks. The copolymerized PNIPA-*co*-acrylic acid gels with more pores showed rapid swelling and deswelling properties by two-step preparation.[8] By incorporating silica particles into polymer networks to prepare porous PNIPA gels,[9] the deswelling process could be greatly enhanced. We have also reported that the swelling and collapsing speeds were greatly improved by introducing a kind of polymeric surfactant micelle into the PNIPA gel.[10]

As to our best knowledge, there is no report so far on the introduction of bilayer membranes into PNIPA gel to improve the volume phase transition rate. We herein present this novel method to ameliorate the shrinking property of the traditional PNIPA gel. A polymerizable nonionic surfactant, *n*-dodecyl glyceryl itaconate [DGI; *n*-$C_{12}H_{25}OCOCH_2C(=CH_2)COOCH_2$-$CH(OH)CH_2OH$], forms bilayer membranes (an iridescent lamellar liquid crystal) in water having the spacing distance of sub-micrometer in the presence of small amounts of ionic surfactant at the temperature above the Krafft point (43 °C).[11] However, this iridescent system is very fragile as environmental conditions change. When temperature decreases, DGI tends to crystallize from the iridescent solution and phase separation takes place. We have interestingly found that after polymerization the periodic structure of poly-DGI (PDGI) bilayer membranes is stable enough at room temperature for a long time. DGI forms onionlike multilayer lamellar vesicles in solution at 55 °C. After polymerization, the onionlike structure still exists, which is proved by the iridescent color. After introducing NIPA monomer and cross-linker, the system is polymerized at 4 °C. We synthesized PNIPA gel in the space of the compartments between the bilayer membranes to obtain this hybrid gel (PDGI−PNIPA gel) (see the Experimental Section in the Supporting Information). It is interesting to note that the PDGI−PNIPA hydrogel shows super-rapid shrinking behavior during the phase transition process; the volume shrinkage of 90% occurs, and the gel attains the complete collapsed state within 15 s. This hybrid gel turns to turbid at the very beginning of the phase transition but still exhibits the rapid shrinking. The phase transition temperature of PDGI−PNIPA is, interestingly, almost the same as that of pure PNIPA gel, and the swelling process of PDGI−PNIPA hybrid hydrogel takes a much longer time than the shrinking one.

The volume phase transition of the hybrid hydrogel was measured by calculating the value of V/V_c, where V and V_c are the gel volumes at the target temperature and at the highest temperature of the present experiment, respectively. It should be noted here[10] that V_c does not represent the volume of the completely collapsed state of pure PNIPA gel, since V and V_c were measured at intervals of 1 h and the samples were not necessarily in the equilibrium state. However, this situation gives little effect on the determination of the phase transition temperature. As shown in Figure 1a, the hybrid gel shows an abrupt volume change at the temperature close to the phase transition one of pure PNIPA gel, i.e., around 34 °C. The water absorbencies (V/V_c) of the PDGI−PNIPA gels are 4−5-fold greater than those of PNIPA gel, which are comparable with our previous result.[10]

The shrinking and swelling processes of the PDGI−PNIPA and PNIPA gels at 40 and 20 °C are shown in parts b and c of Figure 1, respectively. It is surprisingly worth noting that the PDGI−PNIPA hybrid hydrogel shows a very rapid phase transition. As one can see from the figure that, within 15 s, the volume change of PDGI−PNIPA hybrid hydrogel is as high as 90%, while the PNIPA gel shows a shrinkage only about 10%. The volume of the PDGI−PNIPA gel is almost constant after 15 s, showing the complete collapse of the network. In contrast, the volume of PNIPA gel is still decreasing even after 405 min, indicating the incomplete collapse of the gel. The so-called "ultra-rapid" phase transition of the PNIPA hydrogel reported so far shows a 70% shrinkage in 5 min.[12] We can call this PDGI−PNIPA hybrid gel with a shrinkage of 90% volume in 15 s as a super-rapid one. The video of this super-rapid shrinking process at intervals is available in the Supporting Information. The swelling process of PDGI−PNIPA is, interestingly, much slower, as can be seen from Figure 1c. For PNIPA gel in imperfect collapsed state, the volume can be recovered over 95% within 100 min, but for PDGI−PNIPA gel, 90% volume can be recovered in 160 min. The PDGI−PNIPA and the PNIPA gels recover the original sizes in 424 and 326 min, respectively. The PDGI−PNIPA gel does not show a rapid swelling behavior, which might be due to the formation of wrinkles of DGI bilayer membranes during the drastic volume shrinkage. The recovery of these plicate bilayer membranes of DGI may take time. The PDGI−PNIPA gel shows a super-rapid shrinking process but a rather slow swelling one during the phase transition. The volume changes of PDGI−PNIPA and PNIPA gel can be visually observed in Figure 2. For a PDGI−PNIPA gel, the cylinder dimensions of 1.55 × 15.5 mm (diameter × length) contract to 0.64 × 7.2 mm, with a volume shrinkage of about 90% just

† Research Institute for Electronic Science, Hokkaido University.
‡ Graduate School of Science, Hokkaido University.
§ JST, CREST.
* Corresponding author: Ph (+81)-11-706-9356; Fax (+81)-11-706-9357; e-mail tsujik@es.hokudai.ac.jp.

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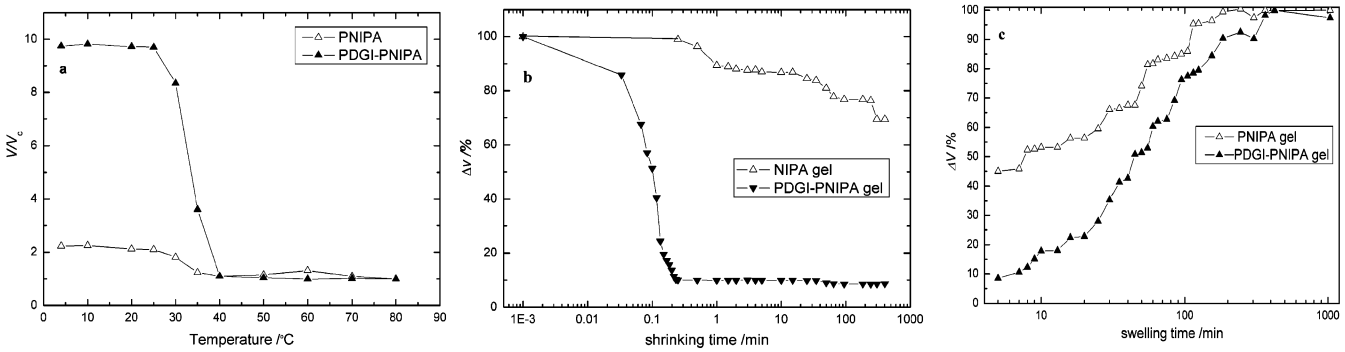

Figure 1. (a) Temperature dependence of shrinking volumes of the gels in pure water. Both PNIPA and PDGI−PNIPA gels show similar phase transition temperature at about 34 °C. Time dependence of the volume change of the PDGI−PNIPA and the PNIPA gels during shrinking (b) and swelling (c) processes, respectively. In the shrinking process, the samples were put directly into water at 40 °C; in the swelling process, the 1-day-shrunk gels were put back into water at 20 °C. ΔV was normalized by the size of the gels before phase transition as 100%.

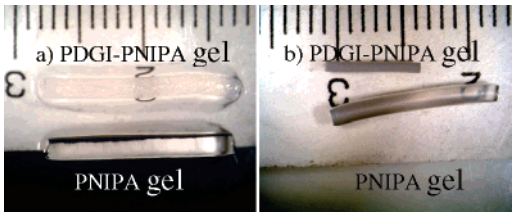

Figure 2. Photographs for hydorgels before (a) and after (b) phase transition at 40 °C. The pictures were taken within 1 min after the samples were put into the warm water (40 °C). The time was so short that the PNIPA gel did not form skin homogeneously yet. The background was changed from black to white in order to make the contrast clear before and after shrinking.

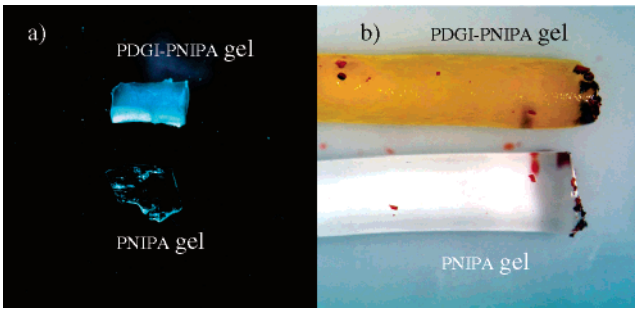

Figure 3. Images of PDGI−PNIPA and PNIPA gels under crossed polarizers (a). The upper image in (a) is PDGI−PNIPA gel and the bottom one is PNIPA gel. In the right photograph (b), the colored gel is PDGI−PNIPA and the colorless one is PNIPA gel. Both gels were kept in water containing Yellow AB crystals for 1 week at room temperature.

within 1 min; in contrast, a PNIPA gel shows a shrinkage from 1.49 × 14.6 mm to 1.43 × 14.3 mm; the volume change is only about 10%. The shrinking and swelling processes are completely reversible and do not show any hysteresis.

For PNIPA gel systems, even though the clear mechanism of rapid shrinking still remains uncertain, several reports have revealed that the rapid shrinkage results from the formation of micelle aggregates and/or clusters of incorporated constituents[10] or grafted side chains[2,13,14] of PNIPA gel during phase transition. It should be noted here that DGI is a kind of nonionic surfactant which forms lamellar bilayers instead of micelles in water phase. Sodium dodecyl sulfate (SDS) was added to DGI to prepare the iridescent system of bilayer membranes, but the gel samples were washed fully in water for a week to remove it. Furthermore, the shrinking and swelling processes were repeated several times before the tests (see the Experimental Section). The super-rapid volume change of the PDGI−PNIPA gel cannot be ascribed to any micellar aggregates or clusters.

It is well-known that the process of swelling and collapsing is collectively diffusion-limited, and their kinetics strongly depend on the sizes of the gels. For spherical gels, Tanaka[15] has shown that the characteristic time of gel swelling and shrinking is determined by the size, R, of the gel and the collective diffusion coefficient, D, of the polymer network as $\tau = R^2/D$. For typical polymer gels, D is on the order of 10^{-7}−10^{-6} cm^2/s, depending on polymer concentration, cross-linking density, etc. For the gels prepared by the same composition and method, one can assume D to be almost the same. By decreasing the size of the gel, the shrinking and swelling properties may be improved. The super-rapid shrinking behavior of PDGI−PNIPA gel can be supposed to have domains divided by PDGI bilayer membranes. By polymerizing DGI mesophase in the iridescent state, the bilayer structures maintain well even after PNIPA network is introduced between them. As shown in Figure 3a, when exposed to polarized light, PDGI−PNIPA gel shows a bright image while PNIPA gel is almost dark. It is evident from this photo that the DGI bilayer membranes (lamellar liquid crystal) still exist in the PDGI−PNIPA gel. When PDGI−PNIPA gel and PNIPA are immersed in water with the presence of an oil-soluble dye, Yellow AB crystals, PDGI−PNIPA gel shows yellowish color after a week while PNIPA gel is still colorless, as shown in Figure 3b. Yellow AB, which is insoluble in water but soluble in the hydrophobic moiety, penetrated into PDGI bilayer membranes and was solubilized there. By observing the hybrid gel with a laser confocal scanning microscope (LCSM) (differential interference contrast, DIC, mode), one can see the domains segmented by PDGI bilayer membranes, as shown in Figure 4. Since the images are observed at DIC mode, the difference of the contrast in the image shows the density and/or refractive index differences. The curved traces in the image may be ascribed to the boundary between the domains of PDGI bilayer membranes and the PNIPA gel phases. As a reference, the figure of simple PNIPA gel without PDGI is inserted. The onionlike multibilayer membrane structures with a diameter of about 20 μm in iridescent state are shown in Figure 2 in the Supporting Information. The LCSM image also give the size of these PDGI bilayer membranes segregated domains to be about 20 μm. The calculated characteristic time of swelling and shrinking by $\tau = R^2/D$ is 10 s, which is very close to our experimental results (15 s). The reason for the super-rapid shrinking but slow swelling behavior of this novel hybrid gel can be explained as follows: once it undergoes the phase transition, each PNIPA domain shrinks, but the PDGI bilayer membranes still keep the original structure for a while, which may favor to form interstices among these domains and facilitate the releasing of water in the gel. As the shrinking going on, the PDGI bilayer membranes are forced to be rumpled by the

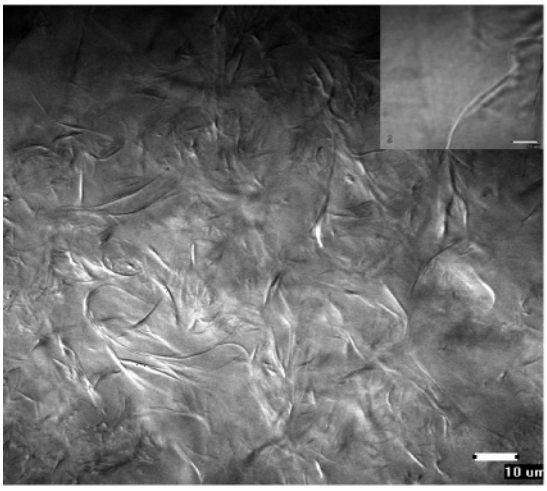

Figure 4. Photograph of laser confocal scanning microscopy of PDGI−PNIPA gel. From the curved traces, domains with the size of several tens of micrometers can be seen. The inserted figure shows the cross-section image of simple PNIPA gel; no domain can be found. (The mark left from cutting was specially chosen to show this is the cross section.) The scale bar is 10 μm.

surrounding PNIPA gel domains and the hybrid hydrogel attains the collapsed state. The crumpled bilayer membranes are not easily recovered to the original extended sheet,[16] and the swelling process of the gel may be slow.

In conclusion, we have successfully incorporated a polymerized nonionic bilayer system into PNIPA gel. This hybrid PDGI−PNIPA gel shows super-rapid shrinking during phase transition, which can be ascribed to the formation of domains of several tens of micrometers in the PDGI−PNIPA gel. The collective-diffusion-dominated phase transition can be greatly accelerated by these numerous independent domains. The PDGI bilayer membranes act as the role of not only dividing the PNIPA gel into numerous small domains but also forming interstices among these domains during drastic shrinking process. Probably because of the folding of PDGI bilayer membranes after the drastic volume shrinkage, the swelling process takes a longer time than the deswelling one. The introduction of polymer bilayer membranes into PNIPA gel provides a new strategy to improve the thermal response of traditional PNIPA gel.

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Supporting Information Available: Experimental details and scheme for the synthesis of PDGI−PNIPA gel, freeze fracture TEM image of iridescent DGI solution, the calculation of the vacant space in the DGI vesicle system, and the video of the super-rapid shrinking process. This material is available free of charge via the Internet at http://pubs.acs.org.

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