

Molecular Association by the Radiation Pressure of a Focused Laser Beam: Fluorescence Characterization of Pyrene-Labeled PNIPAM

J. Hofkens, J. Hotta, K. Sasaki,* and H. Masuhara*

Department of Applied Physics
Osaka University, Suita, Osaka 565, Japan

T. Taniguchi and T. Miyashita

Institute for Chemical Reaction Science
Tohoku University, 2-1-1 Katahira
Aoba-ku, Sendai 980-77, Japan

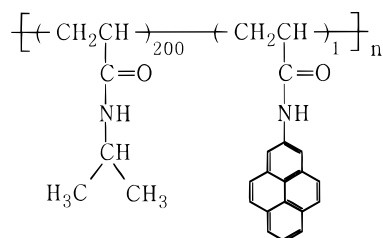
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Recently, we have reported quite novel and interesting laser induced behavior of poly(*N*-isopropylacrylamide) (PNIPAM) in aqueous solutions.^{1–3} Irradiation via a microscope by a CW laser beam of 1064 nm gives absorption through the vibrational overtone band of H₂O and locally heats up the solution at the focal spot. As a result, the phase transition of the polymer is induced, leading to the coil to globule transition of the polymer.^{4–9} Simultaneously, the focused laser beam exerts radiation force upon the molecular aggregates, due to the Lorentz force upon Rayleigh particles,^{10–12} resulting in a single micro-particle.

In order to demonstrate clearly the role of the radiation force upon molecular assembling in the polymer solution, we have carried out two different experiments. In the first experiment we have succeeded in forming a microparticle in a D₂O solution of PNIPAM where photothermal temperature elevation is not induced because of the red shift of the overtone band.^{1,2} In a second experiment, an aqueous solution of poly(*N*-isopropylacrylamide-*co*-*N*-octadecylacrylamide) containing sodium dodecylsulfate (SDS) was investigated. The interaction of SDS with the octadecyl chains is known to result in partially negative charged polymer chains. Due to the electrostatic repulsion the collapse of the polymer chains is normally not realized even by temperature elevation. However, particle formation could be seen when a focused IR laser beam was applied on the solution.³ From these experiments we have concluded that molecular assembly by radiation pressure is a quite general phenomenon.

The question remains whether the structure of a single microparticle formed by the radiation pressure effect is similar

to the structures of the submicrometer aggregates formed by temperature elevation. As the fluorescent probe method is excellent to monitor local structures of polymers, pyrene labeled PNIPAM (Py-PNIPAM) was synthesized as a fluorescent probe labeled PNIPAM polymer. *N*-Isopropylacrylamide (NIPAM) (Eastman Kodak) was recrystallized from a benzene/*n*-hexane mixture. *N*-(1-Pyrenyl)acrylamide (Py) was synthesized by the reaction of 1-aminopyrene with acryloyl chloride. Py-PNIPAM was prepared by free radical polymerization of NIPAM with Py in dimethylformamide (DMF) at 60 °C using AIBN as a thermal initiator. The molecular weight (M_w) for the copolymer was determined to be 1×10^5 by GPC. The ratio of NIPAM monomer units over pyrenyl units was 200/1.



Py-PNIPAM

The intensity ratio of the 0–0 vibrational band (375 nm) over the 0–2 vibrational band (395 nm) in the fluorescence spectrum of pyrene increases as the environmental polarity increases.¹³ Furthermore, diffusion is not efficient in polymer associates, hence excimer fluorescence reflects high local concentration or dimer configuration in the ground state.

The microparticle formation process was here monitored by CCD camera. Before introducing the 1064 nm laser beam of ca. 100 mW, a clear and transparent aqueous solution of 3.6 wt % Py-PNIPAM was observed under the microscope. After switching on the laser, a single particle could be seen. The particle formation process (Figure 1) was similar to that reported before for aqueous solutions of nonlabeled PNIPAM.²

Fluorescence measurements under a confocal microscope were done as previously reported.¹⁴ Fluorescence spectra of pyrene labeled PNIPAM in H₂O are given in Figure 2. The intensity ratio of the 0–0 and the 0–2 bands was about unity before irradiation and weak excimer fluorescence was found as a tail in the 450–600-nm region. This means that the micropolarity around the pyrene chromophore in water is rather high and that the association of the chromophore is inefficient. After 2 min irradiation, a small particle is formed in which the micropolarity is much lower than in the original solution and a small increase in excimer fluorescence can be observed. Upon prolonged irradiation the particle becomes more apolar and the polymer chains seem to be aligned in such a way that a substantial increase in excimer fluorescence can be seen. In H₂O both photothermal and radiation pressure effects are involved as reported previously,^{1–3} hence it is considered that the assembly structures are determined by both effects.

To separate photothermal effect we conducted similar experiment in D₂O where temperature elevation is practically neglectable. As summarized in Figure 3, micropolarity was decreased and excimer formation was enhanced upon irradiation, which resembles the behavior in H₂O, but the tendency was clearer in D₂O than in H₂O. The fluorescence spectra obtained by just

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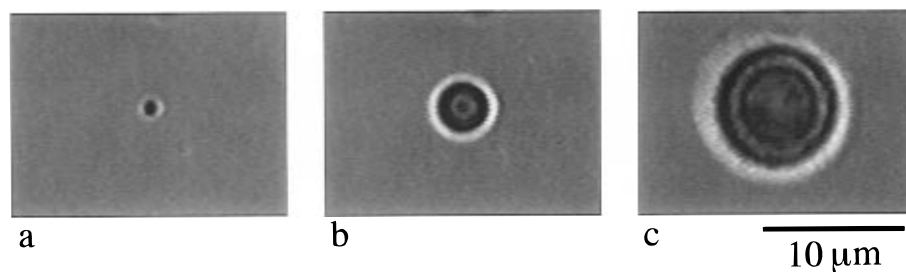


Figure 1. Photographs during a laser induced phase transition in an aqueous Py-PNIPAM solution (3.6 wt % in H₂O, $P_{1064} = 200$ mW, initial temperature (T_{init}) was 22 °C): (a) irradiation time (t_{ir}) = 30 s, diameter = 1 μm ; (b) $t_{\text{ir}} = 240$ s, diameter = 4 μm ; (c) $t_{\text{ir}} = 540$ s, diameter = 10 μm .

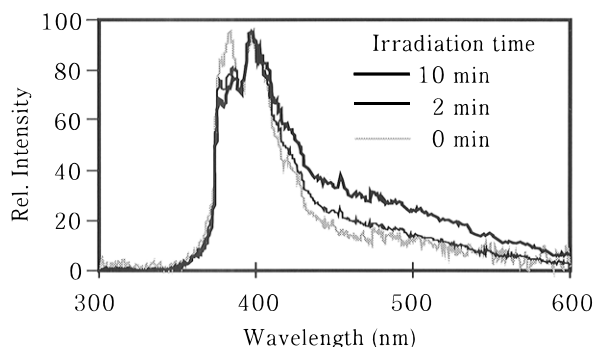


Figure 2. The fluorescence spectra of Py-PNIPAM (3.6 wt % solution, 313 nm excitation wavelength) in water at different irradiation times. The spectra are normalized at the 0–2 vibrational band.

temperature elevation (Figure 3b) are quite different from the spectra upon irradiation. The particle formed by temperature elevation did not show appreciable excimer formation, although apolar character around the pyrene chromophore is similarly observed. The fluorescence spectral data indicate complete different structures of the assembled PNIPAM particle formed by radiation pressure and temperature elevation.

This fact is strongly supported by the former observations on formation and disappearance behaviors of the single particle.² The formation process in D₂O is extremely slow compared to temperature elevation. The particle formed in H₂O after short irradiation disappears instantaneously after blocking the laser beam, while a particle with the same size in D₂O disappears slowly in 60 s, indicating a more tightly packed particle.

In general the collapsed polymer chains in aqueous solution form a more apolar environment for the bonded pyrene chromophore and the mobility of the chromophores is restricted due to their association. Consequently appreciable excimer fluorescence is not expected; however, the present results in D₂O are completely opposite. Therefore, it is concluded that a new molecular assembling mechanism is achieved by the radiation pressure of the focused laser beam. The organization of molecular structures is of course responsible for the physical and chemical properties as well as for the function-

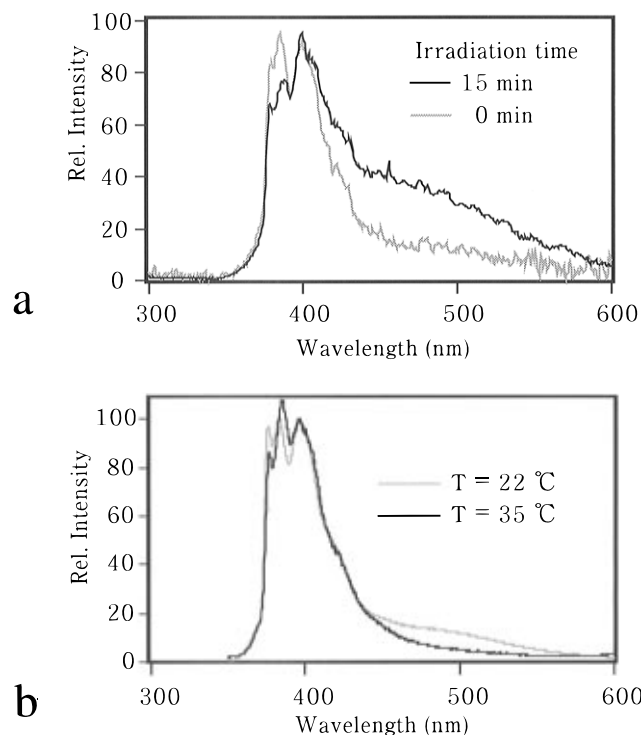


Figure 3. The fluorescence spectra of Py-PNIPAM (3.6 wt % solution, 313 nm excitation wavelength) in D₂O: (a) at different irradiation times and (b) at different temperatures. The spectra are normalized at the 0–2 vibrational band.

ality of the organizes, hence the radiation pressure effect is expected to open a new way to create new functional materials.

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