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Infrared Laser-Induced Photo-Thermal Phase Transition of an Aqueous Poly(*N*-isopropylacrylamide) Solution in the Micrometer Dimension

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The phase transition of an aqueous poly(*N*-isopropylacrylamide) solution (PNIPAM, wt% = 1.8—3.6%) was induced by the irradiation of a focused (ca. 1 μm) 1064-nm laser beam; this brought about the formation of a single PNIPAM microparticle. The diameter of the particle was controlled to 2—9 μm through the laser power, polymer concentration, and solution temperature. The primary origin of particle formation was the photo-thermal phase transition of the polymer solution through the local heating of water (H_2O) by the laser beam. The characteristic features of the phenomena, including manipulation of the PNIPAM particle by the incident laser beam and the role of radiation force for the particle formation, are discussed.

Stimulus-responsive materials are very much concerned with special references to the development of functional and intelligent materials, such as actuators and artificial muscles.[1,2] Among the various external stimuli (i.e., temperature, solution pH, and electric field) and light signal is quite unique, since a light beam can be focused to a very minute spot and easily switched on/off. As an example, we previously reported that polyacrylamide gels having triphenylmethyl cyanide (TPMCN) as a light absorber showed a photoinduced volume expansion in water, and demonstrated that the response time of the volume change was shortened by reducing the gel size from millimeter to micrometer.[3,4] In this case, TPMCN, itself, absorbs the incident light energy, and subsequent ionization of the excited state chromophore induces a volume expansion through a change in the osmotic pressure between the gel and the surrounding water phase. Besides such a photochemical effect, light can also be utilized as a heat source. Actually, Suzuki and Tanaka recently reported that the volume shrinkage of a poly(*N*-isopropylacrylamide) (PNIPAM) gel in water could be controlled by local heating of the polymer networks through the absorption of a 488-nm laser beam by a dye chromophore covalently-linked to the polymer backbone.[5]

Although UV light has been frequently used as a heat source (as mentioned above), infrared (IR) light, particularly and IR laser beam, is quite interesting, since a *focused* IR laser beam can be utilized as both a heat source and a light source for the optical manipulation of a microparticle in solution. Optical manipulation is essentially based on the *radiation force* generated by the refraction of a light beam through a particle.[6,7] Since longer wavelength light is favorable for avoiding light absorption by a particle, an IR laser beam is commonly used as a light source for optical manipulation. In a series of publications we have reported on the noncontact and nondestructive manipulation of various microparticles by a focused 1064-nm laser beam (*laser manipulation*; described later in detail).[8—16]

A focused IR laser beam has a high potential for both inducing thermally-induced phenomena and the manipulation of various materials in the micrometer dimension. *Radiation force* is also expected to play a role in controlling the conformations and/or aggregation states of polymers in solution, so that an inside look at intra- and inter-molecular interactions of polymers will be obtained. If this is the case, furthermore, such an approach will also be extended to molecular systems, such as micelles and vesicles. In order to test such possibilities, we studied a photo-thermal phase transition of an aqueous PNIPAM (not cross-linked) solution by an IR laser beam. PNIPAM has received current interest as a stimulus-responsive polymer, since the aqueous solution shows a phase transition at around 31—32 °C (phase-transition temperature; T_c), below which the solution is homogeneous and clear, though it becomes turbid above T_c due to the precipitation of fine PNIPAM particles.[17] We have expected that

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the phase transition of the solution and aggregation states of PNIPAM particles above T_c can be controlled by a laser beam or radiation force.

In this paper we report on the characteristic features of the laser-induced phase transition of an aqueous PNIPAM solution,[18] and discuss the factors which control the phenomena. The laser manipulation of a PNIPAM microparticle produced by the phase transition and an important role of radiation force for particle formation are also described.

Experimental

Chemicals: PNIPAM was prepared by the radical polymerization of *N*-isopropylacrylamide (1.4 g in 100 mL of water) in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (100 μg) and ammonium peroxodisulfate (0.1 g). In order to avoid precipitation of the polymer above T_c, the reaction was performed at 30 °C for 8 h. The polymer was purified by repeated decantations from an ethanol–water mixture. The molecular weight of the polymer (M_w) was determined to be 1×10^6 on the basis of intrinsic viscosity (η) measurements in water and the relation between M_w and η reported by Winnik,[19] $\eta = 4.58 \times 10^{-4}\, M_w^{0.93}$. 1-Anilinonaphthalene-8-sulfonate (ANS, Nacalai) and D_2O (99.8%, Nacalai) were used as supplied. Water (H_2O) was purified by deionization and distillation (Yamato Autostill WG 25).

Apparatus: All of the experiments were performed under an optical microscope (Nikon, Optiphot XF) unless otherwise noted. A 1064-nm laser beam from a CW Nd^{3+} : YAG laser (Spectron, SL-903U) was introduced to the microscope and focused into a ca. 1 μm spot through an objective lens (magnification = 100, numerical aperture (NA) = 1.30) of the microscope. A sample solution was placed between two glass plates and set on the microscope stage. The phase-transition behavior was monitored by a CCD camera (Sony, DXC-930) equipped to the microscope. The laser power irradiated onto a sample solution (abbreviated as P_{1064}) was determined by reported procedures.[10] For fluorescence measurements, a PNIPAM solution containing ANS as a probe (2×10^{-3} mol dm^{-3}) was excited by a 355-nm laser beam (Quanta Ray DCR-II, Nd^{3+} : YAG laser, pulse width ca. 7 ns, 10 Hz), which was introduced to the microscope coaxially with the 1064-nm laser beam. Special care was taken to monitor the ANS fluorescence from a PNIPAM particle by setting a pinhole in front of a monochromator (McPherson, 2035); the fluorescence was then analyzed by a photodiode array detector (Princeton Instruments, DSIDA). Other details concerning the experimental set up have been described elsewhere.[20] Absorption and steady-state fluorescence measurements (10 mm optical path length quartz cell) were conducted using a Shimadzu UV3100 spectrophotometer and a Hitachi F4010 spectrofluorometer, respectively. The temperature of the sample solution was controlled by a thermoheater equipped to the microscope stage, and was monitored by a thermocouple. All of the experiments were performed under air-saturated conditions.

Results and Discussion

General Features of Laser-Induced PNIPAM Microparticle Formation: Figure 1a and 1b show optical micrographs of an aqueous PNIPAM solution (3.6 wt%) below (25 °C) and above (34 °C) T_c (=31—32 °C), respectively. Below T_c, the polymer chains are in coil structures and the solution is transparent. Above T_c, on the other hand, the chains associate with each other to form water-insoluble particles, due to a large increase in the hydrophobicity of the polymer. The polymer-chain conformation changes from a coil to a globular structure upon heating, as has been known the coil-globule transition of a single polymer chain.[21,22] Above T_c, submicrometer PNIPAM particles were precipitated in the entire region of the sample solution, appearing as black spots in Fig. 1b. The results were essentially analogous to those reported by Heskins and Guillet,[17] and Winnik.[19]

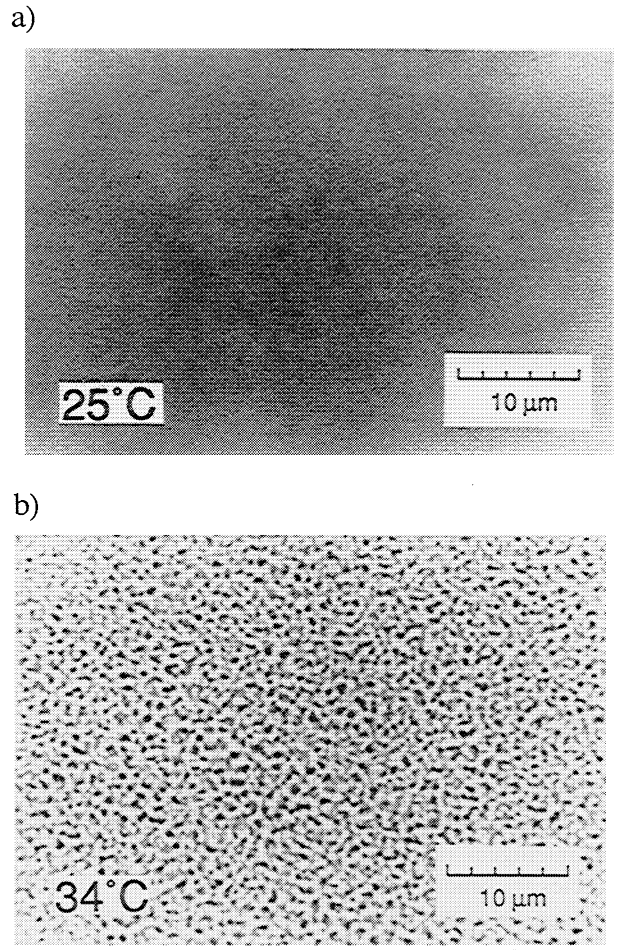

Fig. 1. Optical micrographs of an aqueous PNIPAM solution (3.6 wt% in H_2O) below (a; 25 °C) and above (b; 34 °C) the phase transition temperature (T_c = 31—32 °C).

At room temperature, a PNIPAM solution (3.6 wt%) was irradiated with a focused (ca. 1 μm) 1064-nm laser beam (laser power; $P_{1064} = 1.2$ W). A typical example of the morphological changes of the solution with the irradiation time (t) is shown in Fig. 2. As clearly shown in Fig. 2a and 2b, the phase transition of the polymer solution took place immediately after laser irradiation and, at $t = 0.5$ s, a PNIPAM particle with the diameter (d) of ca. 3 μm was produced in the vicinity of the focal spot of the laser beam. Furthermore, a careful inspection of Fig. 2b indicated that the particle was surrounded by submicrometer PNIPAM particles. At $t = 5.0$ s (Fig. 2c), although the diameter of the particle was almost the same as that at $t = 0.5$ s, the morphology in the periphery of the particle was changed. Upon further irradiation, a PNIPAM particle with $d \approx 7$ μm was produced, as shown

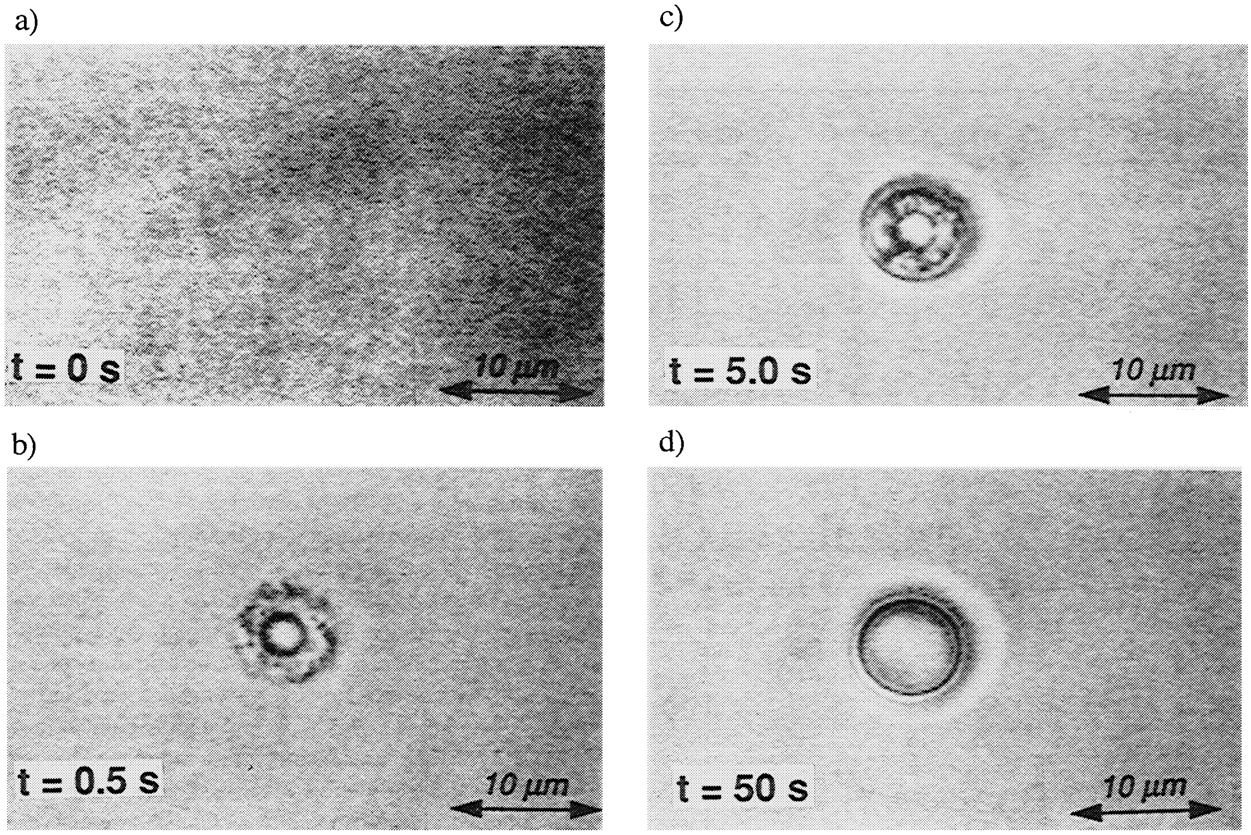

Fig. 2. Optical micrographs during 1064-nm laser-induced phase transition of an aqueous PNIPAM solution (3.6 wt% in H_2O). a; before laser irradiation, b; irradiation time (t) = 0.5 s, c; $t = 5.0$ s, and d; $t = 50$ s. $P_{1064} = 1.2$ W at 20 °C.

in Fig. 2d ($t = 50$ s). It is noteworthy that the surface of the particle at $t = 50$ s is very smooth as long as the observation is made under an optical microscope. Furthermore, the structure around the particle observed during the initial stage of laser irradiation ($t = 0.5$ or 5.0 s) is not discernible in Fig. 2d. The formation and growing-in of a PNIPAM particle with t indicate aggregation of a number of globular-structured polymers.

We measured the time-response profile of d during laser irradiation, as summarized in Fig. 3. In this study we defined d as the diameter of the PNIPAM particle, with the surrounding structure observed in Fig. 2b and 2c being neglected; d was determined based on the video data. The increase in the particle diameter to ca. 4 μm was very fast and almost finished within 100 ms. Further laser irradiation rendered a gradual increase in d, which reached an equilibrium value ca. 7 μm) at $t > 50$ s. The morphological changes in the particle and its surrounding were analogous to those shown in Fig. 2c and 2d. Namely, this slow process at $0.1 < t < 50$ s accompanied the changes in the morphology around the PNIPAM particle. The fast and slow processes in particle formation are very important results to deduce the mechanism (as discussed later in detail). When the laser was turned off, the microparticle disappeared with a time constant ca. 200 ms (Fig. 3b). The formation and dissolution of the PNIPAM particle was highly reversible for several cycles without any appreciable change in the equilibrium diameter. The formation of a single PNIPAM particle with a diameter of several micrometers is markedly in contrast to the thermal phase transition of the solution in the dark, by which a number of submicrometer particles are produced, as demonstrated in Fig. 1. The preparation of PNIPAM particles of several micrometers is only possible by the present method with a focused IR laser beam.

Origin of Photo-Thermal Phase Transition by a Focused Laser Beam: Since PNIPAM does not absorb the laser beam at 1064 nm, the present particle formation cannot be ascribed to a direct photoresponse of the polymer, itself. Therefore, water (H_2O) as the solvent should play an essential role in particle formation. Actually, H_2O absorbs at 1064 nm as the spectrum shows in Fig. 4 (measured in a 10 mm optical path length cuvette), while D_2O is almost transparent at this wavelength. These spectra are in good agreement with the reported ones,[23] and the absorption of H_2O at 1064 nm has been assigned to the overtone band of the OH stretching mode. It is very important to note that PNIPAM particle formation cannot be observed in D_2O (polymer concentration = 3.6 wt%, $P_{1064} = 1.43$ W, 20 °C). These results clearly indicate that particle formation is induced by the absorption of the laser beam by H_2O and a subsequent phase transition of the polymer solution via the photo-thermal local heating of H_2O.

The conversion of the photon energy to heat was roughly estimated as follows. We assume that the photon energy of a 1064-nm laser beam absorbed by a spherical H_2O droplet (radius (R) = 1 μm) is converted to heat (Q), and that local heat

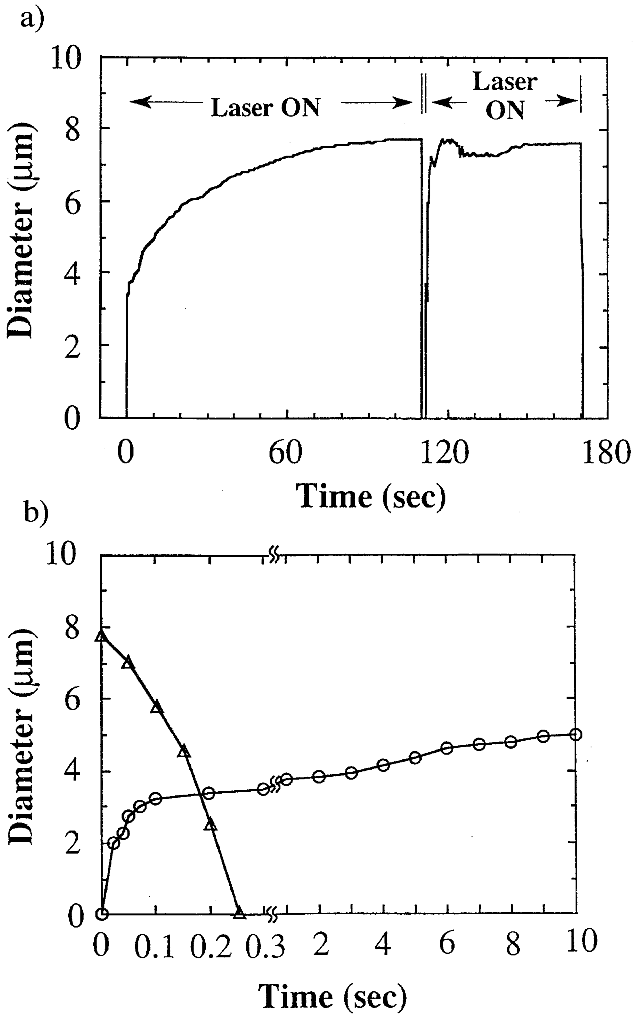

Fig. 3. Time-response profiles of 1064-nm laser-induced PNIPAM microparticle formation and dissolution (a). The initial time-response profiles of the particle formation (○) and dissolution (△) (b). $P_{1064} = 1.2$ W, 20 °C, and PNIPAM = 3.6 wt% in H_2O.

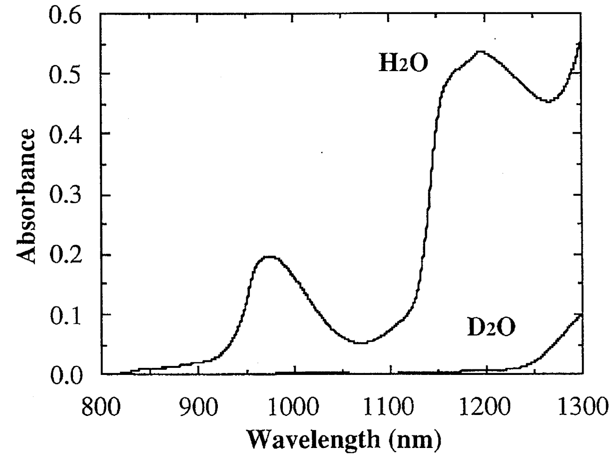

Fig. 4. Absorption spectra of H_2O and D_2O in the near infrared region (optical path length = 10 mm).

is equilibrated by the surrounding solution phase. In such a case, the relevant temperature increase in the droplet (ΔT) can be calculated by the equation[24] $\Delta T = Q/4\pi\varkappa R$, where $\varkappa$ is the thermal conductivity of H_2O. Q was estimated from the absorbance of H_2O at 1064 nm (absorbance $= 5.6\times10^{-6}$ for 1 μm optical path length) and P_{1064}. At $P_{1064} = 1.2$ W, ΔT was calculated to be ca. 4 °C for a droplet with a volume of 1 μm^3. In the actual experiments, however, the focused (ca. 1 μm) laser beam is irradiated on the solution with a large cone angle (ca. 120°) due to the use of a large NA (1.30) objective lens, so that water is heated over a larger volume than 1 μm^3. The larger is the volume heated, the lower is the cooling rate by the surrounding solution phase, since the surface area/volume ratio of a droplet decreases with increasing R. This is one of the primary reasons for the formation of a PNIPAM particle (d = 4—7 μm) having a size larger than the incident laser beam (ca. 1 μm; discussed again later). The experimental results given in Figs. 2 and 3 indicate that ΔT by 1064-nm laser irradiation is sufficiently high to induce a phase transition of the polymer solution.

The photographs in Fig. 2 suggest the formation of a spherical PNIPAM particle. However, this is not necessarily warranted, since the shape of the laser beam is conical (as mentioned above). The laser-beam pattern influenced the particle formation, and reproducible results, such as those in Fig. 3, were obtained only when a TEM_{00} Gausian beam was used as a light source. This indicates that the spatial distribution of a photon density near to the focal spot of the laser beam is very important. Furthermore, a balance between Q and the cooling rate governs particle formation. Although Q is generated in a conical volume, cooling of the local heat by the surrounding solution proceeds isotropically. Therefore, we suppose that the shape of the particle produced by the photo-thermal phase transition will be spherical, or nearly spherical, although an observation of the cross section of the particle under an optical microscope is very difficult at the present stage of the investigation.

Factors Controlling a Laser-Induced Photo-Thermal Phase Transition: In order to further confirm the photothermal effects, we examined the factors governing PNIPAM particle formation in detail. As shown in Fig. 5, particle formation can be induced above a certain P_{1064} value, depending on both the solution temperature before laser irradiation and the polymer concentration. When the polymer concentration is identical (3.6 wt%), as an example, particle formation at 20 °C is observed with $P_{1064} > 0.7$ W (b), while the threshold P_{1064} is ca. 0.3 W at 23 °C (a). Namely, the lower is the solution temperature, the higher is the laser power necessary for the phase transition. The threshold P_{1064} value thus increases with decreasing the solution temperature. At a given P_{1064}, the cooling of local heat is more efficient at a lower solution temperature. Therefore, the diameter of the particle becomes larger with elevating the solution temperature and increasing P_{1064}. When the solution temperature is identical (20 °C), on the other hand, a decrease in the PNIPAM concentration brings about an increase in the threshold P_{1064}, and then the formation of a smaller particle (b and c). Since a

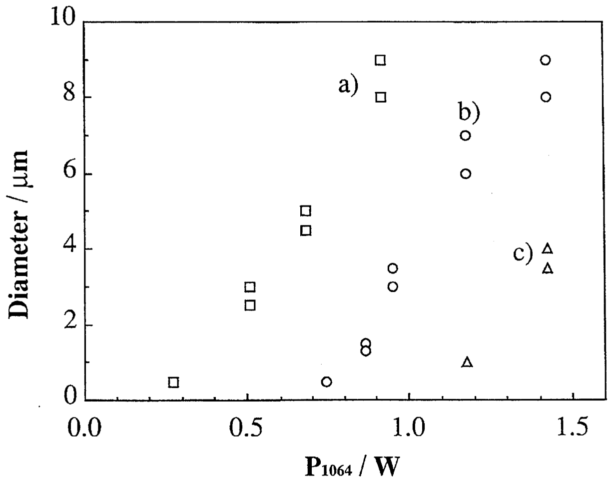

Fig. 5. P_{1064} dependencies of the diameter of the PNIPAM microparticle produced by 1064-nm laser-induced phase transition in H_2O. a; PNIPAM = 3.6 wt% at 23 °C. b; PNIPAM = 3.6 wt% at 20 °C. c; PNIPAM = 1.8 wt% at 20 °C.

high concentration favors interpolymer association, a larger PNIPAM particle can be produced by increasing the polymer concentration. All of the results, including the absence of the phase transition in D_2O, prove that the primary origin of the PNIPAM particle formation in photo-thermal local heating of H_2O by the 1064-nm laser beam.

On the basis of the results given in Fig. 5, we conclude that the diameter of a PNIPAM particle can be controlled to 2—9 μm through P_{1064}, the solution temperature, and the polymer concentration. This is particularly unique for preparing a single PNIPAM particle having an arbitrary diameter, which cannot be attained by the thermal phase transition in the dark.

Fluorescence Probe Study on a Photo-Thermal Phase Transition: The micropolarity in the PNIPAM particle will be much lower than that in the surrounding water phase due to the hydrophobic nature of the polymer above T_c. Since the fluorescence maximum wavelength and intensity of 1-anilinonaphthalene-8-sulfonate (ANS) are known to be highly sensitive to the solvent polarity,[25,26] the phase transition of the solution can be followed spectroscopically through fluorescence measurements of a PNIPAM–ANS solution. Before discussing the fluorescence characteristics of ANS before and after a photo-thermal phase transition, we describe the results for a bulk ANS–PNIPAM solution.

As shown in Fig. 6, the maximum wavelength and intensity of ANS fluorescence are strongly dependent of the temperature ([ANS] = 2×10^{-3} mol dm^{-3}, PNIPAM = 3.6 wt%, excitation wavelength = 355 nm). The spectra were obtained by a conventional method using a 10 mm optical path length cuvette and a spectrofluorometer. Below T_c (25 °C), the fluorescence spectrum exhibits a peak (λ_{max}) at around 520 nm ($\nu_{max} = 1.92\times10^4$ cm^{-1}; a), while that above T_c (34 °C; $\lambda_{max} = 466$ nm, $\nu_{max} = 2.15\times10^4$ cm^{-1}; b) shifts to a shorter wavelength by 54 nm (2230 cm^{-1}). According to the solvent dependence of the spectrum,[25,26] a λ_{max} of 520 or 466 nm corresponds to a polarity (ε) in ethanol/H_2O of 1/4 (v/v, $\varepsilon\approx69$) or acetone–ethanol ($\varepsilon = 20.7$—24.6), respectively. Furthermore, the fluorescence intensity increases considerably upon heating. It has been reported that a decrease in ε from 69 to 20.7—24.6 results in an increase in the fluorescence quantum yield of ANS from 0.02 to 0.37—0.31,[25,26] indicating that ANS is located in or in the vicinity of the precipitated PNIPAM particles. The results are in good agreement with the changes in the fluorescence characteristics of ANS with the solvent polarity; we can thus conclude that the micropolarity in the globular-structured PNIPAM polymer chains above T_c is very low compared with that in a homogeneous solution below T_c.

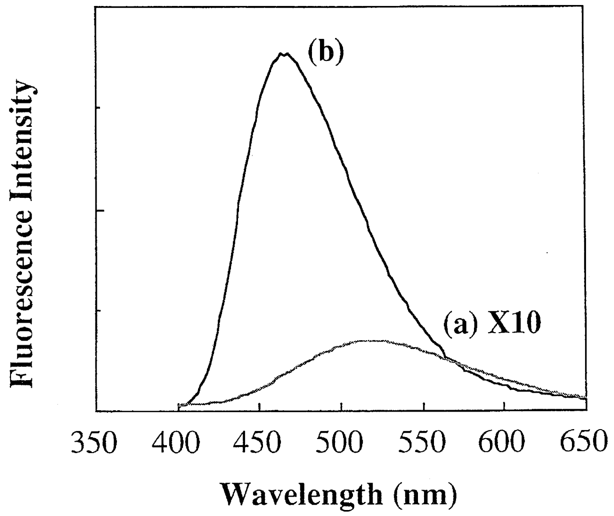

Fig. 6. Fluorescence spectra of ANS below (a; 25 °C) and above (b; 34 °C) the phase transition temperature of the PNIPAM solution (3.6 wt% in H_2O) in the dark. Recorded with a conventional method with a quartz cell (10 mm optical pathlength) and a fluorometer.

Analogous results were obtained when an aqueous PNIPAM–ANS solution was irradiated by a 1064-nm laser beam (Fig. 7; $P_{1064} = 1.4$ W, 20 °C). In this experiment, both 1064-nm and pulsed 355-nm laser beams were irradiated coaxially to the sample solution in order to monitor the ANS fluorescence from a PNIPAM particle produced by the photo-thermal phase transition. The fluorescence of ANS showed $\lambda_{max}\approx475$ nm ($\nu_{max} = 2.11\times10^4$ cm^{-1}; b), and was highly intense compared with that before 1064-nm laser irradiation (a). λ_{max} of ca. 475 nm indicates that the micropolarity in the PNIPAM particle is as low as that in ethanol/H_2O = 9/1 (v/v)—*N*,*N*-dimethylformamide ($\varepsilon = 30.1$—36.71).[25,26] A considerable amount of water molecules is excluded from the polymer chains upon PNIPAM particle formation. The phase transition of an aqueous PNIPAM solution, similar to that by thermal heating in the dark (Fig. 6), is induced by 1064-nm laser-beam irradiation.

Simultaneous Laser Manipulation of a PNIPAM Particle by a 1064-nm Laser Beam: A 1064-nm laser beam can act as a light source for the noncontact and nondestructive manipulation of a PNIPAM particle (*laser manipulation*). As previously reported, laser manipulation of a microparticle in solution is based on the refraction of a light beam through

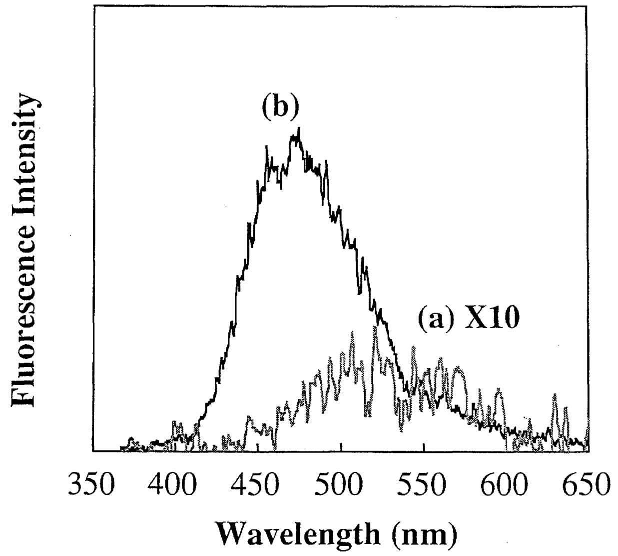

Fig. 7. Fluorescence spectra of ANS before (a) and during 1064-nm laser irradiation (b) to the PNIPAM solution (3.6 wt% in H_2O). Observed under an optical microscope.

a particle. According to the conservation law, the amount of momentum change before and after light refraction at the particle/solution boundary (ΔP) should be exerted to the particle at a direction opposite to that of ΔP ($-\Delta P$). The sum of $-\Delta P$ generated at all areas of the particle irradiated by the laser beam is the driving force of laser manipulation (called the *radiation force*). When the refractive index of a particle (n_1) is higher than that of the surrounding medium (n_2), the force is directed to the focal spot of the laser beam.[8,10,11,16] Therefore, the particle is trapped and manipulated in the vicinity of the focal spot of the laser beam.[8—16]

As shown in Fig. 8, actually, a PNIPAM particle produced by the photo-thermal phase transition (the particle at the center of the photograph) was manipulated by the incident 1064-nm laser beam. The Brownian motion and viscous flow of the particle were suppressed by the laser beam, while a polystyrene particle as a reference sample (not irradiated) was transferred along the X (a) or Y direction (b) with the movement of the microscope stage. As described in the preceding section, PNIPAM polymer chains are dehydrated above T_c, and the refractive index of PNIPAM ($n_1 = 1.508$)[27] is higher than that of water ($n_2 = 1.33$).[29] Therefore, the refractive-index condition for laser manipulation (i.e., $n_1 > n_2$) is satisfied upon particle formation. This is the first demonstration of simultaneous PNIPAM microparticle formation and manipulation by an IR laser beam.

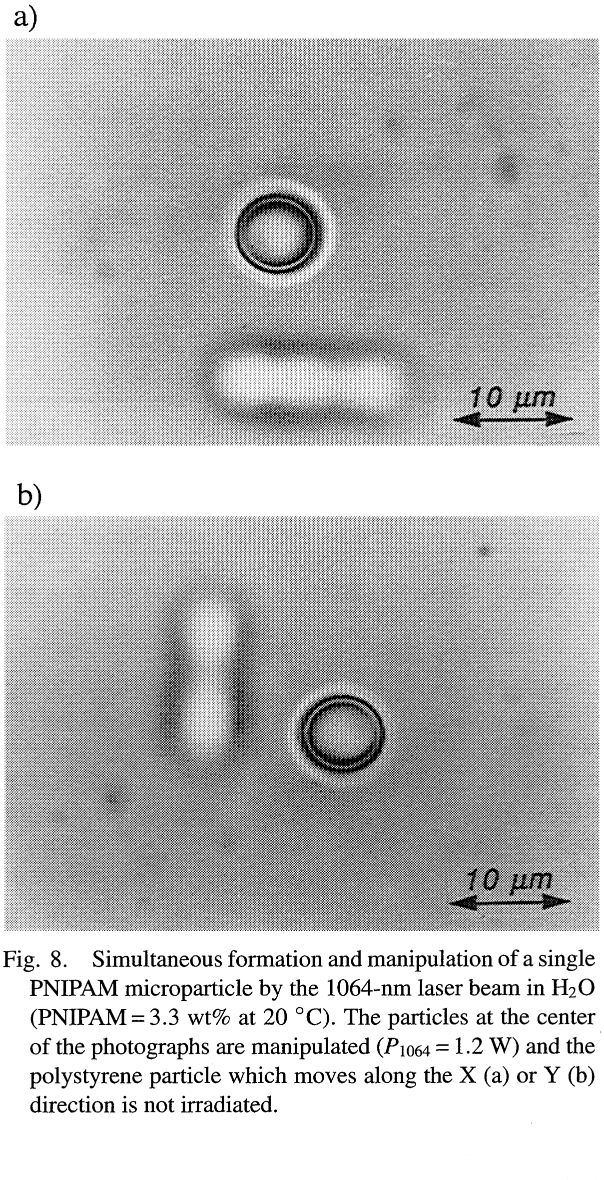

Fig. 8. Simultaneous formation and manipulation of a single PNIPAM microparticle by the 1064-nm laser beam in H_2O (PNIPAM = 3.3 wt% at 20 °C). The particles at the center of the photographs are manipulated ($P_{1064} = 1.2$ W) and the polystyrene particle which moves along the X (a) or Y (b) direction is not irradiated.

A Role of Radiation Force for Particle Formation: The morphologies of the PNIPAM particle and its surroundings change along with the laser irradiation time, and the surface of the particle becomes smooth upon prolonged irradiation (Fig. 2). Since the local heat generated by laser irradiation is not expected to exceed the glass transition temperature of the polymer ($T_g = 145$ °C),[27,28] the change in the morphologies is not ascribed to a thermal effect. Therefore, the radiation force plays an important role in PNIPAM particle formation. Above T_c we suppose that the globular-structured polymer chains, or very minute particles whose total volume and density are sufficient for light refraction, are attracted towards the laser beam through a weak, but finite, radiation force.[30] Indeed, we experimentally confirmed that submicrometer PNIPAM particles produced above T_c in D_2O were attracted and concentrated by a 1064-nm laser beam, as shown in Fig. 9. At 34 °C, the phase transition of the solution in the dark gave submicrometer PNIPAM particles, as can be recognized by a number of small black spots (a). Upon 1064-nm laser irradiation, a relatively large black spot was produced (b; $t = 0.5$ s) and, the diameter of the spot increased to 10 (c; $t = 4.4$ s)—14 µm (d, $t = 75$ s). Growing-in of the spot during 1064-nm irradiation indicates an aggregation of the PNIPAM submicrometer particles. Since the photo-thermal effect is neglected in D_2O, the driving force for the attraction and concentration of the particles should be the radiation force of the laser beam.

According to these discussions concerning the role of the radiation force, the results given in Figs. 2 and 3 are explained

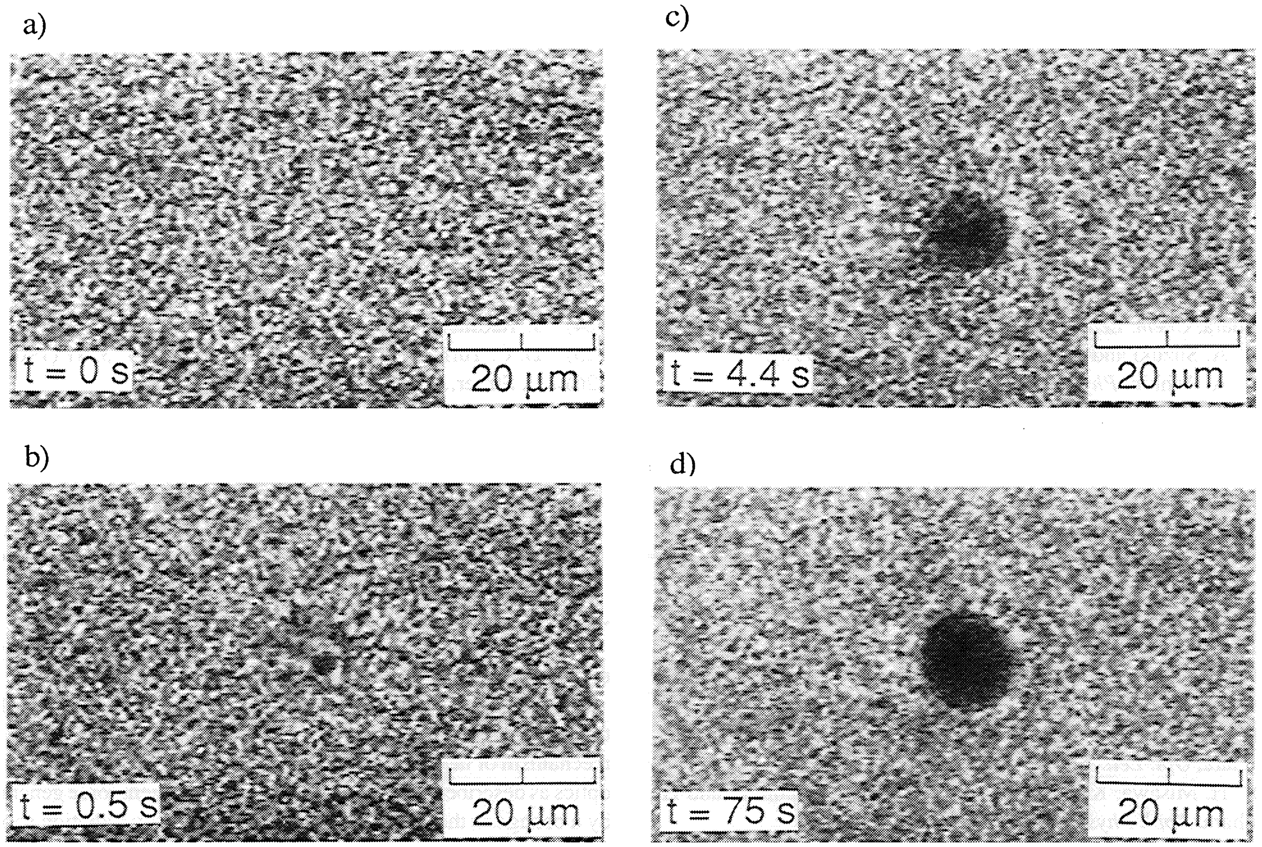

Fig. 9. Attraction and concentration submicrometer PNIPAM particles by the 1064-nm laser beam in D_2O at 34 °C. The dark spot at the center of the photographs grows-in with laser irradiation time. PNIPAM = 3.6 wt% and $P_{1064} = 0.75$ W.

as follows. The particle formation consists of both fast ($t <$ 100 ms) and slow ($t >$ 100 ms) processes (Fig. 3). Since the primary origin of particle formation is the photo-thermal local heating of water, the fast process can be well explained by the relevant phase transition of the solution. Once small PNIPAM particles with submicrometer or smaller sizes are produced, they are attracted to the focal spot of the laser beam by the radiation force, as in the case of Fig. 9, which renders a single PNIPAM particle with $d \approx 4$ μm ($t < 100$ ms, Fig. 2b). Since the formation of a PNIPAM particle leads to an increase in the thermal conductivity of the solution near to the focal spot, the solution temperature in the periphery of the particle becomes higher than that predicted from the equation of ΔT. This results in the structures around the PNIPAM particle shown in Fig. 2b and 2c through the phase transition of the solution in this region. As demonstrated in Fig. 9, small particles are gradually attracted to the higher laser-intensity region (i.e., focal spot) during several tens of seconds. We suppose that the slow particle formation process in Fig. 2 and 3b, accompanying the morphological changes of the structure around the PNIPAM particle, can be explained based on the same reasoning as that for the results in Fig. 9. For particle dissolution, switching off the laser leads to a disappearance of the force attracting the submicrometer particles, and to a simultaneous cooling of the solution by the water phase. A very fast dissolution of the PNIPAM microparticle may therefore be accounted for partly by the radiation force as well. The radiation force certainly plays an important role in PNIPAM particle formation.

Conclusion

The photo-thermal phase transition of an aqueous PNIPAM solution by an IR 1064-nm laser beam is quite unique since: i) fast and reversible microparticle formation and dissolution are attained, and ii) a relatively large PNIPAM microparticle, which cannot be obtained thermally in the dark, is arbitrary prepared and manipulated in three-dimensional space. The diameter of the particle was also shown to be controlled over 2—9 μm through P_{1064}, the polymer concentration, and the solution temperature. Since PNIPAM particles of several micrometers can be prepared only by the present method, the photoinduced formation and simultaneous manipulation of a PNIPAM particle by an IR laser beam is promising for the preparation and applications of PNIPAM-based photoresponsive materials of micrometer dimension.

It is worth noting that the radiation force has been demonstrated to play an important role in particle formation through the attraction and concentration of polymer chains by the incident laser beam. In addition to the role as a light or heat source, lasers can be used to modulate the conformation and/or aggregation states of polymer chains, micelles, and vesicles. Further studies, including an elucidation of the explicit role of the radiation force for microparticle formation, will be reported in a separate publication.[20)]

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