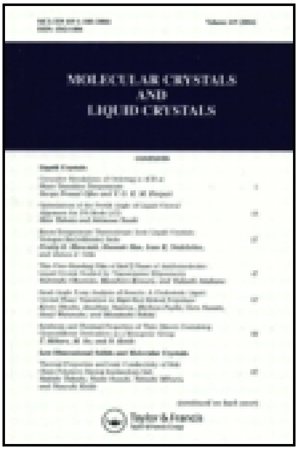

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Laser Induced Phase Transition in Aqueous Solutions of Hydrophobically Modified Poly(N-Isopropylacrylamide)

Johan Hofkens [a], Jun-Ichi Hotta [a], Keiji Sasaki [a], Hiroshi Masuhara [a], Herman Faes [b] & Frans De Schryver [b]

[a] Department of Applied Physics, Osaka University, Suita, Osaka, 565, Japan

[b] Department of Organic Chemistry, KULeuven, Celestijnenlaan, 200 F, Belgium

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LASER INDUCED PHASE TRANSITION IN AQUEOUS SOLUTIONS OF HYDROPHOBICALLY MODIFIED POLY(N-ISOPROPYLACRYLAMIDE).

JOHAN HOFKENS[1], JUN-ICHI HOTTA[1], KEIJI SASAKI[1], HIROSHI MASUHARA[1], HERMAN FAES[2], FRANS DE SCHRYVER[2]
[1]Department of Applied Physics, Osaka University, Suita, Osaka 565, Japan
[2]Department of Organic Chemistry, KULeuven, Celestijnenlaan 200 F, Belgium

Abstract : Phase transitions of amphiphilic copolymer solutions can be achieved by irradiating aqueous solutions of this polymer with an IR-laser beam. As a result, a single microparticle up to 15 μm is formed, whereas thermal heating of the solution results in submicrometer particles. Both the photo-thermal effect (due to absorption of 1064 nm by the H_2O overtone) and the radiation force cause the unusual large particle formation (up to 15 μm). Furthermore, the present study shows that the conformational distribution and associations of polymers in solution can be controlled with the radiation force of a focused laser beam.

INTRODUCTION

Poly(N-isopropylacrylamide)(PNIPAM), an amphiphilic polymer, containing hydrophobic and hydrophilic segments in a single molecule, shows interesting solution properties, especially in water. Heskins and Guillet[1] reported a reversible phase transition at a LCST (lower critical solution temperature) of 31 degree Celsius for PNIPAM in water. Since then, several experimental studies of this transitions have been reported.[2-11] A wide variety of experimental approaches, including light scattering, microcalorimetry, fluorimetry and so on have been used to elucidate the principals of this phase transition. Several authors reported that the water molecules near the hydrophobic segments form hydrogen bonds among themselves.[12-15] This arrangement of the water helps to keep the polymer in a rather random coil conformation. When the temperature is increased, the random thermal energy of the water molecules suffices to disrupt the hydrogen bonds. The well solvated random coils shrink to a state of thightly packed globular particles, followed by the onset of aggregation of individual chain molecules and the solution turns out to be inhomogeneous.

Recently, some papers were published dealing with the laser induced phase transition in aqueous PNIPAM solutions.[16,17] Normally, heating of polyacryamide solutions results in phase separation and the formation of submicrometer particles. By exposing PNIPAM solutions to a IR-laser beam, a single particle up to 25 μm was formed. Evidence was found for the influence of 'radiation pressure' upon this phase transition . The goal of this paper is to elucidate the use of the radiation force of a focused IR.-beam to control associations and conformations of polymers in solution. The polymer used in this study is a hydrophobically modified polyacrylamide polymer, PNIPAM-C18/68 (poly-(N-isopropyl-acrylamide-co-N-octadecylacrylamide, the number 68 is referring to the fact that for each 68 monomers, there is one octadecyl chain incorporated). The physical properties of amphiphilic polymers depend to a large extent on their chemical composition and the relative amount of hydrophobic to hydrophilic moieties. The hydrophobically modified polyacrylamides are known to form polymeric micelles [4,5] in such a way that there hydrophobic character is protected from the water phase. Hydrophobic probes can be dissolved in this polymeric micelles. Several attempts have been made to construct stimuli-responsive polymer solutions and gel systems which undergo phase transition by external stimulation, such as photons and chemicals.[6]

OPTICAL TRAP

Electromagnetic momentum will manifest itself as a radiation force or pressure whenever the momentum of an incident field is changed by deflection or absorption. The use of the radiation pressure as an optical trap for microparticles was first demonstrated by Ashkin.[18-21] More recently, Masuhara et al. proposed three-dimensional manipulation of microparticles by the radiation force of a single focused IR-laser beam.[22-26]

The physical origin of radiation force in single beam traps is most obvious for particles in the Mie size regime, where the diameter is large compared with the wavelength λ. Ray optics can be used to describe the scattering and optical momentum transfer to the particle.[18, 21, 22] If the refractive index of the particle has no imaginary part (no absorption) and a larger real part than that of the surrounding medium, then the particle will be attracted to the focused beam and will be three-dimensionally trapped in the vicinity of the focal point, against the thermal Brownian motion, gravity and convection.

Ray optics can not be applied to particles whose diameters are much less than the wavelength of the used light (Rayleigh particles). Wave optics are necessary for understanding the radiation pressure exerted on these small particles. According to the Rayleigh scattering theory, a particle whose diameter is much smaller than the wavelength of the used light works as a single electric dipole. The dipole experiences the Lorenz's force exerted by the optical electromagnetic field.[21, 22] This force corresponds to the radiation pressure[27] and can be written as the sum of the scattering force (F_{scat}, derived from the change in direction of a pointing vector) and the gradient force (F_{grad}, an electrostatic force acting on the dipole in the inhomogeneous electric field). When n_p (the refractive index of the particle) > n_m (the refractive index of the medium), then the gradient force is directed to the high electric field intensity region. If F_{grad} exceeds F_{scat}, there is a barrier for the particles to escape from the focal region. For a focused IR.-beam the value of $R=F_{grad}/F_{scat}$ is usually larger than 1 at the position of maximum gradient as the gradient force usually is stronger than the scatter force, and effective trapping occurs (optical trap). As calculated by Ashkin,[18] particles as small as 9 nm can be trapped (depending on the refractive indices of the particle and medium, focused spot size and laser power). For PNIPAM-C18/68 polymer chains (molecular weight of 100000 in THF, for details on the synthesis see reference 28), the hydrodynamic radius in water is reported [28] to be around 30 nm for solutions containing 0.4 w/v % copolymer. The refractive index of the PNIPAM-

C18/68 in the dehydrated or globule state is around 1.5, [29] higher than the refractive index of water (1.33), so all conditions are fulfilled to see optical trapping. A schematic visualization of the particle formation (via an IR-laser beam) in a PNIPAM-C18/68 solution is given in figure 1.

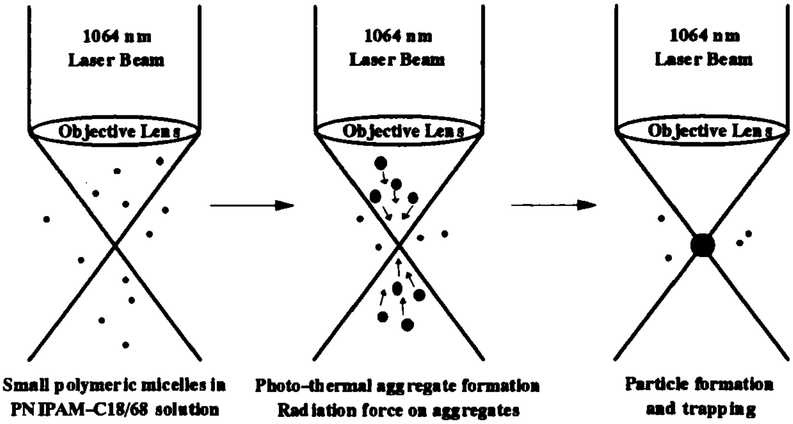

FIGURE 1 : Schematic representation of laser induced particle formation in PNIPAM-C18/68.

RESULTS AND DISCUSSION

PNIPAM-C18/68 in H_2O

The PNIPAM-C18/68 copolymer, used in the experiments, exhibits lower critical solution temperature (LCST) of 27-29 °C. Thermal heating results in the formation of submicrometer particles, leading to clouding of the solution. Photo-irradiation of the solution with an IR-laser beam (1064 nm, CW Nd^{3+}:YAG) through the objective lens (x 100, NA = 1.3) of an optical microscope (focused spot size ≈ 1 μm) leads, after a certain time of exposure, to the formation of a 1 μm particle. The particle starts to grow upon prolonged irradiation. A typical example of the morphological changes of the solution as a function of the laser irradiation time is shown in figure 2.

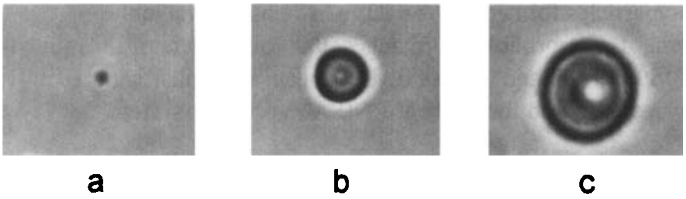

FIGURE 2 : Pictures of the morphological changes in a 0.45w/v % solution of copolymer after irradiation with an IR-laser beam (155 mW); a) t_{ir} =10 s, b) t_{ir} =150 s, c) t_{ir} = 300 s See Color Plate I.

The dependence of the particle diameter as a function of the laser power, for a certain concentration, is given in figure 3. The diameter increases with increasing laser power, but a maximum diameter is achieved at a certain laser power (~185 mW for all concentrations on copolymer). Higher laser power results in a faster achievement of this diameter, but does not lead to larger particles. Laser power above 220 mW leads to fast particle formation but the particle is not stable. As it reaches the maximum diameter, the particle disappears (after several minutes of irradiation) and one can clearly observe a convection in the sample solution. As explained before, the particle, with an appropriate size, is trapped against thermal Brownian motion, gravity and convection. As the particle grows, the gravity force will increase. With increasing laser power, also the temperature gradient induced in solution will increase. Therefore we consider that the trapping force will be overcome by the other forces at a certain laser power.

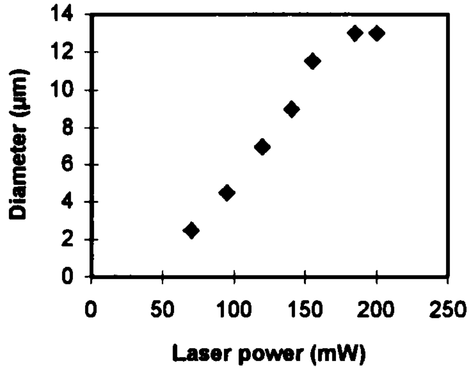

FIGURE 3 : Diameter (error smaller than 1 µm) of the laser induced particle as function of the applied laser power for a 0.45 w/v % copolymer solution (diameter measured after 10 minutes of irradiation). Particles formed above 220 mW are not shown since they disappeared after 6 to 7 minutes.

After blocking the laser beam, the particle desintigrates and irregular microparticles (flocs) can be seen. These microparticles continue to exist even after cooling down of the solution. The presence of this particles after the measurements indicates that the multipolymeric particles formed are too large to redissolve quickly.

In general, the morphologic changes that occur when an aqueous solution of PNIPAM-C18/68 is irradiated with an IR-laser beam are similar with the previous reported changes that were observed for the neat PNIPAM-polymer system.[30]

PNIPAM-C18/68 in D_2O

Hotta et al.[31] recently demonstrated that fusion of swelled micelles (to form a visible micelle) can be achieved with the radiation force of a focused IR.-beam. As PNIPAM-C18/68 is known to form small polymeric micelles, we tried to check whether these micelles could be gathered by the radiation force and whether a visible particle could be formed. In order to avoid temperature effects, the experiment was done in carefully prepared D_2O solutions (to avoid contamination with water, the polymer was dried under vacuum for several days and the solution preparation was conducted under dry N_2 atmosphere). The polymeric micelles are initially too small to cause visible scattering of a HeNe-laser beam (focused at the same position as the IR-laser beam) through the microscope. Irradiation of a 0.33 w/v % solution of PNIPAM-C18/68 in D_2O (185 mW) led to the scattering of a HeNe laser beam (at the focal point of the IR.-beam) after 30 seconds. Prolonged irradiation (>240 s) resulted in a visible microparticle with a diameter of a few micrometer (slightly larger than the focused spot size). Similar results were reported for the PNIPAM-homopolymer, although in the latter case longer irradiation times were required.[30]

At the current stage, the microparticles are believed to result from a radiation force induced phase transition (the polymer chains are forced so close together that it becomes thermodynamically preferable to assume the folded shape). The reported results suggest that the structure of the microparticles obtained with a combination of radiation force and photo-thermal effect (H_2O) and the structure of the microparticles obtained as result of the radiation force only (D_2O) might be different. As the fluorecence probe technique is known to be an excellent method to measure micropolarity and microviscosity as well as small structural differences[4,5], fluorescence measurements on hydrophobically modified polyacrylamide polymer containing pyrene are currently undertaken to confirm these eventual differences.

PNIPAM-C18/68 in H_2O in the presence of surfactant

A situation with a strong interaction between copolymer and cosolute, involving strong adsorption of the cosolute to the polymer, rendering the polymer more polar and increasing its solubility, is thought to be significant mainly with amphiphilic cosolutes. These often bind strongly to nonionic polymers and are expected to have dual effects. The alkyl chains introduce hydrophobic groups whereas the introduction of charged groups increases the polymer polarity resulting (at low electrolyte and polymer concentration) in a strong interpolymeric repulsion. The change in cloudpoint will depend on the balance between those two effects and will, hence, be sensitive to the presence of counterion or of (simple) electrolyte. In the absence of added salt an increase in solubility is expected because the electrostatic effect dominates. [32,33]

We followd the diameter of the laser induced particles in aqueous PNIPAM-C18/68 solutions, containing increasing concentrations of SDS (sodium dodecyl sulphate) and C16PyrCl (cetylpyridinium chloride) (laser power was 185 mW, all diameters were measured after 10 minutes of irradiation). As can be seen in figure 4, for both surfactants there is a substantial decrease in particle diameter, even at surfactant concentrations (0.01 mM) far below the critical micelle concentration (CMC) of the surfactants (1 mM and 8 mM for C16PyrCl and SDS, respectively). Faes et al.[28] observed that clouded solution of PNIPAM-C18/68 (temperature is above LCST) gradually became transparent as surfactant is added. The fact that we observed microparticles in solutions containing as much as 20 mM surfactant gives a clear indication of the influence of the radiation force on the particle formation process. The radiation force is apparently strong enough to overcome the electrostatic repulsion between the polymer chains.

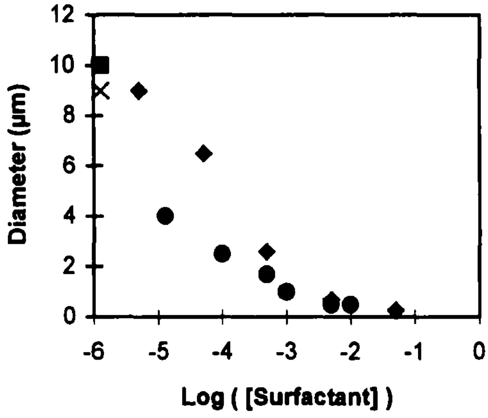

FIGURE 4 : The diameter of the observed particle as a function of the concentration on surfactant (● : SDS in a 0.25 w/v % solution of polymer, x : the same solution without SDS, ◆ : C16PyrCl in a 0.33 w/v % solution of polymer, ■ : the solution without C16PyrCl); all diameters were measured after 10 minnutes of irradiation.

We also studied the influence of the neutral surfactant polyoxyethylene(23)-laurylalcoholether (Brij35). Figure 5 shows a substantial increase in the particle diameter at neutral surfactant concentrations below the CMC.

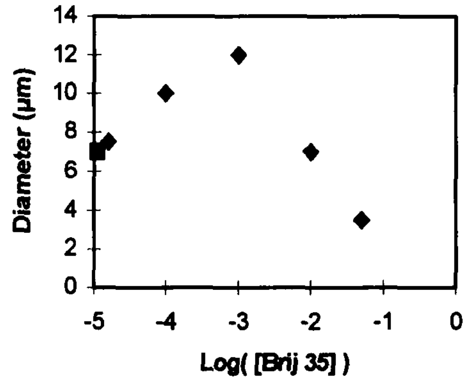

FIGURE 5 : The diameter of the observed particle as a function of the concentration on neutral surfactant (◆ : Brij35 in a 0.25 w/v % solution of copolymer, ■ : the same solution without surfactant); all diameters were measured after 10 min of irradiation.

A sharp decrease in the particle diameter is observed around the CMC of the neutral surfactant . Until now, the reason for the increase and the sharp decrease in the diameter is not understood. A more systematic approach of these phenomena is currently undertaken.

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