Polymer
Journal

Laser-Induced Reversible Volume Phase Transition of a Poly(*N*-isopropylacrylamide) Gel Explored by Raman Microspectroscopy

By Yasuyuki TSUBOI,* Masayuki NISHINO, and Noboru KITAMURA*

A micro-rod of poly(*N*-isopropylacrylamide) (PNIPAM) in a D_2O solvent undergoes reversible shrinkage/swelling induced by a focused near infrared (1064 nm) laser beam. Since the solvent is transparent at 1064 nm, the origin of the phenomenon is ascribed not to photothermal effects but completely to an interaction between the gel and the photon pressure generated by the laser beam. Features of this laser-induced shrinkage such as the dynamics and the effects of the combination of heat and photon pressure are clarified and compared with the normal thermo-responsive volume phase transition of a PNIPAM gel. The local structure of the rod of gel upon laser-induced shrinkage was investigated in detail by means of spatially-resolved micro-Raman spectroscopy. The Raman spectra obviously showed dehydration of the polymer chains around the shrunken area of the gel. As a result, the shrinkage was revealed to be a volume phase transition triggered by photon pressure. Furthermore, the fundamental mechanism for the laser-induced volume phase transition is discussed briefly on the basis of Flory-Rhener's model taking into account the χ parameter, which depends on the volume fraction of the polymer.
KEY WORDS: Optical Microscope / Infrared Laser Beam / Optical Trapping / Photon Pressure / Hydration / Dehydration / Thermo-responsive Polymer /

Poly(*N*-isopropylacrylamide) (PNIPAM) gel is a typical stimuli-responsive polymeric material. PNIPAM gels and their derivatives exhibit reversible volume phase transitions in aqueous solutions in response to changes in temperature, the chemical composition of the solvent, pH, hydrostatic pressure, and so on. For the thermo-responsive phase transition, PNIPAM gel is in a swollen phase below a critical temperature, and in a collapsed phase above the temperature.[1–4] The phase transition is governed by the energetic balance between the hydrophilic and hydrophobic interactions of the polymer chains. The fundamental mechanistic aspects and theoretical modeling of such a volume phase transition are of great interest, and have been developed on the basis of the theory of Flory-Rhener.[5,6] In addition to short-range weak interactions such as the hydrophilic/hydrophobic interactions and the role of the osmotic pressure, it has been experimentally demonstrated that long–range Coulomb forces between polymer chains induce a frustrated volume phase transition in a polyampholyte gel. Thus, a polymer gel is a prototype that can be used to gain an understanding of biomolecules and biological systems governed by short-range interactions such as hydrogen bonding and hydrophobic/hydrophilic interactions as well as by long-range Coulomb interactions.

Based on such stimuli-responsive volume changes, the potential applications of these materials have grown extensively in the past decade; drug delivery, bio-sensing, flexible actuators, and chemical extraction.[7,8] In addition to these examples, some researchers have recently reported some novel applications of the volume phase transition of PNIPAM gels with reference to optical micro-devices. Hu *et al.* demonstrated that a 3-dimensional microparticle array made of PNIPAM gel particles exhibited opal-like-coloration responding to temperature.[9] Takeoka and Watanabe fabricated a mesoporous PNIPAM gel by means of template synthesis using closely-packed self-assembled colloidal silica crystals.[10] The fabricated gel exhibits brilliant opalescence that shows fast optical-switching in response to a thermo-responsive volume phase transition of the gel. Also, Reese *et al.* developed a fast (nanosecond) photonic crystal switching device by using PNIPAM nano-gel colloidal particles that self-assemble into crystalline colloidal arrays.[11] The fast switching was achieved by rapid shrinkage of the PNIPAM nano-gel particles by a temperature jump. In addition, very recently, Dong *et al.* demonstrated adaptive liquid micro-lenses fabricated in a micro-fluidic device.[12] In the device, the thickness of the liquid micro-lens was adjusted by a surrounding ring made of a PNIPAM gel that shrinks in accordance with a change in pH, and the pH was controlled by injection of a chemical reagent through a micro-channel inside the device. For further development of such novel devices using the gels, it would be advantageous to be able to control the volume phase transition of the gel by a novel perturbation capable of accessing the gel with high spatial resolution in a non-contact-mode.

In 2000, Juodkazis and Misawa *et al.* discovered a quite intriguing phenomenon for a micro-rod of PNIPAM gel. They demonstrated that a focused near-infrared laser beam induced reversible shrinkage in the gel.[13] It was confirmed that the origin of the shrinkage could be ascribed to a pure electro-magnetic perturbation, the so called photon pressure (radiation force), rather than to effects of local heating. One of the

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan
*To whom correspondence should be addressed (E-mail: twoboys@sci.hokudai.ac.jp (YT) and kitamura@sci.hokudai.ac.jp (NK)).
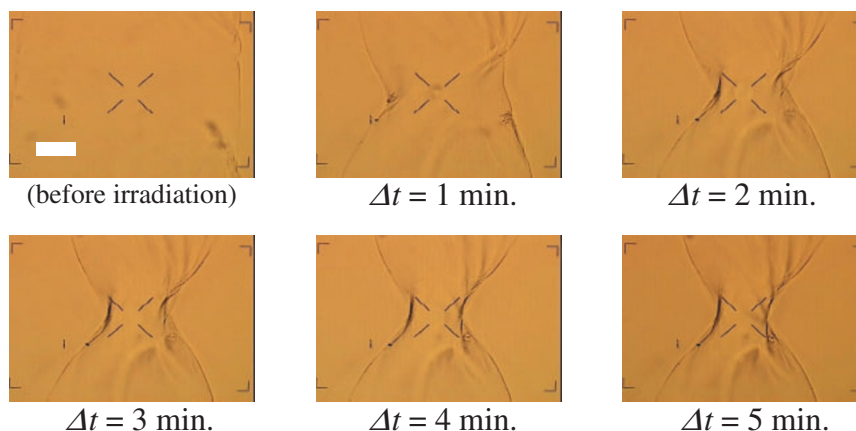
Figure 1. Optical micrographs for the temporal evolution of laser-induced shrinkage of a micro-rod of PNIPAM gel (P_{eff} = 270 mW). The observation was made at room temperature. The time (Δt) after starting laser irradiation is given in the figure. The scale bar = 50 μm.

features of great interest in laser-induced gel shrinkage is that the shrinkage takes place up to several tens of micrometers away from the irradiation spot. Although laser-induced reversible shrinkage of polymer gels possesses a wealth of scientific interest as well as potential applications to actuators, sensors and optical devices, as described above, the detailed behavior and mechanism of laser-induced shrinkage still remains unclear. To address this issue, an effective approach is to reveal the chemical structure of the gel under photon pressure.

In this study, we used spatially-resolved Raman microspectroscopy in order to ascertain the chemical structure of the gel upon laser-induced shrinkage. As we have demonstrated in relevant work on the assembly of PNIPAM polymer chains (phase separation/phase transition) in aqueous solutions induced by photon pressure, Raman microspectroscopy is a powerful tool for analyzing the local structure of PNIPAM systems, since the hydrated/dehydrated polymer structure is reflected in their Raman spectra with high sensitivity.[14] Also, the laser power and temperature dependences of the laser-induced shrinkage of PNIPAM gels were investigated in detail. The local structure of a micro-rod of PNIPAM gel under photon pressure is presented and the laser-induced shrinkage is confirmed to originate from a real volume-phase transition.

EXPERIMENTAL

Micro-rods of PNIPAM gel were synthesized using the following procedure.[2] *N*-Isopropylacrylamide (Wako, Guaranteed grade) was purified, and polymerized in D_2O (Wako, 99.99%) inside a glass micro-capillary tube by free-radical polymerization using *N*, *N'*-methylenebisacrylamide (Wako, Guaranteed grade) as a crosslinker, and ammonium persulfate (Wako, Guaranteed grade) and sodium bisulfate (Sigma-Aldrich) as an initiator and a polymerization accelerator, respectively. The molar ratio of the crosslinker to the monomer was 0.01 (monomer:crosslinker = 100:1). The polymerized PNIPAM gel was taken out of the tube, and then soaked and washed in D_2O. Crosslink density of the gel was

2×10^{-2} that was caluculated using $2N_c/(N_c + N_m)$ where N_c and N_m are molar concentration of the crosslinker and the monomer, respectively. The volume phase transition temperature (T_v) of the gel rod was determined to be 307 K in D_2O.

Details of the experimental apparatus have been reported elsewhere.[14,15] Briefly, a CW Nd^{3+}:YAG laser ($\lambda = 1064$ nm, Spectron Laser System, SL-902T) and a CW Ar^+ laser ($\lambda = 488$ nm, Coherent, Inova 70) were used for generating photon pressure and excitation for Raman scattering of the sample, respectively. The laser beams were introduced coaxially into an inverted optical microscope (Nikon, ECLIPSE E300) and the sample was irradiated through an oil-immersion objective lens (NA = 1.30 or 0.65). The 488 nm laser beam was scanned spatially using a galvano mirror system inserted between the laser and the optical microscope. Raman scattered light passing through two holographic notch filters (for 488 and 1064 nm) was detected by a cooled CCD camera (Andor Tec.) equipped with a polychromator. The effective laser power (P_{eff}; laser power after passing through the objective lens) was measured using a power meter (Ophir, NOVA). All the measurements were carried out at room temperature (21 + 1 °C).

RESULTS AND DISCUSSION

General Features of Laser-induced Shrinkage of the PNIPAM Gel

When the 1064 nm laser beam was focused on the central area of a micro-rod of PNIPAM gel in D_2O under the optical microscope, a large shrinkage of the gel was induced around the irradiated point, leading to the formation of a "waist" in the micro-rod.[13] Figure 1 displays optical micrographs for the temporal evolution of the shrinkage of the gel ($P_{eff} = 270$ mW). The observation was made at room temperature. The gel started to shrink immediately after laser irradiation. The shrinkage was appreciable after 1 min and reached an equilibrium state at 3 min. Although the laser focal point was very small compared with the size of the rod, with the diffraction-limited spot size being 1.22λ/NA ~ 1.5 μm, the shrinkage occurred at a distance of more than a hundred micrometers

away from the focal point. Since D_2O is transparent at the laser wavelength (absorption coefficient at 1064 nm is $< 0.2\,cm^{-1}$), any photothermal effects (*i.e.*, temperature rise) are negligible in the irradiated area.[13,16–18] Therefore, the origin of the laser-induced shrinkage of the gel observed here is photon pressure as previously described.

The present shrinkage behavior is similar to that found previously by Juodkazis and Misawa *et al.*, except that the time scale (Δt) is different. In their work, the equilibrium point was achieved within a few seconds ($\Delta t < 5\,s$). The diameter (d_0) of the PNIPAM gel rod prepared in the present work was 250–300 μm, which is larger than that used in the preceding work, $d_0 = 50$–80 μm. The difference in the shrinkage time scale can be interpreted in the framework of a theory developed by T. Tanaka *et al.*[19,20] The time required to reach the equilibrium volume of a gel should be proportional to the square of the characteristic length of the gel due to the collective diffusive process of the gel network. That is, $\Delta t < 5\,s$ for $d_0 = 50$–80 μm roughly corresponds to $\Delta t \sim 2\,min$ for $d_0 = 250$–300 μm.

The degree of shrinkage is evaluated as d_w/d_0 where d_w and d_0 are the diameter of the waist of the gel rod at equilibrium and the initial diameter of the gel rod, respectively. In Figure 2(a), d_w/d_0 is shown as a function of $P_{eff.}$. Measurements was carried out at room temperature. With $150\,mW < P_{eff.} < 200\,mW$, the shrinkage is somewhat small; $d_w/d_0 > 0.8$. On increasing $P_{eff.}$ the shrinkage becomes more apparent and d_w/d_0 reaches a minimum value at 0.23 when $P_{eff.} > 270\,mW$.

The dynamics of the shrinking of the gel rod are shown in Figure 2(b); $d(t)/d_0$ is plotted against the time (t) after switching on the laser at various laser powers, P_{eff}. The dynamics of gel shrinkage/swelling has been modeled by Tanaka *et al.* on the basis of the concept of collective diffusion of the polymer chain network. The time-dependence of gel shrinkage ($d(t)/d_0$) is expressed by the following equation,[21,22]

$$d(t)/d_0 = d_w/d_0 - C\exp(-t/\tau) \qquad (1)$$

where τ is the time constant for gel shrinkage and C is a constant; $C = 6/\pi^2\,(d_w - d_0)$. As shown in Figure 2(b), the data are well fitted by eq. (1), and we can evaluate τ. The time constant τ is plotted against P_{eff} in Figure 2(c), which shows τ decreasing linearly with P_{eff}. Although it is difficult to explain the linear relation at present, we have shown that the rate of shrinkage become faster with increasing $P_{eff.}$.

In the above, we have revealed a common feature of thermally induced volume phase transition and laser induced shrinkage of the gel in so much as each has a threshold value, temperature and P_{eff}, respectively. In addition, according to previous work,[13] it has been suggested that the volume phase transition temperature, T_v, shifts to a lower value when a photon pressure is exerted on a rod of gel. In order to understand the role of photon pressure in shrinkage in comparison with that of thermal energy, we investigated the shrinkage behavior of a gel rod by varying P_{eff}. The results of this are shown in Figure 3. As seen in Figure 3(a), the
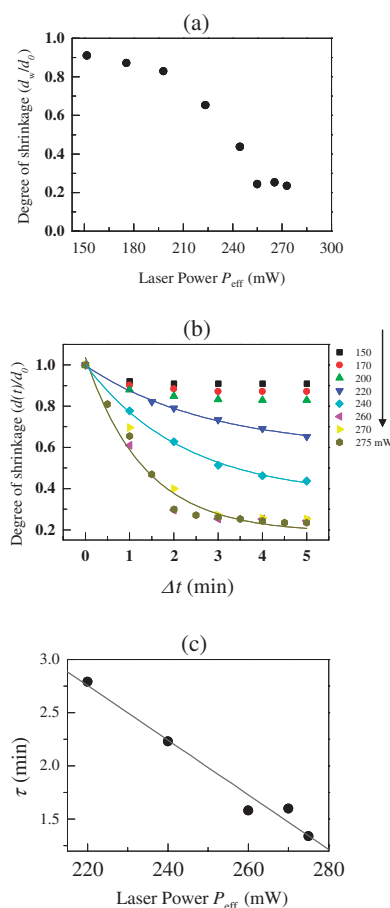

Figure 2. Laser power (P_{eff}) dependence of the dynamics of shrinkage of a micro-rod of PNIPAM gel. Measurements were carried out at room temperature. (a) Degree of shrinkage at equilibrium (d_w/d_0) as a function of P_{eff}. (b) Temporal evolution of the degree of shrinkage ($d(t)/d_0$) for various P_{eff}. The solid lines are best fits based on eq. (1). (c) Laser power dependence of the time constant for shrinkage obtained from the curve fitting.

shrinkage behavior is very sensitive to P_{eff}. T_v shifts to lower temperatures with increasing P_{eff}. In Figure 3(b), T_v is plotted against P_{eff}, which shows that T_v decreases *linearly* with increasing P_{eff}. This means that photon pressure can drive gel shrinkage, as can the rise in temperature. Note that the range of P_{eff} in the figure is less than the threshold value required to induce shrinkage at room temperature. The strength of the photon pressure is proportional to P_{eff} (as noted later), and it is revealed that *ca.* 150 mW of P_{eff} corresponds to a temperature rise of about 10 K (evaluated from the slope of the linear relationship) for inducing shrinkage.

Raman Microspectroscopy of a Gel upon Volume Phase Transition

It has been established that the volume phase transition of a thermo-responsive gel such as PNIPAM in an aqueous solution is due to dehydration and hydration of the polymer chains in the shrinkage and swelling processes, respectively. Therefore, observation of the dehydration of PNIPAM polymer chains upon shrinkage would be direct evidence of the volume phase
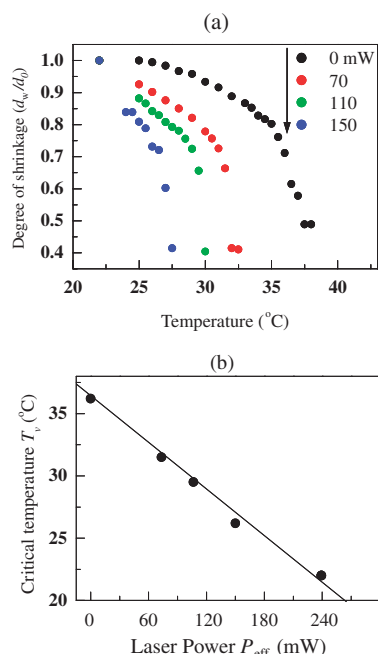
Figure 3. Effect of photon pressure upon thermally-induced gel collapse. (a) Temperature dependence of the degree of shrinkage ($d(t)/d_0$) at various P_{eff}. (b) Volume phase transition temperature (T_v) as a function of P_{eff}.
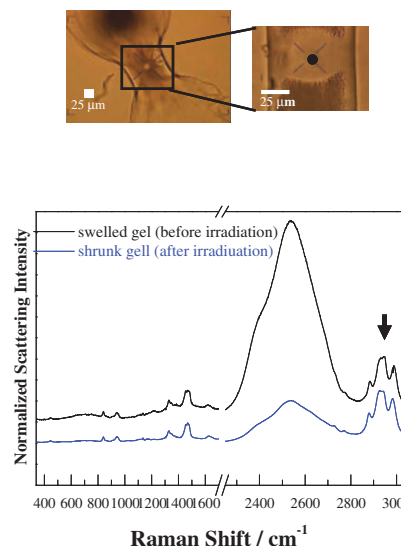

Figure 4. Raman spectra of swollen (before laser irradiation, black line) and shrunken (after laser irradiation, blue line) PNIPAM gels. The spectra are normalized at 2940 cm^{-1}, shown by the arrow. The 1064 nm laser beam was focused at the center of the micro-rod of PNIPAM gel, and the Raman spectra were measured at the point marked by a dot in the optical micrographs. Laser power; P_{eff} = 270 mW.

transition in the laser-induced shrinkage described above. Figure 4 shows the Raman spectra of a micro-rod of PNIPAM gel in D_2O before and after laser irradiation, together with optical micrographs of the gel. The spectra were taken at the focal point of the 1064 nm laser beam and normalized to the intensity at around 2900 cm^{-1} responsible for the symmetric/ asymmetric C-H stretching of the –CH$_3$ group of the gel. In the wide wavenumber region, various vibrational peaks are clearly observed. Spectral changes upon laser-induced shrinkage are discussed on the basis of expanded spectra (Figure 5).

In the region 2200–2800 cm^{-1}, we see broad and intense Raman signals that are ascribed to the O-D stretching mode of D_2O (Figure 5(a)). The signal intensity of the band upon shrinkage clearly decreases, signifying that the D_2O molecules are excluded from the focal point where photon pressure has been applied. Below 1000 cm^{-1}, two peaks at 840 and 940 cm^{-1} assigned to various -C-C- skeletal stretching modes were found to be insensitive to laser irradiation (Figure 5(b)). In the region 1400–1500 cm^{-1}, the band due to the -CH$_2$- bending vibration (1450 cm^{-1}) overlaps that of the amide II mode, which is mainly due to the N-H vibration (Figure 5(c)).[23] Close to the amide II band, a weak peak can also be seen at around 1600–1650 cm^{-1} (Figure 5(d)).[23] This signal can be ascribed to the C=O vibrations, and is referred to the amide I band. In the higher wavenumber region (> 2800 cm^{-1}, Figure 5(e)), four characteristic vibrational peaks were detected and assigned to the C-H stretching modes of the PNIPAM gel: symmetric C-H stretching of -CH$_3$ (2880 cm^{-1}), antisymmetric C-H stretching of -CH$_2$- (2920 and 2945 cm^{-1}), and antisymmetric C-H stretching of -CH$_3$

(2980 cm^{-1}).[14,24] These Raman bands before and after laser irradiation are slightly different, suggesting a structural change in the PNIPAM gel upon shrinkage. In particular, the change in the methylene C-H stretching vibrational band that splits into two peaks at 2920 and 2945 cm^{-1} gives us direct information about the hydration and dehydration of the PNIPAM gel upon shrinking. Before laser irradiation, the latter peak (at 2945 cm^{-1}) is more intense compared with the intensity of the former (at 2920 cm^{-1}). After laser irradiation resulting in shrinkage, the relative intensity of the two peaks is clearly reversed.

Such spectral behavior can be interpreted as follows. It has been shown by Raman spectroscopy of a thermo-responsive polymer that the C-H stretching band of the polymer main chain exhibits a slight low-frequency shift by dehydration of the C-H group in the main chain.[24–26] The change in the relative intensity of the peaks of the antisymmetric CH stretching of -CH$_2$- (2920 and 2945 cm^{-1}) upon shrinkage is ascribed to dehydration of the methylene chain of the polymer backbone in the globular state. Therefore, the changes in the relative peak intensities, as shown by inversion of the signal intensities at 2920 and 2945 cm^{-1}, are evidence of the volume phase transition. Indeed, similar spectral changes were also observed for the thermally-induced volume phase transition of a PNIPAM gel. It should be noted that similar spectral changes have also been observed for thermo-responsive phase separation and laser-induced phase separation (particle formation) in aqueous PNIPAM solutions.[14] The spectral change featuring inversion of the relative intensities of the two peaks is common behavior in the phase transitions of PNIPAM systems.
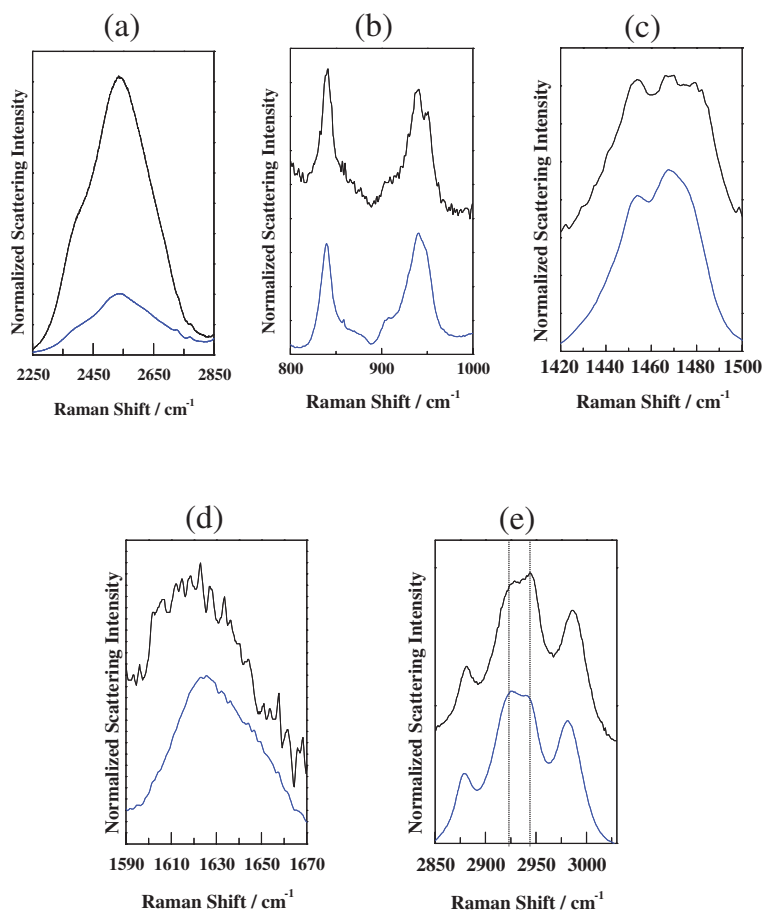
Figure 5. Expanded Raman spectra of Figure 4 for swollen (before laser irradiation, black line) and shrunken (after laser irradiation, blue line) PNIPAM gels. The assignment for each vibrational peak is described in the text.

Raman Mapping Around the Focal Point for a Gel

Dehydration of the PNIPAM polymer chains upon shrinkage was thus confirmed at the focal point of the laser beam where the photon pressure was strongly exerted. As previously described, one striking feature of this phenomenon is that the gel shrinkage takes place up to several tens of micrometers (more than 100 micrometers) away from the focal point of laser irradiation. Therefore, it is valuable to perform Raman microspectroscopy to explore the chemical structure not only at the focal point but also around the whole shrunken area of the PNIPAM gel.

Position-dependent Raman spectra of the gel (Raman mapping) in volume phase transition are displayed in Figure 6. In the Raman mapping, photon pressure was applied by the focusing the 1064 nm laser beam on the center of the rod, while the position for Raman excitation at 488 nm was scanned in three different directions using a galvano mirror optical system: along the long axis of the rod, perpendicular to the long axis, and in an oblique direction. All the spectra have been normalized to the intensity at $2920 \, cm^{-1}$. The C-H stretching bands of the PNIPAM gel and the O-D stretching band of the solvent can be seen in the figure. Along the long axis of the rod (Figure 6(a)), the relative intensity of the O-D stretching band

to the C-H stretching band increases slightly as the detection position becomes further from the center of the rod. Also, perpendicular to the long axis (Figure 6(b)), the relative intensity of the O-D stretching band to the C-H stretching band increases as the detection position moves further from the centre, and the degree of increase is much clearer than that in Figure 6(a). The degree of hydration (water content) increases abruptly in the vicinity of the interface between the polymer and liquid phases. In the oblique direction (Figure 6(c)), the behavior of the spectra is intermediate between the above two cases (Figure 6(a) and 6(b)): the relative intensity of the O-D stretching band to the C-H stretching band gradually increases as the detection position moves further from the center. Thus, Raman mapping of the rod clearly reveals the spatial distribution of the degree of hydration (water content) of the PNIPAM polymer chains (*i.e.*, water content in the gel) upon volume phase transition. The degree of hydration increases gradually moving away from the focal point of the laser beam and then increases abruptly at the interface.

Mechanism of Volume Phase Transition Triggered by Photon Pressure

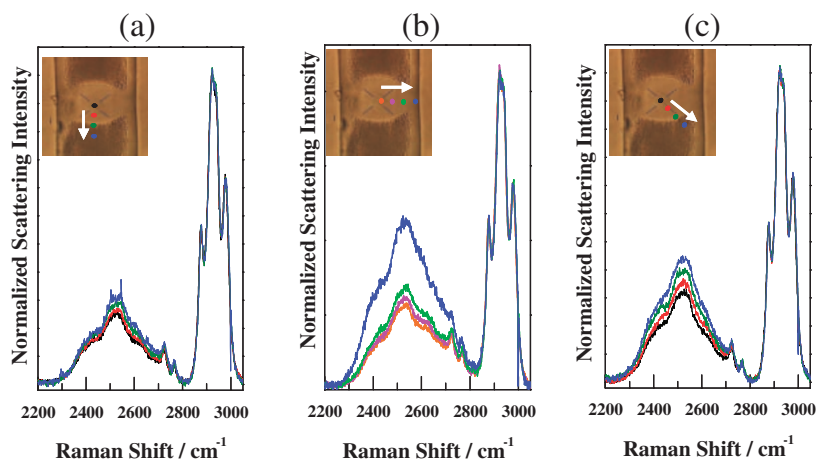The origin of photon pressure is the dipole gradient force

Figure 6. Spatially-resolved Raman spectra for the shrunken area (waist) of a micro-rod of PNIPAM gel. The spectra were measured at points along three axes, which are marked by different colored dots. (a) Along the long axis of the micro-rod. (b) Along the short axis (perpendicular to the long axis). (c) Along an oblique axis. Laser power; $P_{eff} = 270\,\text{mW}$.

which can be expressed on the basis of the Lorentz force as;[27–29]

$$F = \frac{1}{2}\alpha\nabla E^2 + \alpha\frac{\partial}{\partial t}(E \times B) \quad (2)$$

where E and B are the electric field strength and the incident magnetic flux density, respectively. α is the polarizability of the material (PNIPAM gel) and is given by

$$\alpha = 4\pi\varepsilon_2 r^3 \frac{(n_1/n_2)^2 - 1}{(n_1/n_2)^2 + 2} \quad (3)$$

where ε_2 is the dielectric constant of D_2O, and, n_1 and n_2 are the refractive indices of the particles and the surrounding medium (D_2O), respectively. In eq. (2), the first term corresponds to the gradient force, while the second term acts on the particles as a scattering force due to the change in the Poynting vector of the incident light. For $n_1 > n_2$, the gradient force is directed towards high intensity electric field regions, *i.e.*, the focal point. In the present case, in which a focused near infrared Gaussian laser beam is used, the gradient force is much stronger than the scattering force. Accordingly, the material receives an attractive force (photon pressure), and if the matter consists of Rayleigh particles, they become trapped at the focal point. The extent of the interaction should be proportional to the laser power (P_{eff}; P_{eff} has a linear relation with E^2). This is the initial interaction that triggers the shrinking of the gel rod.

On the other hand, the fundamental mechanism underlying the present phenomenon, the volume phase transition of the gel rod, can be illustrated in terms of a change in the osmotic pressure due to photon pressure. In a swollen gel, an interaction of hydration of polymer chains is prior to a hydrophobic interaction among polymer chains, while the mutual relation between the two interactions is inverted in a shrunk gel, as described in the introductory part. When a gel is immersed in a liquid, it can undergo a volume-phase transition in response to changes in external conditions such as the temperature, the

solvent, pH, an electric field, and light. The competing forces exerted on the gel are a rubber elasticity, a polymer-polymer affinity and hydrogen ion pressure, etc. The sum total of these competing forces resulting in the osmotic pressure, determine the equilibrium volume of the gel. The phase transition in a gel has been analyzed in terms of the osmotic pressure (Π) given by Flory-Rhener's equation.[5,6]

$$\Pi = \frac{n_p k_b T}{V_0}\left[\frac{\phi}{2\phi_0} - \sqrt[3]{\frac{\phi}{\phi_0}}\right] - \frac{k_b T}{v_c}[\chi\phi^2 + \ln(1 - \phi) + \phi] \quad (4)$$

where ϕ is the volume fraction of the polymer network and χ is Flory's χ-parameter. k_b is the Boltzmann constant and T is the temperature. V_0, n_p, and v_c are the standard volume of the gel, the total number of chains in the gel, and the molar volume of D_2O, respectively. Judging from the Raman spectra (Figure 4), relative signal intensity of polymer chain ($\sim 2900\,\text{cm}^{-1}$) and water ($\sim 2500\,\text{cm}^{-1}$), ϕ at the focal point at shrinkage was quintupled by laser irradiation as compared to the swollen gel (before irradiation).

According to the model proposed by Erman and Flory, the parameter χ that characterizes the solvent-polymer interaction is a function of the volume fraction of the polymer chains:[3,4,30]

$$\chi = \chi_1 + \chi_2\phi \quad (5)$$

For a gel such as PNIPAM that exhibits a first-order phase transition, χ_2 is required to be greater than $1/3$. By combining eq. (4) and (5), we can illustrate the ϕ-dependence of Π, as shown in Figure 7. The positive and negative differential coefficients ($d/d\phi$) of the curves induce swelling and shrinkage of the gel, respectively. As seen in the figure, the dependency of Π on ϕ is very sensitive to χ_1. A slight increase in χ_1 (with $\chi_2 = 0.56$[30] causes a dramatic variation in the curves, and a region where shrinkage occurs (where the differential coefficient is negative) appears when $\chi_1 = 0.465$ and 0.470.

We consider the following mechanism to be responsible for the laser induced volume phase transition. When photon pressure is exerted on a gel having a ϕ-dependence of Π with
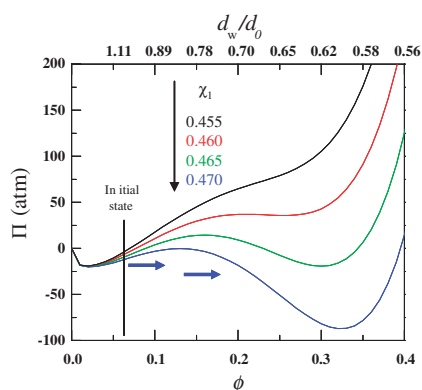
Figure 7. Simulated curves of the ϕ-dependence of Π on the basis of eqs. (4) and (5). The curves were obtained with $\chi_2 = 0.56$ and varying χ_1 as noted in the figure. The initial state (the equilibrium state before laser irradiation) is also shown, and the equilibrium shifts in the direction of the arrows due to photon pressure.

$\chi_1 > 0.47$, local shrinkage at the irradiated spot is induced, resulting in a local increase in ϕ. Then, as the equilibrium is broken at the focal point due to the local change in χ, shrinkage of the 3D-polymer network propagates outwards from the focal point according to the curves shown in Figure 7. Thus, once a local shrinkage in the gel is triggered by photon pressure of a tightly focused laser beam with a focal point comparable to its wavelength, then the volume of the collapsed state can be much larger that the initially illuminated point due to the collective motion of the polymer chains.[19] Based on the above mechanism, local irradiation by the $1.5\,\mu m$ spot triggers shrinkage of the rod extending over a hundred micrometers or so, while the force to exclude water molecules gradually become weaker moving away from the focal point. Thus the experimental results observed can be explained by this mechanism.

CONCLUSIONS

We have demonstrated the overall process of reversible volume phase transition of a rod-shaped PNIPAM gel triggered by photon pressure applied by a focused near-infrared laser beam. The time scale needed for laser-induced volume phase transition is roughly proportional to the inverse of the square of d_0, as is generally observed in thermally-induced volume phase transition. The time constant (τ) for laser-induced shrinkage was shown to decrease linearly with P_{eff}. Furthermore, the photon pressure accelerates the dynamics of volume phase transition, and shifts T_v towards lower temperatures. The photon pressure and heat act cooperatively to induce volume phase transition. T_v decreases linearly with increasing P_{eff}; with $P_{eff} = 150\,mW$ equivalent to $\Delta T = 10\,K$, although the origin of the linear relationship is unclear at present and a further study is necessary. Moreover, the local structure of a rod of PNIPAM gel was revealed in detail by means of Raman micro-spectroscopy. At the focal point, where the photon pressure is exerted, dehydration (exclusion of heavy water molecules) is promoted, based on which we can conclude that the laser-induced shrinkage is a volume phase transition. The distribution of the water content, *i.e.* the degree of hydration/dehydration of the polymer chains, depends upon the position around the focal point. The degree of hydration increases gradually moving away from the focal point, and it increases abruptly approaching the interface between the gel and the liquid. The laser-induced volume phase transition can be understood within the framework of the Erman-Flory model. Thus, laser light can reversibly control the volume phase transition of micro-gels in a non-contact mode, which will open new channels to promising potential applications of gels, such as micro-optical devices and micro-actuators.

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