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Poly(N-isopropylacrylamide) Microparticle Formation in Water by Infrared Laser-Induced Photo-Thermal Phase Transition

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Irradiation of a focused 1064 nm laser beam to an aqueous poly(N-isopropylacrylamide) solution resulted in the reversible microparticle (diameter ≈ 7 μm) formation through local heating of water by the laser beam and subsequent phase transition of the polymer solution. The microparticle produced was simultaneously manipulated in three-dimensional space by the incident 1064 nm laser beam.

Laser light can be focused into a wavelength-order spot so that lasers play crucial roles for both inducing and elucidating chemical reactions in μm-subμm domain.1) Since laser light is easily switched on and off, furthermore, various chemical and physical phenomena would be controlled in μm-subμm dimensions. Another characteristic feature of a focused laser beam is "*radiation force*" generated by refraction of a laser beam through a microparticle.2) This particular force enables noncontact and nondestructive manipulation of various microparticles in solution ; *laser trapping/manipulation*. Indeed, we recently demonstrated three-dimensional manipulation of individual microparticles such as polymer latex particles, microcapsules, and so forth undergoing Brownian motion in solution.3,4) Chemistry in μm domains will be certainly opened through lasers and related techniques. As an example of laser-induced chemistry in μm dimensions, we report reversible microparticle formation/dissolution of poly(N-isopropylacrylamide), PNIPAM, in water by a focused 1064 nm laser beam.

PNIPAM was prepared by heating an aqueous solution (100 ml) of N-isopropylacrylamide (1.4 g), N,N,N',N'-tetramethylethylenediamine (100 μg), and ammonium persulfate (0.1 g) at 30 °C for 8 h. The polymer was purified by repeated decantations from ethanol-water. Molecular weight (M_w) of the polymer was determined to be 1×10^6 on the basis of intrinsic viscosity ($[\eta]$) measurements in water and the relation ; $[\eta] = 4.58 \times 10^{-4} M_w^{0.93}$.5) PNIPAM dissolved in deionized water (3.6 weight %) was placed between

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two quartz plates and set on the stage of an optical microscope (Nikon, Optiphoto XF). The sample solution was then irradiated by a focused (≈ 1 μm spot) 1064 nm laser beam from a CW Nd^{3+}:YAG laser (Spectron, SL-903U) through a microscope objective (magnification = 100, numerical aperture (NA) = 1.30). Effective laser power irradiated to the sample solution (P_{1064}) was determined to be 1.2 W by the reported method.3) Further details on the experimental setup have been reported in elsewhere.3)

An aqueous PNIPAM solution exhibits a phase transition at 31 - 32 °C (a lower critical solution temperature : LCST), above which the polymer chains associate with each other to form water-insoluble subμm polymeric particles owing to a large increase in hydrophobicity of the polymer.6) At ambient temperature (20 ± 0.1 °C), the solution is homogeneous and clear while photoirradiation of a focused 1064 nm laser beam (P_{1064} = 1.2 W) leads to instantaneous PNIPAM microparticle formation in the vicinity of the focal spot of the laser beam as typically shown in Fig. 1. Growing-in of the particle to a diameter (d) of ≈ 4 μm was very fast (within 100 ms, Fig. 2), whereas prolonged irradiation rendered a gradual increase in d (Fig. 3). At irradiation time over 40 s, the diameter of the particle reached to an equilibrium value (≈ 7 μm). When the laser was turned off, the microparticle disappeared with a time constant of ≈ 150 ms (Figs. 2 and 3). Formation/dissolution of the microparticle was highly reversible for several cycles without any appreciable change in the equlibrium diameter of the particle. Recently, Suzuki and Tanaka reported that crosslinked PNIPAM gels exhibited volume shrinkage in water with absorbing incident light by dye chromophores attached to the gel.7) In the present system, however, PNIPAM itself does not absorb at 1064 nm. H_2O possesses absorption around 1064 nm due to several OH vibration modes while D_2O scarcely absorbs at this wavelength.8) Since the PNIPAM microparticle formation cannot be observed in D_2O, the phenomenon is induced by absorption of the 1064 nm laser beam by H_2O and subsequent phase transition of the polymer solution via photo-thermal local heating of H_2O.

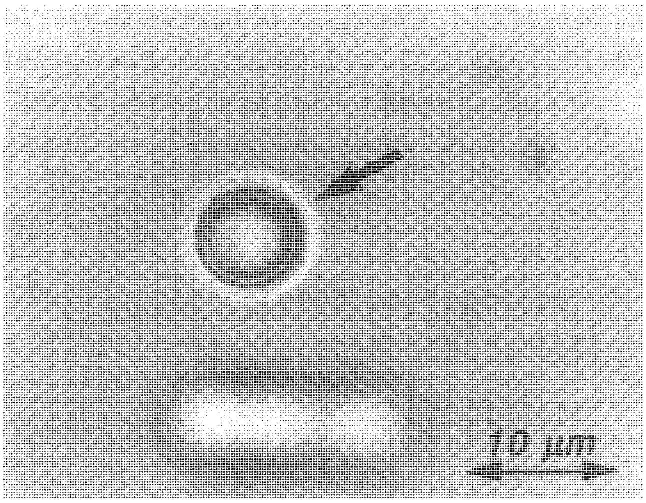

Fig. 1. Photo-thermal phase transition of PNIPAM in water by a focused 1064 nm laser beam. The particle indicated by the arrow is produced upon laser irradiation and manipulated simultaneously by the incident laser beam (P_{1064} = 1.2 W, 20 ± 0.1 °C).

If one assumes that a 1064 nm laser beam absorbed by a spherical H_2O droplet with the radius (R) of 1 μm is converted to heat (Q) and heat generated is equilibrated with the surrounding water phase, the relevant temperature increase in the droplet (ΔT) can be calculated by, $\Delta T = Q/4\pi\kappa R$, where κ is thermal conductivity of H_2O.9) Q was estimated by absorbance of H_2O at 1064 nm (5.6×10^{-6} for 1 μm optical path). For P_{1064} = 1.2 W,

ΔT was calculated to be ≈ 4 °C for 1 μm^3. In the actual experiments, the laser beam is irradiated to the solution with a large cone angle (≈120 °) due to the use of a large NA (1.30) objective lens, so that water is heated in a larger volume than 1 μm^3 and, therefore, ΔT would be much higher than 4 °C. At 20 °C, the particle formation can be observed at $P_{1064} > 0.7$ W, while the laser power necessary to produce a PNIPAM particle decreases with raising a solution temperature. The results clearly indicate that photothermal phase transition of the polymer solution via local heating of H_2O is a primary origin of the phenomenon. It is worth emphasizing, however, that a PNIPAM particle produced upon laser irradiation is much larger than those produced above LCST in the dark (d < 1 μm). Furthermore, the surface of the particle is very smooth as far as the resolution of an optical microscope (Fig. 1). We suspect that the present results will not be explained by laser-induced local heating of the solution alone and that the 1064 nm laser beam itself plays an important role for the PNIPAM microparticle formation.

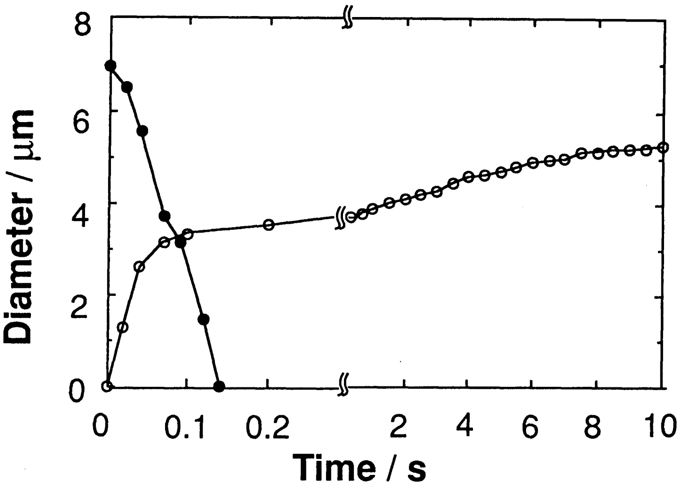

Fig. 2. Initial time-response profiles of PNIPAM microparticle formation (open circles ; laser on) and dissolution (closed circles ; laser off) in water.

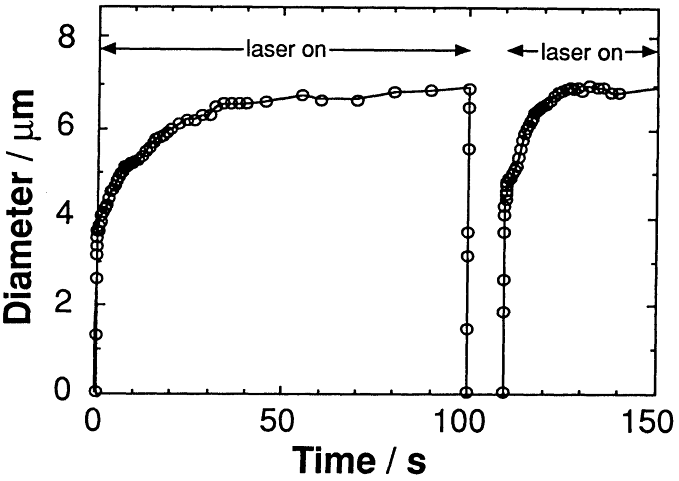

Fig. 3. Reversible PNIPAM microparticle formation/dissolution in water.

Once a PNIPAM microparticle is produced upon photoirradiation, the 1064 nm laser beam is refracted by the particle. The amount of the momentum change upon refraction (ΔP) should be conserved and, therefore, ΔP (radiation force) is exerted to the particle as discussed in detail elsewhere.[2,3] When the refractive index of the particle is higher than that of the surrounding medium, the particle is optically trapped by the laser beam.[2] Indeed, a PNIPAM particle is trapped and manipulated by the incident 1064 nm laser beam. In Fig. 1, the PNIPAM particle indicated by the arrow remains to be always focused in the photograph while a poly(methyl methacrylate) latex particle dispersed in water as a reference particle (not irradiated) moves along the X direction with flow of the solution. Besides the X direction, the particle was optically manipulated along the Y and Z (laser beam axis) directions similar to the previous results on laser manipulation of various microparticles.³⁾

The aggregated PNIPAM polymer chains above LCST whose volume and density are enough for refraction of the laser beam would be attracted towards the focal spot of the laser beam through small but finite radiation force exerted to the aggregated polymer chains. Indeed, we experimentally confirmed that subμm PNIPAM particles above LCST in D_2O were attracted and concentrated by the 1064 nm laser beam. Since the photo-thermal effect is neglected in D_2O as mentioned above, driving force for attraction and concentration of the particles would be radiation force of the laser beam. To the best our knowledge, this is the first demonstration for laser control of molecular aggregation. The PNIPAM particle formation in H_2O (Fig. 1) will be therefore responsible for both radiation force and local heating of H_2O by the 1064 nm laser beam.

The photo-thermal phase transition of PNIPAM by an infrared 1064 nm laser beam is quite unique since, i) fast and reversible microparticle formation/dissolution is attained, and ii) a relatively large PNIPAM microparticle ($d \approx 7$ μm) which cannot be obtained thermally in the dark is arbitrarily prepared and manipulated in three-dimensional space. The present results could be further applied to laser-controlled microactuators, microdevices, drug delivery systems, and so forth. Further studies including elucidation of explicit roles of radiation force on the microparticle formation are in progress and the detailed discussion will be made in forthcoming publications.

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