Laser Manipulation and Assembling of Polymer Latex Particles in Solution

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ABSTRACT: Three-dimensional laser manipulation of polymer latex particles in solution was demonstrated. Polymer latex particles with a diameter of several microns were spatially aligned in arbitrary patterns (letters and geometrical figures) by repetitively scanning a focused laser beam (1064 nm) under an optical microscope. Irradiation of nanosecond or picosecond 355-nm laser pulses on individual laser-trapped polymer particles in a sample solution containing polymerizable vinyl monomers and a photoinitiator brought about permanent fixation of the particles in three-dimensional structures. Possible roles of the laser trapping/manipulation techniques in studying the chemistry and physics of polymeric microparticles are also discussed.

Introduction

The spatial and temporal coherency of a laser beam has been so far applied to various areas of research in polymer science.[1,2] As an example, laser fluorescence spectroscopy with nanosecond to picosecond time resolution is now recognized as a potential means to study the dynamic aspects of polymer solutions and solids. Indeed, microenvironmental properties of polymer solutions and solids such as viscosity, polarity, segmental motion, and so forth have been extensively studied on the basis of laser fluorescence spectroscopy and related techniques. Lasers also play important roles in polymer science as represented by Raman spectroscopy, laser light scattering, and so on. Besides spectroscopy, a laser beam is intense and can be focused into a wavelength-order spot, and lasers have been used as light sources for microfabrication of polymer solids[3] and photopolymerization in solution. Laser ablation[4] and three-dimensional stereolithography[5] are such examples.

A unique characteristic of a laser beam, scarcely applied to chemistry, is the radiation force generated by refraction of a laser beam through a microparticle.[6,7] Under appropriate conditions as described later, the radiation force is exerted to a microparticle, and this particular force can be used for noncontact and nondestructive manipulation of individual microparticles undergoing Brownian motion in solution: *laser trapping/manipulation.* If one can manipulate individual particles, for example, spectroscopic characterization and chemical modification/fabrication of particles could be arbitrarily performed by combining laser trapping/manipulation with other laser techniques. In this article, we report laser manipulation of individual polymer latex particles by a single-beam or multibeam laser technique and demonstrate photochemical fixation of the particles to create three-dimensional micron-sized structures. Possible roles of laser trapping/manipulation in the chemistry and physics of polymeric microparticles are also discussed.

Principle of Laser Trapping

Laser trapping of a microparticle(s) was experimentally shown by Ashkin in 1970.[6] According to Ashkin, the principle of "laser trapping" is as follows.[6,7] We assume that a particle is irradiated by a focused laser beam as illustrated in Figure 1. Refraction of a light ray B by a spherical particle with refractive index n_1 in the medium (refractive index n_2) leads to a light momentum change, $\Delta\mathbf{P} = \mathbf{P}_1 - \mathbf{P}_0$, where $\mathbf{P}_0$ and $\mathbf{P}_1$ are light momentum before and after refraction, respectively. If n_1 is larger than n_2, $\Delta\mathbf{P}$ should be exerted to the particle with a direction opposite to that of $\Delta\mathbf{P}$ (i.e., $-\Delta\mathbf{P}$) owing to conservation laws. The same is true for a light ray A except for the direction of $\Delta\mathbf{P}$. The sum of $-\Delta\mathbf{P}$ at each point of the particle irradiated by the laser beam is the radiation force (**F**) exerted on the particle. It is noteworthy that $-\Delta\mathbf{P}$ possesses both axial ($\Delta\mathbf{P}_a$) and transaxial ($\Delta\mathbf{P}_t$) components (Figure 1), and **F** directs to the high-intensity region of the laser beam depending on the contributions of $\Delta\mathbf{P}_a$ and $\Delta\mathbf{P}_t$ to $-\Delta\mathbf{P}$. When the particle is irradiated by a laser beam with a large cone angle as shown in Figure 1, the contribution of $\Delta\mathbf{P}_a$ to $-\Delta\mathbf{P}$ and, therefore, to **F** becomes dominant so that the particle is levitated and trapped in the vicinity of the focal point of the laser beam. Contrarily, if the particle is irradiated with a small cone angle through an objective lens, the contribution of $\Delta\mathbf{P}_t$ to $-\Delta\mathbf{P}$ becomes more important as compared with that of $\Delta\mathbf{P}_a$. In such a case, the particle is not levitated but manipulated in the XY plane depicted by the focal point of the laser beam. Steering of the laser beam focused by an objective lens with a large numerical aperture therefore leads to three-dimensional manipulation of the particle. The laser trapping/manipulation method certainly has potential for performing various studies on individual polymeric microparticles.

Experimental Section

Laser Trapping/Manipulation System. An experimental setup for the laser manipulation of micron-order particles is shown in Figure 2. A 1064-nm TEM_{00} mode Gaussian beam from a CW Nd^{3+}:YAG laser (Spectron, SL903U or SL902T) was used as a trapping light source and was focused into a sample solution (~1-μm spot) through an objective lens (×100, NA = 1.30) of an optical microscope (Nikon, Optiphoto XF or 2). A sample solution was placed between two quartz plates and was set on the stage of the microscope. For single laser beam trapping, a particle was laser trapped in the focal spot of the laser beam.[8] For multibeam scanning laser manipulation, the laser beam was split into two beams by a polarizing beam splitter (PBS), and each beam was modulated by two sets of galvano mirrors (GM; GSI, G325 DT).[9] The two trapping laser beams were scanned independently in the plane of the sample solution. The galvano mirrors were controlled by a controller (Marubun, TI-325) and a computer (NEC, PC9801RA).

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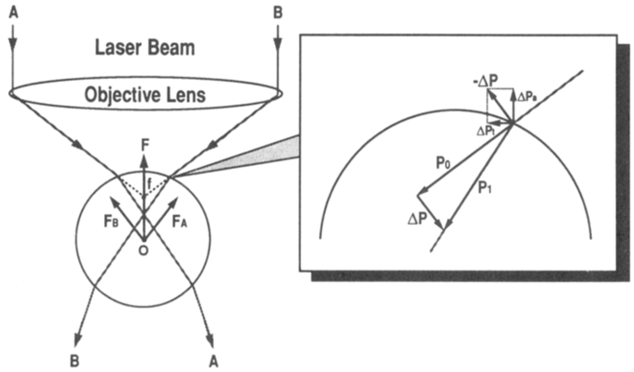


Figure 1. Principle of laser trapping.

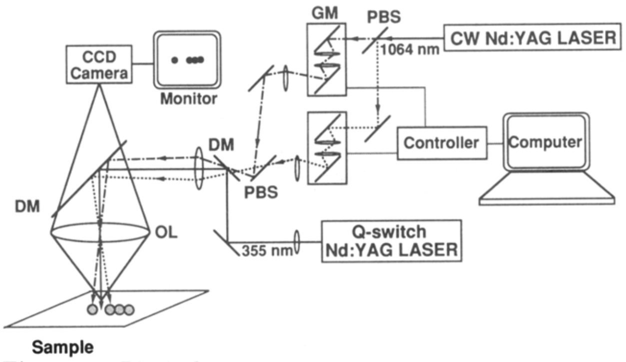
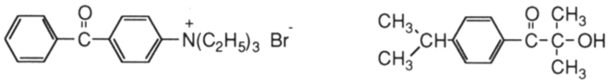


Figure 2. Block diagram of multibeam laser manipulation–reaction system. PBS, polarizing beam splitter; GM, galvano mirrors; DM, dichroic mirror; OL, objective lens.

Chart I
Structures and Abbreviations for the Radical Photoinitiators



Photopolymerization in a sample solution was performed by irradiation of a 355-nm pulsed laser beam from a Nd^{3+}:YAG laser (Quantel, YG501-10, pulse width ~30 ps, or Quanta-Ray, DCR-II, pulse width ~7 ns). Since both trapping (1064 nm) and excitation (355 nm) laser beams were introduced coaxially into the microscope by the use of a dichroic mirror (DM), a laser-trapped microparticle(s) or the vicinity of a trapped particle(s) was correctly irradiated by the pulsed laser beam.[10] Both trapping beam power and excitation beam power at the individual microparticles, P_{1064} and P_{355}, respectively, were determined by the reported methods.[8] All the behavior occurring in the sample solution was monitored by a CCD camera–video monitor set (Sony, DXC-750, BVU-950, and PVM-1442Q) equipped to the microscope.

Materials. The synthesis and purification of (4-benzoylbenzyl)triethylammonium bromide (BBA; structure is shown in Chart I) were reported previously.[11] 1-(4-Isopropylphenyl)-2-hydroxy-2-methylpropan-1-one (Darocur 1116, Merk) and other chemicals (all Nacalai Tesque Inc.) were used without further purification. Poly(methyl methacrylate) (PMMA, Soken Chemical and Engineering Co., Ltd.) and polystyrene (PSt, Polysciences Inc.) latex particles were used as received.

Results and Discussion

Laser Manipulation of Microparticles in Solution. Laser trapping of an individual particle such as a PMMA ($n_1 = 1.49$)[12] or PSt ($n_1 = 1.59$)[12] latex particle with a diameter of 0.25–10 μm was easily attained by irradiating the particle with a focused 1064-nm laser beam in a relatively low refractive index medium such as water ($n_2 = 1.33$),[13] ethylene glycol ($n_2 = 1.43$),[13] or diethylene glycol ($n_2 = 1.45$).[13] In Figure 3, the PSt particle indicated by the arrow is optically trapped in water by a laser beam with $P_{1064} \sim 200$ mW, while other particles move along the X direction due to flow of the sample solution. Similarly, laser trapping of the particle along the Y and Z (along the laser beam axis) directions was also attained. Besides PMMA and PSt particles, we confirmed three-dimensional laser manipulation of a melamine resin microcapsule containing a dye/toluene solution, liquid oil droplets, titanium dioxide, glass beads, biocells, and so forth in an appropriate medium which satisfies n_1 (particle) > n_2 (medium).[8,14] It is noteworthy that, although the radiation force exerted on a particle is on the order of several pN, the radiation force is strong enough to suppress Brownian motion of micron-order particles in solution at room temperature.[8] A simple calculation indicates that a high temperature limit for laser trapping of a particle (1-μm diameter) within a 1-μm sphere is ~7000 K assuming the radiation force to be as small as 1 pN.[8,15]

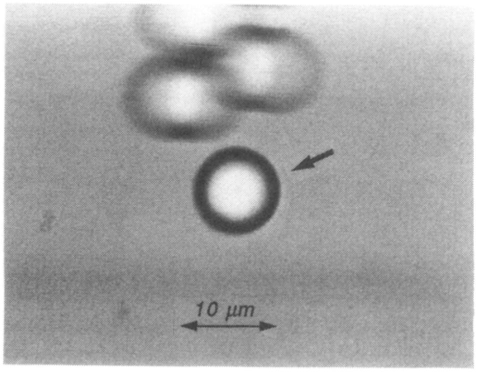


Figure 3. Laser trapping of a PSt particle in water. The particle indicated by the arrow is trapped by the 1064-nm laser beam (P_{1064} = ~200 mW at room temperature).

Laser trapping/manipulation of an arbitrary number of microparticles is quite important for chemical application of the technique. Burns et al. have reported that a number of particles can be laser trapped in the interference fringes of a laser beam(s).[16] We also demonstrated that PMMA latex particles in water were spatially aligned in concentric circles or a line image of a 1064-nm laser beam.[15] However, these spatial patterns of particles are essentially based on interference of an incident laser beam(s), so there is severe limitation in producing arbitrary spatial patterns. Therefore, we developed a new technique, *laser scanning micromanipulation*.[17] If a focused trapping laser beam is repetitively scanned in the plane of a sample solution (XY plane) with a repetition rate faster than the time scale of the Brownian motion of a particle, the particles will be optically trapped in the locus of the scanning laser beam. The trapping laser beam focused into a ~1-μm spot was arbitrarily scanned in a sample solution by modulating the galvano mirrors (see also Figure 2).

Figure 4 shows a typical example of laser scanning manipulation of PSt (diameter ~2 μm) particles in ethylene glycol, demonstrating spatial alignment of PSt in the pattern of "μm". The pattern was also manipulated in the lateral (XY) direction without deformation by controlling the movement of the galvano mirrors. Scanning manipulation of particles is dependent on P_{1064}, the repetition rate (R) of the laser beam, the diameter of the particle (d), and the viscosity (η) of the surrounding medium. For manipulation of small particles in a low-η medium, fast scan of the laser beam is absolutely necessary owing to fast Brownian motion of the particle. Furthermore, Brownian motion of particles becomes faster with

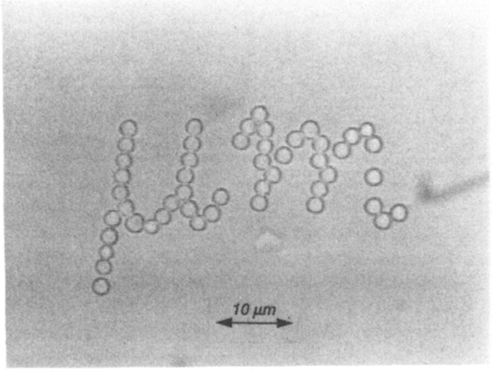


Figure 4. Spatial pattern formation of PSt particles in ethylene glycol. P_{1064} = 145 mW, repetition rate = 13 Hz at room temperature.

decreasing d, and R should be larger for smaller particles. With increasing number of particles to be trapped in a pattern, on the other hand, the average P_{1064} irradiated to each particle in the pattern decreases. Therefore, higher P_{1064} is required for laser trapping of a larger number of particles. For the data in Figure 4, the spatial pattern of PSt was produced with R = 13 Hz and P_{1064} = 145 mW (η in ethylene glycol = ~26 cP at 15 °C).[13] The spatial pattern of the particles disappears immediately after switching off the laser beam owing to Brownian motion of the particles.

Photopolymerization on a Single Laser-Trapped Particle. To fix spatial patterns of laser-trapped particles, in situ photopolymerization of a sample solution under laser trapping conditions will be promising. Therefore, we explored simultaneous laser trapping–photochemical fixation of PSt particles in polymerizable vinyl monomer solution.

PSt particles (d = ~1 μm) were dispersed in an aqueous solution of acrylamide (AM, 2.0 M), N,N'-methylenebisacrylamide (MBA, 2.0×10^{-2} M), and (4-benzoylbenzyl)triethylammonium bromide (BBA, photoinitiator, 5.7×10^{-2} M). Individual PSt particles were optically manipulated in the solution by the 1064-nm laser beam (P_{1064} = 75 mW) similar to the result in Figure 3. With a single PSt particle being optically trapped, the trapped particle was irradiated with nanosecond 355-nm laser pulses (~7 ns) with P_{355} = ~2.2 μJ μm^{-2} pulse^{-1}. After pulsed laser irradiation for several seconds, photopolymerization of AM and MBA proceeded in the vicinity of the particle. The formation of a polyacrylamide gel on the PSt particle was observed as shown in Figure 5a. Further irradiation of the 355-nm pulses (several tens of seconds) resulted in a growing-in of the gel, and the PSt particle was completely covered with the AA–MBA gel (Figure 5b).

The primary process of the present photopolymerization will be hydrogen abstraction from the nπ^* excited triplet state of BBA. Although the nπ^* absorption band of BBA in water is not clearly resolved (shoulder at ~330 nm) owing to the presence of a strong $\pi\pi^*$ transition (λ_{max} = 254 nm), the excited-state properties of BBA have been reported to be very similar to those of benzophenone;[11] the lowest excited triplet state is an nπ^* transition. Photopolymerization of AM and MBA was more efficient on or in the close vicinity of a PSt particle as compared with that in the bulk phase without a particle. The results suggest that the nπ^* excited triplet state of BBA abstracts a hydrogen from a PSt particle, possibly from a tertiary hydrogen of the main-chain PSt (the PSt particle used is not cross-linked). BBA and the vinyl monomers are water soluble, and these molecules will not penetrate deeply into PSt owing to the hydrophobic nature of the interior of the particle. The excited BBA will thus abstract hydrogen from the surface PSt group of the particle. However, the molar extinction coefficient of BBA at 355 nm is quite small (80 M^{-1} cm^{-1}). Both direct and two-photon absorption of the 355-nm laser pulse(s) by BBA will be responsible for initiation of polymerization (discussed again later). Furthermore, the excitation 355-nm laser pulse is focused into a micron-order spot, so that the excited triplet BBA and, therefore, radical species such as BBA and vinyl monomer radicals will be produced in very high concentrations around the focal spot of the laser beam. This could be one of the possible reasons for efficient photopolymerization.

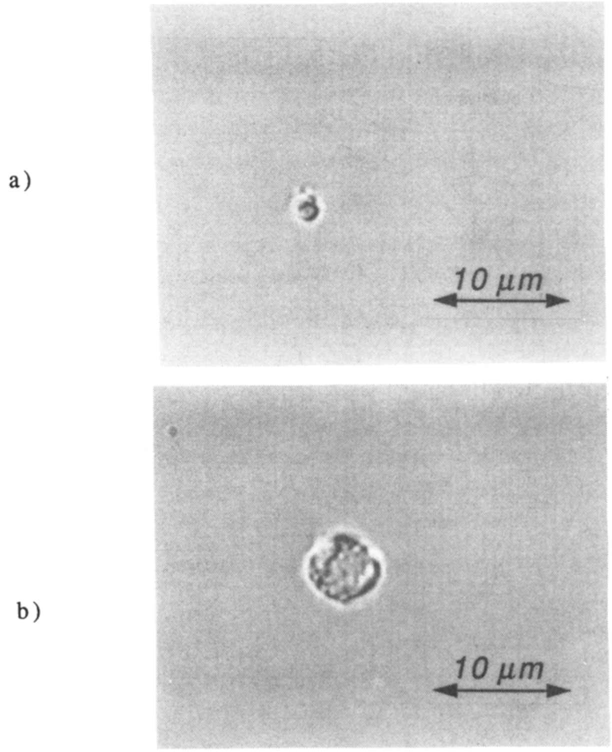


Figure 5. Photopolymerization on a single laser-trapped PSt particle in an aqueous solution of AM (2.0 m), MBA (2.0×10^{-2} M), and BBA (5.7×10^{-2} M).

Photopolymerization of vinyl monomers in the vicinity of a focal spot of a laser beam is not unusual since three-dimensional stereolithography has been already established. In stereolithography, André has reported that spatial resolution of photopolymerization in a viscous prepolymer solution by a focused laser beam was ~5 μm.[5] In the absence of the trapping laser beam and PSt particles, an aqueous solution of AM, MBA, and BBA placed between two glass plates was irradiated by nanosecond 355-nm laser pulses with the glass plates being moved along the XYZ directions. Photopolymerization of AM and MBA proceeded three-dimensionally, following the locus of the laser beam. In a typical experiment, the focused 355-nm laser beam was moved from the bottom to the top glass plate of the sample cell. Polymerization of the monomers produced a rod-shaped AM–MBA gel with a diameter and a length (distance between the two glass plates) of several microns and ~40 μm, respectively. It should be noted that the 355-nm laser beam was focused into a ~1-μm spot by an objective lens with a large numerical aperture (NA = 1.30). This implies that the sample solution is irradiated by a large cone angle of the laser beam (~120°). Nevertheless, the formation of the AM–MBA gel was confined to the vicinity of the focal point of the 355-nm

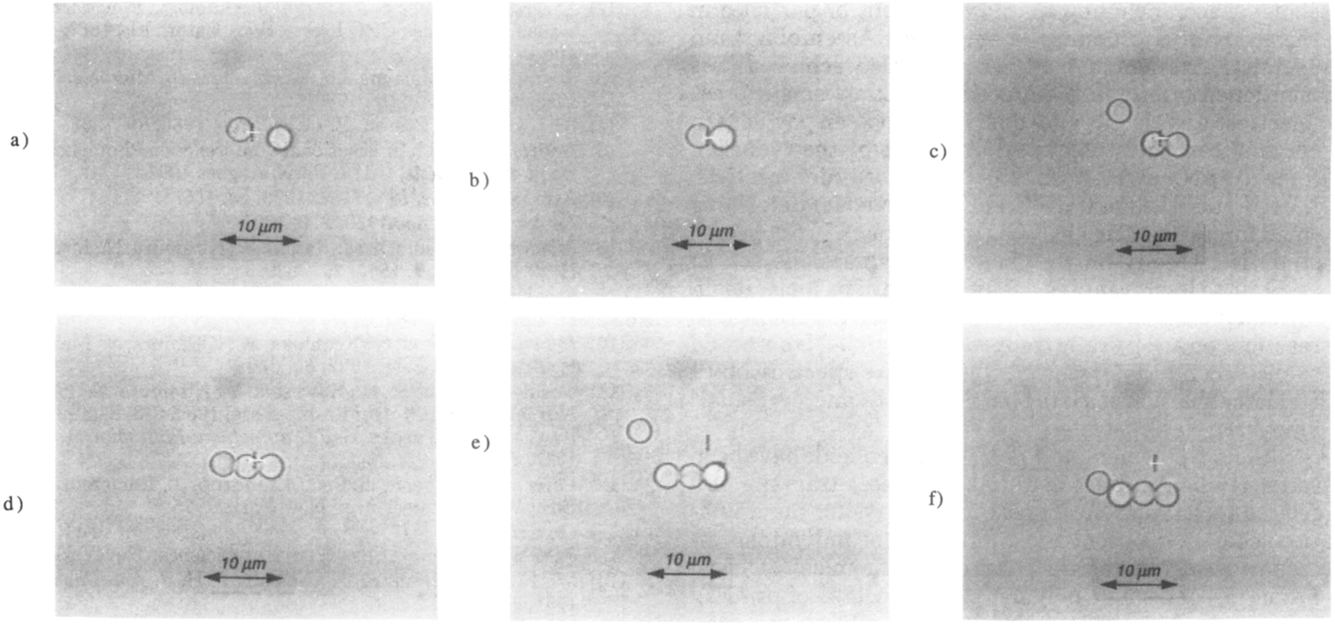


Figure 6. Photochemical assembling of PSt particles in an ethylene glycol solution of AA (1.9 M), MBA (2.6×10^{-2} M), and Darocur 1116 (5.0×10^{-2} M). The cross (+) in the figure represents a computer marker for the 1064-nm laser beam position.

laser beam. The results also support two-photon absorption of the 355-nm laser pulses by BBA as the primary process of photopolymerization.

Assembling of Laser-Trapped Particles by a Multibeam Laser Technique. In principle, the method described in the preceding section can be applied to assemble an arbitrary number of polymer latex particles. In these experiments, PSt particles (~3-μm diameter) dispersed in an ethylene glycol solution of acrylic acid (AA, 1.9 M), MBA (2.6×10^{-2} M), and Darocur 1116 (photoinitiator, 5.0×10^{-2} M) were used as the sample solution.

The multibeam laser trapping technique in Figure 2 was employed to manipulate many PSt particles as typically shown in Figure 6a, where two particles were optically manipulated independently by two 1064-nm laser beams. The particles always follow the locus of each trapping laser beam with $P_{1064} = 290$ mW and a scanning rate of 2.0 μm/s. The two particles were forced to come into contact, and the contacting area between the particles was irradiated with picosecond laser pulses (355 nm, ~30 ps). Darocur 1116 has been reported to be an efficient photoinitiator for radical polymerization,[18] so that absorption of the laser pulse by Darocur induces photopolymerization of AA and MBA. After 355-nm irradiation for several seconds, polymerization of the vinyl monomers took place in the vicinity of the two contacting PSt particles. Although we cannot see any morphological change on the particles, the two particles were stuck together as confirmed by the fact that the two particles never separated even after the trapping laser beams were switched off (Figure 6b). Gelation of the monomers in the interfacial layer of the particles analogous to the results in Figure 5 could lead to permanent fixation of the two PSt particles. To estimate the adhesive forces between the two particles, the focal points of the trapping laser beams were separated from each other by more than 3 μm. However, the particles were not divided at all. Since the radiation force generated by the laser beam is on the order of several pN, the adhesive forces are larger than several pN.

Analogous procedures of laser trapping–photopolymerization were performed successively to assemble an arbitrary number of PSt particles with any desired geometry. An important key technique to assemble the particles is as follows. Since two 1064-nm laser beams are used for trapping, the two particles stuck together (Figure 6b) should be manipulated by one laser beam to manipulate the third particle by the other beam (Figure 6c). If we irradiate the two-PSt-particle structure (Figure 6c) by one trapping laser beam at a fixed focal point, the structure rotates to satisfy the most stable trapping conditions with respect to the direction of $-\Delta \mathbf{P}$ (Figure 1) and is trapped with the structure being directed to the laser beam axis (i.e., perpendicular to the photograph in Figure 6c). Under such circumstances, controlled laser manipulation–assembling of the particles is not possible. Therefore, one trapping laser beam was repetitively scanned (12.5 Hz) between the two ends of the structure to keep and manipulate the structure in the plane of the sample solution. This was essential to assemble many latex particles by laser trapping. With the structure trapped by the scanning laser beam, the other trapping beam was used to manipulate the third particle (Figure 6c). The particle was then fixed to one end of the two-PSt-particle structure as demonstrated in Figure 6d. Similar procedures were repeated to construct a microstructure consisting of four PSt particles (Figure 6e,f). In these procedures, the particles were optically lifted up in the sample solution to avoid adhesion of PSt with the sample glass plate.

Besides polymer latex particles, we recently succeeded in laser manipulation of micrometer iron particles, carbon black particles, and so forth by the scanning laser manipulation technique.[9] Therefore, the present laser manipulation–photopolymerization method will be further extended to create various microstructures consiting of polymer particles, metal particles, and so on. We expect that such approaches will lead to new composite materials with various chemical functions.

Laser Trapping/Manipulation in Chemistry of Polymer Particles. The laser trapping/manipulation and related techniques were shown to be highly promising for studying the chemistry and physics of polymer microparticles randomly dispersed in solution. Micrometer-order particles were freely manipulated in three-dimensional space, including spatial alignment of particles in the locus of a scanning laser beam. Assembling and chemical fixation of particles were also achieved. As mentioned briefly in the preceding section, small forces (electrostatic, elastic, etc.) operating between particles in solution can be estimated on the basis of the radiation force (~pN) exerted on a micrometer-order particle. Indeed, such studies were recently reported for determing small forces operating in living organisms.[19,20] Analogous study is certainly worth doing for polymer colloids. In addition to laser trapping/manipulation of particles itself, introduction of an excitation laser beam can induce various reactions on an optically trapped particle(s). Nanosecond to picosecond time-resolved fluorescence spectroscopy[21] and laser ablation of a latex particle[8] and a microcapsule[14] have been demonstrated.

Although polymer latex particles and colloids have been so far studied as bulk materials, the laser trapping and related techniques have opened new ways for manipulation, characterization, and fabrication of individual microparticles. Characterization of the chemical/physical properties of a single polymer particle will be of primary importance for designing new functional polymer particles. Elucidation of interactions between particles is also indispensable in understanding the properties of colloidal solutions. Although experimental studies on laser trapping and related phenomena have just started in the fields of chemistry, its application is expected to be very broad, and various chemical applications of the present techniques are now being studied in this project.

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