A Single Droplet Formation from Swelled Micelles by Radiation Pressure of a Focused Infrared Laser Beam

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Radiation pressure due to photon momentum change was prospected by Newton, theoretically proved by Maxwell, and experimentally confirmed by Lebedev.[1] Based on the radiation pressure, a micrometer particle in solution can be trapped by a laser beam, which was demonstrated for the first time by Ashkin.[2] The Brownian motion of microparticles is completely suppressed without any contact and destruction, hence the trapping method is very useful to treat microparticles in solution. We have developed this method further to manipulate a single or plural microparticle(s) freely in three-dimensional space by introducing a computer-controlled pair of galvano mirrors; scanning laser micromanipulation.[3] Now, chemical applications are conducted by combining this method with fluorescence spectroscopy, photochemical reaction, laser ablation, and electrochemistry using a microelectrode.[4] It is also known that radiation pressure is exerted upon Rayleigh particles that are smaller than the wavelength. Therefore, spectroscopy and chemistry of a single molecular assembly, quantum particle, and so on in solution is expected.

The radiation pressure exerted on such a Rayleigh particle is expressed as follows,[5]

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

where E and B are electric field strength and magnetic flux density, respectively. α is an equivalent polarizability of the particle under the dipole approximation and is given by

$$\alpha = 4\pi\epsilon_b r^3 \frac{(n_a/n_b)^2 - 1}{(n_a/n_b)^2 + 2} \qquad (2)$$

where r is the radius of the particle, n_a and n_b are the refractive indices of the particle and the surrounding medium, respectively, and ϵ_b is the dielectric constant of the medium. The first term of eq 1 is an electrostatic force acting on the dipole in the inhomogeneous electric field, which is called a gradient force. When $n_a > n_b$, the polarizability is positive, so that the gradient force attracts a particle to the focal point. The second term is derived from the change in the direction of the Poynting vector, which is called a scattering force which pushes the particle along the beam direction. Since the gradient force is usually much stronger than the scattering force when a laser beam is focused onto the particle, the radiation pressure works for trapping Rayleigh particles in the vicinity of the focal point.

Recently we have succeeded in trapping polymer chains of poly(*N*-isopropyl acrylamide) and its hydrophobically modified copolymer in aqueous solution and in demonstrating a single-particle formation by focusing an infrared laser beam under a microscope.[6−8] As a result a single particle was observed at the focal point, which is due to a change from coil (extend) to globule conformations. However, this precipitation in bulk solution is well-known as a phase transition of the polymer solution and the homogeneous distribution of the gel particles is brought about by temperature elevation, pH change, and concentration increase of additive ions.[9] The experiments on radiation pressure effect upon the polymer solution are accompanied by a temperature elevation due to absorption of the laser beam (1064 nm) by H_2O via O−H vibrational overtone bands. Thus, a single-particle formation by a focused laser beam is brought about by a complicated mechanism. In order to demonstrate clearly a radiation pressure effect upon molecular association and to show the applicability in more general terms, we here report aggregation and fusion processes of micelles in aqueous solution where long-chain polymers are not present.

The micelle was prepared by vigorously stirring a 10-mL aqueous solution of sodium dodecyl sulfate (SDS, 1.7×10^{-2} mol/L) and 0.2 mL of xylene for 1 min, and then 0.1 mL of 1-pentanol was added with additional stirring for 30 min. Futhermore, the solution was mixed with 90 mL of distilled water, and stirred again for 30 min. For fluorescence measurement aromatic molecules were added to xylene in advance. The size of the swelled micelles was estimated to be smaller than 100 nm, since it was difficult to observe the micelles with an optical microscope (Zeiss, UMSP50) by which we could identify polymer latex particles with a diameter of 200 nm.

A fundamental beam (1064 nm) of a CW Nd:YAG laser (Spectron, SL902T) was introduced into the microscope and focused on a ∼1 μm spot by an objective lens (magnification ×100, NA = 1.3), which was used as a trapping light (350 mW). The radiation pressure upon a swelled micelle (∼100 nm) is calculated at $\sim 3 \times 10^{-13}$ N. The aqueous solution of swelled micelles was sandwiched between two quartz plates (thickness 350 μm) and placed on a sample stage of the microscope. Quartz plates were separated by 80-μm spacers and the focal point of the trapping beam was set to 10 μm below the upper quartz plate. The irradiation effect upon the behavior of swelled micelles was monitored with a transmission image of a component tungsten lamp of the microscope or with a back-scattering image of He−Ne laser light which was coaxially introduced into the microscope. These images were taken by a CCD camera. Fluorescence spectra excited by a mercury lamp (313 nm) were observed with an intensified multichannel spectrophotometer (Hamamatsu Photonics, PMA10). The detection area was limited to a 2-μm spot by a pinhole. As a reference experiment, it was demonstrated with this system that 63-nm polystyrene latex and 20-nm gold particles could be trapped.

After a trapping laser was irradiated onto the sample solution, the back-scattering intensity of He−Ne laser increased gradually as shown in Figure 1. This indicates that the refractive index at the focal point becomes different from that of the surrounding homogeneous dispersed solution. As the refractive index of the swelled micelle is higher than that of water because of contained xylene (n_a = 1.49), the present behavior can be ascribed to an aggregation of the swelled micelles. After prolonged irradiation (>100 s), a single small droplet was observed at the focal point in a transmission image, and its

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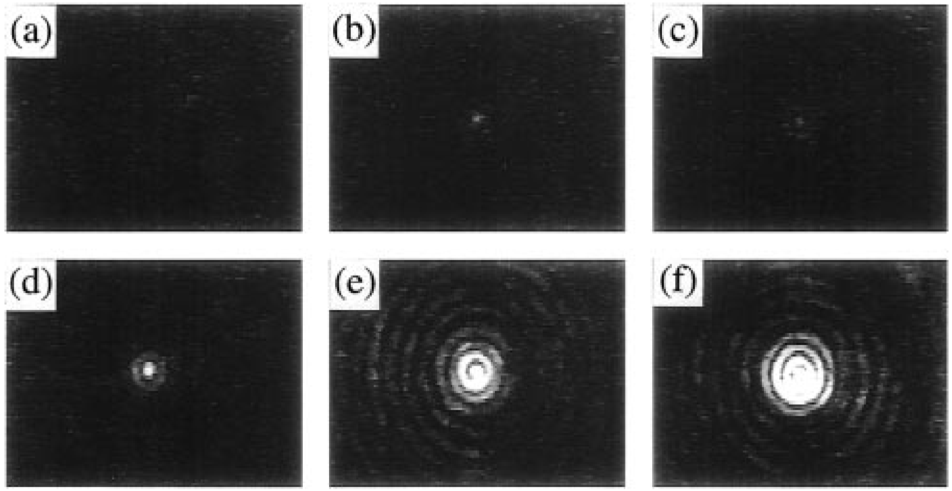

Figure 1. He−Ne laser scattering images of aqueous swelled micellar solution at (a) 0 (before irradiation of the trapping laser), (b) 30, (c) 90, (d) 150, (e) 240, and (f) 300 s after starting irradiation, respectively, which shows aggregation of swelled micelles and droplet formation in solution. He−Ne laser and trapping infrared beam were focused coaxially onto the same position.

diameter increased to ∼1 μm. After a few hundred seconds, growth of the droplet saturated and its diameter was fixed. Switching off the trapping laser, the droplet underwent Brownian motion without dissolution and disappeared immediately from the ocular field. If the sample solution was irradiated again, the aggregate was again formed, which was confirmed repetitively.

Electronic excitation of component molecules is difficult with the present laser beam, since micellar molecules and water have no electronic absorption at 1064 nm. However, an overtone band of the O−H vibration is clearly measured in a cell of 1 cm path length. Thermal excitation may be induced to some extent, since a high power laser beam was focused to a diffraction limit under the microscope. Indeed, it was pointed out that temperature elevation of a few degrees at the focal point is attained when a 1064-nm laser of 1.2 W was focused.[6] To examine the photothermal effect, therefore, we conducted the same experiment in D_2O, whose absorption at the wavelength is negligibly small. We confirmed the quite similar laser-induced aggregation process was also reproduced in this solvent, hence the effect is excluded as a probable reason. We consider that the aggregation of swelled micelles is induced by radiation pressure, which is supported by the following estimation. Under the present conditions, the potential energy well which is formed by the focused infrared laser beam and in which micelles are trapped is calculated to be 1.4×10^{-19} J. On the other hand, the thermal energy with which micelles move as Brownian particles is 4.1×10^{-21} J, hence the Brownian motion is completely suppressed.

An interesting question here concerns whether the generated droplet is just aggregated micelles or a single fused droplet. To discriminate these possible states, an intermolecular excitation energy transfer experiment was performed. Micelles containing an energy donor molecule and those with an acceptor molecule were prepared separately, and immediately after mixing both micellar solutions the irradiation experiment was carried out under the same conditions as described above. It is expected that the fluorescence spectra of the dispersed solution will be ascribed to the donor if fusion of aggregated micelles is not realized. On the other hand, if a single droplet where both donor and acceptor molecules are dissolved is formed, fluorescence spectra will be dramatically changed by energy transfer. Xylene solutions of pyrene (7.1×10^{-2} mol/L) and perylene (1.1×10^{-3} mol/L) were used for preparing swelled micelles, because pyrene−perylene is a representative pair for showing efficient energy transfer in solution. At 313 nm pyrene molecules are excited efficiently, and actually only pyrene monomer fluorescence was detected at 370−420 nm before introducing the trapping laser beam. Association and dissociation of micelles are in general possible, and consequently pyrene and perylene may be contained together in individual swelled micelles leading to intermolecular energy transfer. However, perylene fluorescence due to the energy transfer process was not observed without the trapping laser beam. Upon 1064-nm irradiation a droplet grew, and perylene fluorescence appeared at 430−530 nm and its intensity increased as shown in Figure 2. Thus, it is well-confirmed that pyrene and perylene were dissolved in the single droplet upon irradiation and energy transfer from pyrene to perylene was induced. This clearly indicates that fusion of the swelled micelles was achieved by radiation pressure.

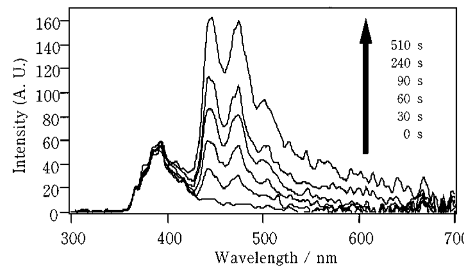

Figure 2. Fluorescence spectral change of aqueous swelled micellar solutions containing aromatic molecules. An excitation light source was a mercury lamp (λ = 313 nm) and only pyrene monomer fluorescence was observed before introducing the trapping laser. Upon prolonged irradiation, perylene fluorescence due to pyrene−perylene energy transfer became relatively intense, indicating fusion of swelled micelles.

It is historically believed that the irradiation effect of light in chemistry is ascribed to photophysical, photochemical, and photothermal processes. The present paper reports for the first time that the radiation pressure effect of a focused infrared laser beam is useful and promising in controlling association and fusion of molecular aggregates in solution. Changing micellar component molecules, we are elucidating physical parameters crucial for exploring novel radiation pressure effects: micelle size, stability, head group of detergent molecules, refractive index, and viscosity of the oil phase, and so on.

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