

Photon Pressure-Induced Association of Nanometer-Sized Polymer Chains in Solution

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The photon pressure effect induced by a focused infrared laser beam upon two kinds of water-soluble carbazoyl-containing copolymers in aqueous solution is shown to result in the formation of single microparticles. The minimum size of the polymer chains at which the photon pressure overcomes the Brownian motion and the electrostatic repulsion is determined to be 10–20 nm. The rate of particle formation and the final particle size are shorter and larger, respectively, as the carbazoyl content of the polymer is higher. This indicates that the polarizability plays an important role in the photon pressure-induced association process.

Introduction

Laser light can be focused to spot diameters of the order of the wavelength of the light, which gives lasers the potential to be used for a variety of chemical and physical applications on the micrometer to submicrometer domain. Studies of molecular photochemical and photophysical processes on these dimensions have become routine in recent years.^{1,2} Another characteristic of a focused laser beam is the “photon pressure”, which was originally proposed by Newton, treated theoretically by Maxwell, and confirmed experimentally by Lebedev.³ The photon pressure is generated by changes in photon momentum as light is refracted as it passes from a medium of one refractive index through a micrometer-sized particle (of a different refractive index).^{4–8} This force enables noncontact and nondestructive manipulation of microparticles in solution; a phenomenon developed recently into the “laser trapping” technique, which may be used for exploratory studies on “chemistry of a single microparticle”.^{1,2}

It is also known that photon pressure is exerted upon Rayleigh particles that are smaller than the wavelength of the light. The photon pressure exerted on such a Rayleigh particle is expressed as follows:⁹

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

where \mathbf{E} and \mathbf{B} are the electric field strength and magnetic flux density, respectively, and ∇ represents a gradient with respect to the spatial coordinates. α is the polarizability of the particle under the dipole approximation, and when the particle in dielectric medium is adopted, it is given by

$$\alpha = 4\pi\epsilon_m r^3 \frac{(n_p/n_m)^2 - 1}{(n_p/n_m)^2 + 2} \quad (2)$$

where r is the radius of the particle, n_p and n_m are the refractive indices of the particle and the surrounding medium, respectively, and ϵ_m is the dielectric constant of the medium. This is because photon pressure is effectively induced by the refractive index difference. The first term of eq 1 is an electrostatic force acting on the dipole in the inhomogeneous electric field, which is called the gradient force. When $n_p > n_m$, 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 and is called a scattering force, which pushes the particle along the beam direction. When the gradient force is expected to be much stronger than the scattering force, the photon pressure traps the Rayleigh particles in the vicinity of the focal point.

One representative application of the photon pressure is a laser lens with which atoms^{10–12} and molecules^{13–16} in a vacuum can be trapped by a focused laser beam. Such studies are considered to open new research fields of control of atomic collision, neutral atom microscopy, nanoscopic deposition, and nanofabrication. The photon pressure can also be used to assemble polymer chains and micelles, as demonstrated recently on aqueous solutions of poly(*N*-isopropylacrylamide) (PNIPAM),^{17–20} sodium dodecyl sulfate/xylene micelles,²¹ and poly(*N*-vinylcarbazole).^{22,23} In the case of PNIPAM, a temperature-induced phase transition is involved, which has complicated interpretation of the mechanism of the molecular assembly, while the molecular assembly of sodium dodecyl sulfate/xylene micelles and poly(*N*-vinylcarbazole) was attributed purely to the photon pressure effect.

To understand the novel molecular association phenomena in solution, it is necessary and indispensable to know the minimum size of molecules/polymers that can be acted upon by the photon pressure and the role of molecular structure under the influence of the photon pressure. We report here the first determination of the minimum size of polymer affected by photon pressure and demonstrate the chemical property that is

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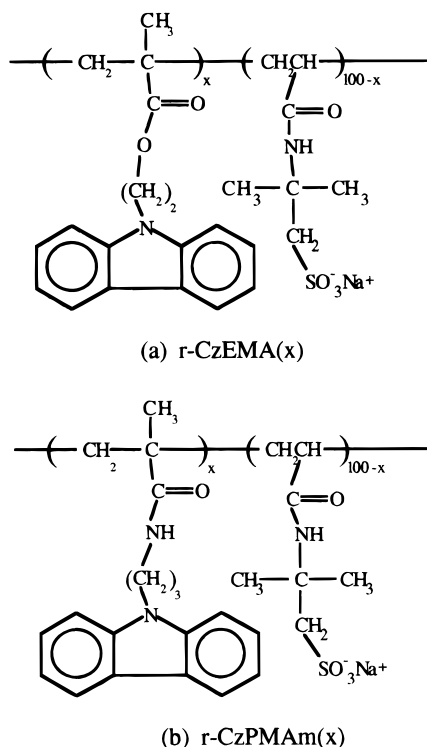


Figure 1. Chemical structures and abbreviations of the random, water-soluble copolymers of (a) sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) and 2-(9-carbazolyl)-ethyl methacrylate (CzEMA), and (b) AMPS and [3-(9-carbazolyl)propyl]methacrylamide (CzPMAm). The carbazole content is given as x in mol %.

most sensitive to the photon pressure effect. Molecular systems examined are aqueous solutions of two series of polymers that have pendant carbazolyl (Cz) groups attached to the polymer backbone by chains of differing lengths and contain varying degrees of ionic and hydrophobic carbazolyl groups.

Experimental Details

The two series of polymers used in this study are random, water-soluble copolymers of sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) and 2-(9-carbazolyl)-ethyl methacrylate (r-CzEMA(x)) and AMPS and [3-(9-carbazolyl)propyl]methacrylamide (r-CzPMAm(x)), where (x) represents the carbazolyl content of the polymer in mol %. The chemical structures and abbreviations of these polymers are given in Figure 1, and details of their synthesis and fluorescence characterization have been published elsewhere.²⁴

The 1064 nm fundamental beam from a CW Nd:YAG laser (Spectron, SL903U) was introduced into an optical microscope (Nikon, Optiphot XF) and focused to a $\sim 1 \mu\text{m}$ spot by an objective lens ($\times 100$ magnification, NA = 1.3). This beam served as the trapping light ($\sim 250 \text{ mW}$). The photon pressure effect on the samples was monitored with either the backscattered image of a HeNe laser aligned collinearly with the YAG beam and focused to the same spot position or with a transmission image of the component halogen lamp of the microscope. Both images could be monitored using a CCD camera/video recorder system.

Solutions of the polymers were prepared to various weight percentages in distilled water (Yamato Autostill WG23) or D₂O (NMR grade, Wako Pure Chemical Industries Ltd.). The samples were prepared on microscope slides with an indentation a couple of hundred micrometers deep and covered with a $\sim 70 \mu\text{m}$ thick coverslip. This arrangement minimized evaporation throughout

the duration of the experiment. The focal point of the trapping beam was set to $\sim 40 \mu\text{m}$ below the bottom of the cover slip.

Molecular weight distribution and radii of gyration information of the polymer samples was obtained using a gel permeation chromatography (GPC) system consisting of a Waters 510 HPLC pump, Waters Ultrahydrogel columns (2000 and 250 Å; $7.8 \times 300 \text{ mm}$; 30#161#C), a Wyatt Dawn-F multiangle laser light scattering (MALLS) instrument, and a Waters 410 differential refractometer (DRI). Triply distilled water containing 0.1 M NaNO₃ was used as the mobile phase and pumped at a flow rate of 0.8 mL/min. MALLS data were collected and analyzed using software supplied by Wyatt.

Results and Discussion

In experiments of this kind, formation of a microparticle due to the molecular association is considered to have occurred when, after the trapping laser beam has been incident on the sample solution for some period of time, the backscattering intensity of the HeNe laser becomes visible. This is ascribed to the increase in the refractive index at the focal point compared to that of the surrounding water ($n = 1.33$) caused by the increasing local concentration of initially homogeneously dispersed polymer chains, at the focal point. The scattered HeNe signal intensity and diameter then increase gradually as the microparticle grows.

An example of a typical backscattering pattern, observed from CzEMA(1) in water as a function of irradiation time is illustrated in Figure 2A. In this case, the onset of visible scattering of the HeNe laser occurred after $\sim 2.5 \text{ min}$ of irradiation. The particle became visible on the transmission image after $\sim 18 \text{ min}$ of irradiation, indicating the formation of a particle of approximately $1\text{--}2 \mu\text{m}$ diameter. This particle remained stable upon further irradiation for over 1 h but grew no larger than it was after $\sim 30 \text{ min}$ of irradiation. Any photothermal effects due to absorption of the 1064 nm beam by overtone vibrational bands of H₂O should be examined, as the temperature elevation at the focal point under the experimental conditions used here is sufficient to induce a phase transition in PNIPAM.^{17–20} The microparticle formation process in D₂O was confirmed to be similar to that in H₂O, although the overtone of D₂O is very weak at 1064 nm. Thus, the photothermal effect is considered not to contribute in the present system.

Microparticles were similarly observed to form in each of the various copolymers studied, but the formation rate (as determined by the onset of visible backscattering of the HeNe beam) and final particle size (determined from the transmission images) appear to vary between the samples. Table 1 summarizes the approximate time taken for the first signs of scattering of the HeNe beam from the various polymer solutions studied. First, the observed onset of formation of a particle of a size capable of being detected through scattering of the HeNe laser occurred in the higher Cz content copolymers in each series sooner than in the lower Cz content copolymers. This effect is even more marked considering that, in these first experiments, the polymer concentration of the solutions used decreased with increasing Cz content (see Table 1) since, due to solubility differences, these concentrations were the highest readily achievable. Second, the onset of scattering from each of the r-CzEMA(x) copolymers in water occurred sooner than for the corresponding r-CzPMAm(x) copolymer of similar Cz content (see Figure 2B).

The results can be explained in terms of photon pressure exerted on the polymer particles, as given in eqs 1 and 2. The

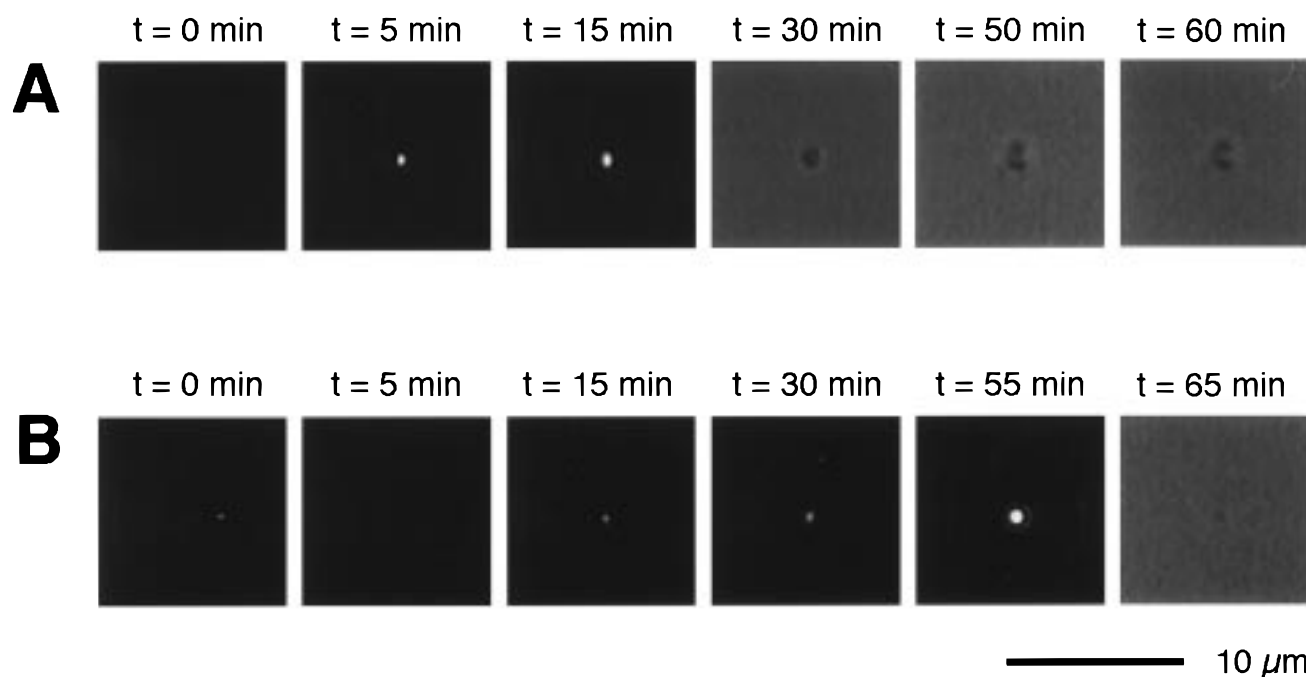


Figure 2. Microscopic images of (A) r-CzEMA(1) and (B) r-CzPMAm(1) in H₂O as a function of irradiation time: (A) CzEMA(1) in H₂O (backscattering images for $t \leq 15$ min and transmission images for $t > 30$ min); (B) r-CzPMAm(1) in H₂O (backscattering images for $t \leq 55$ min and transmission images for $t = 65$ min).

TABLE 1: Polymer Properties and Formation Times of Single Microparticles^a

r-CzEMA(<i>x</i>)	<i>M_w</i>	<i>R_G</i>	<i>R_G'</i>	wt % in H ₂ O	time in H ₂ O (min)	wt % in D ₂ O	time in D ₂ O (min)
<i>x</i> = 1 mol %	2×10^5 ^b	16.7	19.9	3.17	~2.5	2.61	~1.3
<i>x</i> = 48 ^c	1.4×10^6	11.4	12.3	0.17	~0.5	0.17	~1
r-CzPMAm(<i>x</i>)							
<i>x</i> = 1 mol %	2.5×10^5	22.9	23.8	3.06	~7.5	2.58	~7
<i>x</i> = 27	2.1×10^6	17.0	21.7	0.92	~4.5	0.87	~4.5
<i>x</i> = 50	6.5×10^5	14.9	16.7	0.49	~1	0.16	~1

^a *M_w* is the weight average molecular weight; *R_G* and *R_G'* are number and weight average radii of gyration, respectively; the highest solution concentrations (wt %) readily achieved, and the times taken for the first signs of particle formation for the various polymers in water and D₂O. ^b A broad molecular weight distribution was obtained. ^c Difficult to dissolve under the conditions required for GPC analysis.

value of n_p in the present systems is expected to increase with increasing Cz content in a given copolymer, and hence the photon pressure is expected to also follow this trend. It is worth noting that polymers in solution whose radius of gyration is 10–20 nm can be trapped by the photon pressure. This is the first report on the photon pressure-induced association of nanometer-sized polymer chains, while polystyrene Latex spheres and Au microparticles of 38 and 36 nm diameter, respectively, have also been reported to be trapped.²⁵

Itoh et al.²⁴ have discussed the differences expected between r-CzEMA(*x*) and r-CzPMAm(*x*), mentioning that the latter copolymers would be expected to have a reduced mutual interaction of the Cz groups as compared to former copolymers due to (i) the longer spacer chain, (ii) the rigidity and/or hydrogen bonding of the amide bond in CzPMAm decreasing the local motion of the side groups, including the Cz chromophores, and (iii) CzPMAm being expected to polymerize with AMPS in a highly random fashion, giving shorter successive sequences of Cz monomers than the CzEMA copolymers. The effective radius of gyration of r-CzPMAm(*x*) is larger than the

corresponding r-CzEMA(*x*) and this, in conjunction with the expected higher Cz density in r-CzEMA(*x*), would result in the effective polarizability of r-CzPMAm(*x*) being smaller than that of the corresponding r-CzEMA(*x*). This would result in a larger photon pressure influence in r-CzEMA(*x*), as observed.

The r-CzEMA(1) sample consistently gave the largest particles, visible by the lamp transmission (Figure 2A). Dissolution of the microparticles upon removal of the trapping beam was very rapid in all cases; the particles disappearing within seconds. This is ascribed to electrostatic repulsion of the copolymers and excludes a possible association before laser trapping. Since the microparticles disappeared very quickly on removal of the trapping beam, it appears that the driving force for solvation is strong but by application of the photon pressure we can overcome this solvation energy.

Conclusions

We have succeeded for the first time in demonstrating the photon pressure-controlled microparticle formation from copolymers of only a few tens of nanometers in size in aqueous solution. The extent of particle formation achieved appears to be dependent on the Cz content in a given polymer, meaning that the polarizability of the Cz group is a key factor determining the photon pressure effect. The length, flexibility, or properties of the chain linking the Cz chromophore to the backbone also affect the particle formation. The radius of gyration of the polymer may also be a major factor in the microassociation process. The contribution to microparticle formation by photothermal processes has also been shown to be far less important in these polymer systems than was the case for PNIPAM. The findings presented are important and indispensable for establishing the micromanipulation method for nanometer-sized polymer chains and related molecular assemblies.

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