Repetitive Contraction and Swelling Behavior of Gel-like Wire-type Dendrimer Assemblies in Solution Layer by Photon Pressure of a Focused Near-infrared Laser Beam

Sadahiro Masuo, Hiroyuki Yoshikawa, Tsuyoshi Asahi, and Hiroshi Masuhara*

Department of Applied Physics, Osaka University, Suita, Osaka 565-0871, Japan

Takafumi Sato, Dong-Lin Jiang, and Takuzo Aida

Department of Chemistry and Biotechnology, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8685, Japan

Received: August 30, 2001; In Final Form: November 6, 2001

Laser manipulation and laser trapping techniques were applied to μm sized gel-like wire-type dendrimer (L3PPE130 and L4PPE8) assemblies, which are formed at drying process of their tetrahydrofuran (THF) solution on a glass substrate. Deformation and extension of single gel-like assemblies were demonstrated with irradiation of a focused 1064 nm laser beam by scanning a microscope stage. In repetitive irradiation experiments, contraction and swelling of the gel-like assembly were observed in response to the switch on and off of the laser beam, respectively, and in the case of the L3PPE130 gel-like assembly, fluorescence spectra detected at a focal point changed accompanying the contraction and swelling behavior. This spectral change means molecular aggregates were formed transiently by photon pressure of the focused near-infrared laser beam.

Introduction

Wire-type dendrimers,[1] L*n*PPE*m* (*n* and *m* show the generation number of dendritic wedges and the average degree of polymerization of backbone, respectively) consist of a rigid and fully conjugated poly(phenyleneethynylene) (PPE) backbone wrapped with flexible poly(benzyl ether) dendritic wedges. Their chemical structures are shown in Figure 1a. Previously, we reported[2] that doughnut-, particle-, and yarn-like self-aggregated structures were formed, depending on the generation number and on the average degree of polymerization of wire-type dendrimers by depositing their THF solutions on a quartz substrate. Such a doughnut structure had already been reported in the evaporation process of some organic solutions about porphyrin derivatives,[3] monomeric collagen,[4] and metal particles.[5] Formation of these molecular assembly structures by utilization of nonequilibrium processes (evaporation) has attracted much attention because it is possible to form nm $\sim$ μm sized unique structures, therefore there are many reports.[6]

On the other hand, in our laboratory, molecular aggregated structures, especially polymer aggregates, were formed by photon pressure of a focused near-infrared laser beam in solution.[7] The laser trapping and laser manipulation techniques combined with ps fluorescence microspectroscopy are our original techniques, and we have established techniques for the formation of polymer aggregates by photon pressure in solution. However, the formed aggregates in solution disappeared when laser beam was cut off. Therefore, we applied the technique to the evaporation process of the cast polymer solution on a solid substrate, and we expect original assemblies characteristic of the irradiation of the near-infrared laser beam to be deposited on the substrate. We attempt here for the first time to explore a novel effect of the focused near-infrared laser beam upon the drying process of the cast THF solution of L3PPE130 and L4PPE8 on glass substrates.

One reason to use the wire-type dendrimers is as follows. The PPE of the backbone and its derivatives[8] has attracted special attention as a light-emitting diode,[9] plastic laser,[10] and polarizer in liquid-crystalline displays,[11] and the optical properties of the PPEs have been investigated extensively in solutions and solid states. It is well known that fluorescence spectra of PPEs change according to whether or not aggregates form, although the detailed mechanism of spectral changes relating to precious conformational and spatial arrangements has remained elusive. Therefore, we can sensitively monitor the aggregate formation during irradiation of the focused laser beam by measuring fluorescence spectra emitted from the focal point. Another reason to use the wire-type dendrimers is that the π-conjugated polymer like PPEs possess high polarizability, therefore, photon pressure of a focused laser beam can affect the molecules with high efficiency. Here, we have demonstrated the deformation of a gel-like wire-type dendrimer assembly, which is generated at drying process, by laser manipulation, and the contraction and swelling behavior of the gel-like assembly in response to the repetitive irradiation of the focused near-infrared laser beam. Although laser trapping and laser manipulation of dendrimer-built vesicles in aqueous solution has been reported,[12] our motivation is different. This report is the first step for the formation of original assemblies by photon pressure during the drying process.

Experimental Section

Wire-type dendrimers, L3PPE130 and L4PPE8 (M_w/M_n = 6.5 and 1.5, respectively), were dissolved in THF (Nacalai Tesque, Spectro-Grade, without further purification), which concentration is 20 mg/L. For removing impurities, the solution was filtered through a membrane filter, pore size 200 nm, before

* Corresponding author. E-mail: masuhara@ap.eng.osaka-u.ac.jp

10.1021/jp013367e CCC: $22.00
Published on Web 01/11/2002

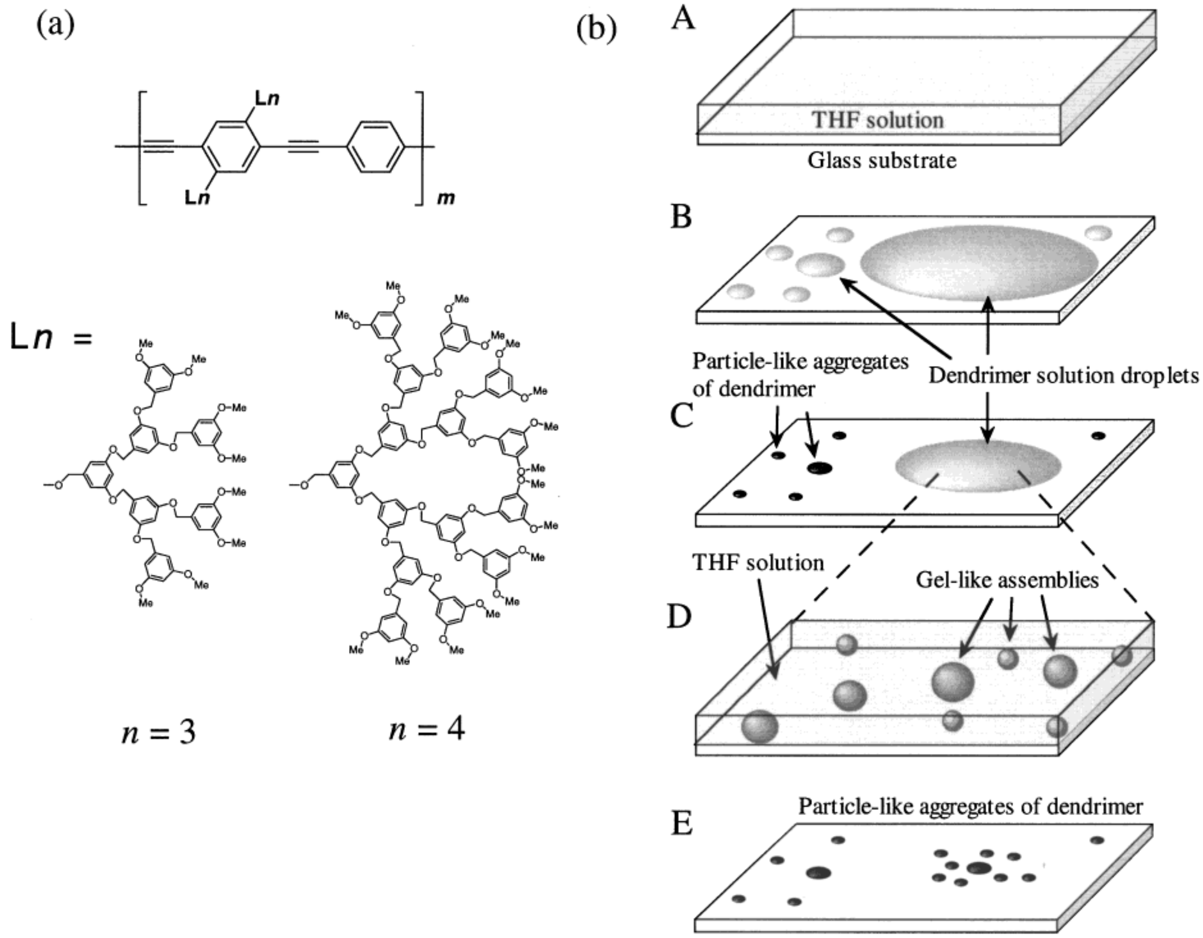

Figure 1. (a) Chemical structures of wire-type dendrimers: *n* and *m* show the generation number of dendritic wedges and the average degree of polymerization of backbone, respectively. (b) Schematic drying processes of the cast THF solution of wire-type dendrimer.

it was cast on the glass substrate (22 $\times$ 32 mm). All glass substrates were washed with detergent solution and immersed in pure water with sonication. The glass substrate was set on an inverted microscope (Olympus, IX70) stage, and after the THF solution (ca. 0.5 mL) was cast on it, it was covered with a glassware (diameter: 12 cm, height: 2 cm) together with THF vessel to prevent rapid evaporation of solvent. All experiments were performed at room temperature (20 °C).

A 1064 nm near-infrared laser beam from a continuous wave (CW) Nd^{3+}: YAG laser (Spectron, SL902T) was used as an optical trapping light source, introduced to the inverted microscope, and focused (spot size: diffraction limit) into the cast solution by an oil immersion objective lens (magnification:100, numerical aperture: 1.35). For measuring fluorescence spectra and images, a CW diode laser at 405 nm (NEOARK, DPS-5001) was used as an excitation light source and introduced through the same optical pass as the CW YAG. The excitation light was focused to a spot approximately 40 μm in size for observation of fluorescence images. Some optical transmission images were obtained during measurement of fluorescence intensity distribution, so that the images are due to the sum of transmission and fluorescence at each position. This is called here the transmission and fluorescence image (Figure 2). For measurement of fluorescence spectra, the excitation light was focused to ca. 1 μm-spot size. The fluorescence spectra were detected by an intensified multichannel spectrophotometer (Hamamatsu Photonics, PMA10). The fluorescence images were taken by a high-sensitivity color CCD camera (FLOVEL, HCC-600) and recorded by a video.

Results and Discussion

When THF solution of L3PPE130 and L4PPE8 were cast on glass substrates, the solvent evaporated gradually and finally particle-like aggregates of dendrimer were formed.[2] The observed drying processes are interesting and are summarized as follows and illustrated in Figure 1b. (1) Initially, the THF solution spread homogeneously all over the substrate (Figure 1b (A)). (2) As solvent evaporated, the THF solution became inhomogeneous and ruptured. As a result, the THF solution was divided into several μm-sized small dendrimer solution droplets, while large droplets (several hundreds of μm in size) also existed during this process (Figure 1b (B)). It is considered that all droplets contain dendrimers at same concentration. (3) Subsequently, the small droplets contracted due to further evaporation, the dendrimers were accumulated in the center, and particle-like aggregates of dendrimer were formed when drying was completed (Figure 1b (C)). On the other hand, the large droplets also contracted due to evaporation, and when the droplet reached a certain concentration, several μm-sized gel-like dendrimer assemblies were formed in the large droplet. It appeared by this condition that gel-like dendrimer assemblies existed in the THF solution pool (Figure 1b (D)). Therefore, it is considered that the gel-like assemblies consist of dendrimers and some amount of THF, and dendrimer molecules randomly orient in these gel-like assemblies such as in a high concentrated dendrimer solution. The behavior may be understood as phase separation. (4) After the dilute solution was dried, the gel-like assemblies gave many particle-like aggregates of dendrimer.

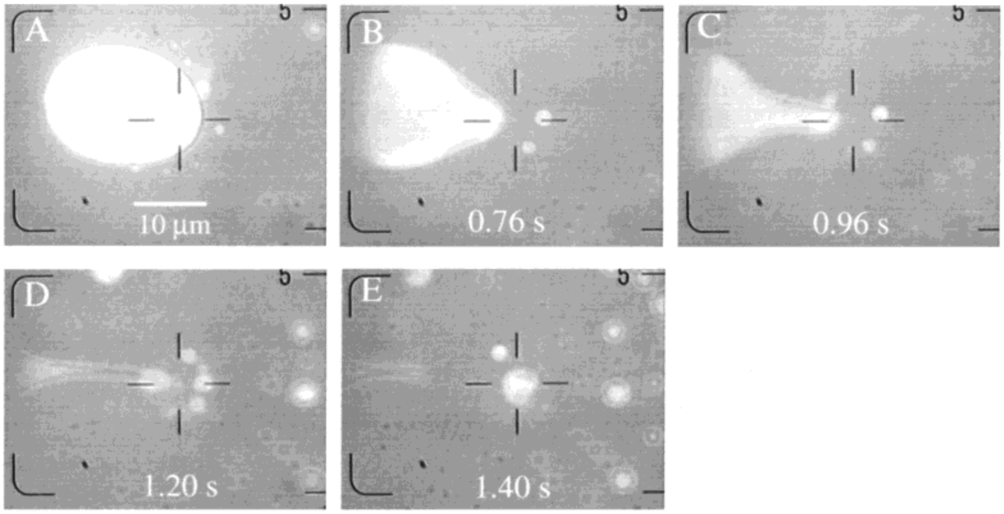

Figure 2. Fluorescence and transmission images of manipulated L3PPE130 gel-like assembly. The beam spot of trapping laser is in the center of each image shown by the crosshairs. The laser power at the beam spot is 12 $MWcm^{-2}$. The times from observation of image A are shown below in each image.

In the present experiment, the 1064 nm laser beam was irradiated to demonstrate laser manipulation of the gel-like assemblies at drying process of the large droplets (Figure 1b (D)). Fluorescence and transmission images of such gel-like assemblies were shown in Figure 2. From Rayleigh scattering theory, the photon pressure by focused 1064 nm laser beam exerts efficiently when the refractive index of the trapping target is higher than that of the surrounding medium.[7h] π-Conjugated polymers including wire-type dendrimers in the gel-like assembly possess high refractive index, and now, around the assemblies, THF solution existed, with a refractive index lower than that of gel-like assemblies. Therefore, the assemblies could be manipulated by the trapping laser. In these images, there are several gel-like assemblies, and the large one in the center of image A was formed by collecting and fusing small ones with laser trapping. As can be seen from images B−D, the large gel-like assembly was extended when the microscope stage was moved to the left with focusing beam ($P_{1064} = 12$ $MWcm^{-2}$) of the gel-like assembly. It is notable that one side of the big gel-like assembly is always pinned at the focal point. In image D, the gel-like assembly was stretched extremely and almost cut off due to further scanning of the stage. After it was broken, small gel-like assemblies around the beam spot were trapped and fused, as in image E. These phenomena mean that photon pressure generated by the focused laser beam can manipulate the gel-like assembly and also may create original assemblies.

Figure 3a shows the fluorescence images of other gel-like dendrimer assemblies, when the gel-like assembly was repeatedly irradiated with a 12 $MWcm^{-2}$ trapping laser. In these fluorescence images, the fluorescence intensity distribution of the gel-like assembly is due to inhomogeneous beam pattern of the excitation CW diode laser, because the image observed by the use of high pressure mercury lamp looked homogeneous. It can be seen from Figure 3a that the gel-like assembly started to contracted as soon as the trapping laser was irradiated to it (faster than video rate: 33 ms), and when irradiation was stopped, the gel-like assembly immediately started to swell. These contractions and swellings were observed repeatedly in response to irradiation and stopping of trapping laser. It is considered that these contraction and swelling behaviors of the gel-like assembly are attributed to the photon pressure. Of course, solvent evaporation due to local heating arising from the absorption of the near-infrared laser beam by the overtone of solvent should be also considered.[7] Thus, we estimated the temperature elevation by use of a recently reported equation[13] as a 1064 nm laser beam was absorbed by THF; however, the estimated value is just 2.4 K at this experimental condition. This value is presumably too small for the evaporation of THF. Therefore, it is considered that the dendrimer molecules were collected at the focal spot by the photon pressure of the focused near-infrared laser beam in the gel-like assembly, which led to the contraction behavior, and when the laser beam was cut off, dendrimer molecules were not trapped at the focal spot, thus, the swelling of the gel-like assembly was observed. The changes of the gel-like assembly diameter corresponding to the repetitive irradiation are shown in Figure 3b. It can be seen that the swelling amplitude of the gel-like assembly after stopping the irradiation decreased with repeating the irradiation of the trapping laser. This decrease is brought about as a result of the evaporation of THF because of the drying process. On the other hand, the diameters of contracted gel-like assemblies are always constant. This means that the same number of dendrimer molecules are always trapped, regardless of the repetitive cycle. These phenomena were observed in both L3PPE130 and L4PPE8 gel-like assemblies, and such a behavior of dendrimer molecules for photon pressure can be confirmed by measurement of fluorescence spectra from the focal spot as follows.

It is interesting to note that contraction and swelling of the gel-like assemblies are accompanied with fluorescence spectral change. The excitation beam spot was spatially identical to that of the trapping laser, and the spot size is about 1 μm. We measured many gel-like assemblies, and found that spectral changes as shown in Figure 4 were observed in response to irradiation and the stopping of the trapping laser. The spectrum labeled “THF solution” shows a peak at 453 nm with a shoulder around 500 nm, and the spectrum labeled “aggregate”, which was detected as a particle-like aggregate of dendrimer after the gel-like assembly was dried completely, shows a new sharp band at 480 nm and a small broad but intense band at 517 nm. Absorption spectra of the particle-like aggregates show a characteristic sharp band, which was well known as an aggregate band, at 470 nm and a broad band at 450 nm (the absorption spectra are not shown here). The spectrum labeled “gel-like assembly”, detected at the gel-like dendrimer assembly, shows a small red-shifted peak at 456 nm and a large contribution around 500 nm relative to the spectrum labeled “THF solution”,

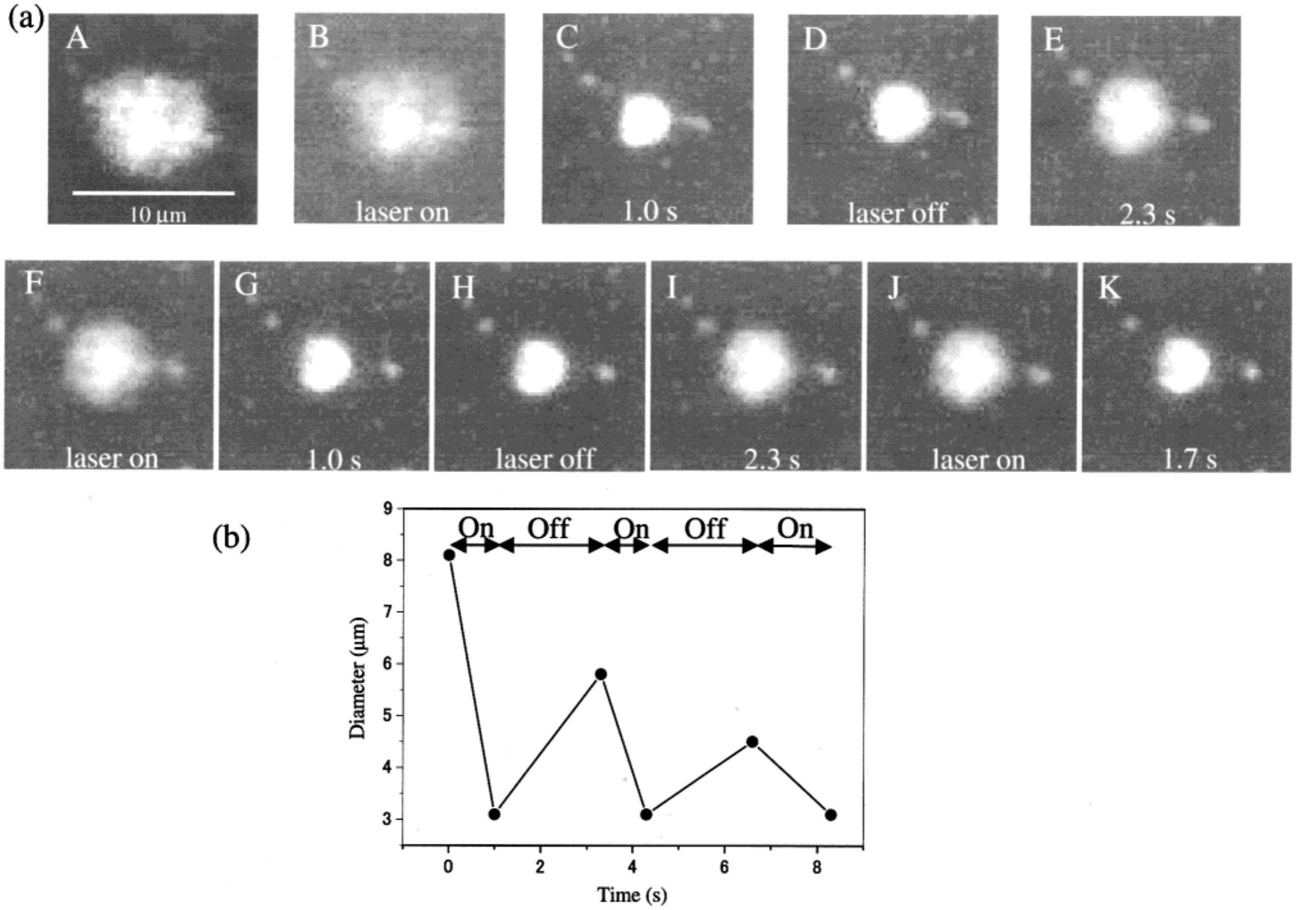

Figure 3. (a) Fluorescence images of L3PPE130 gel-like assembly observed during repetitive irradiation of trapping laser. The "laser on" and "laser off" labels indicate the time when irradiation is started and stopped, respectively. The times from "laser on" or "laser off" are shown below in each image. (b) The diameter change of the L3PPE130 gel-like assembly diameters corresponding to the repetitive irradiation.

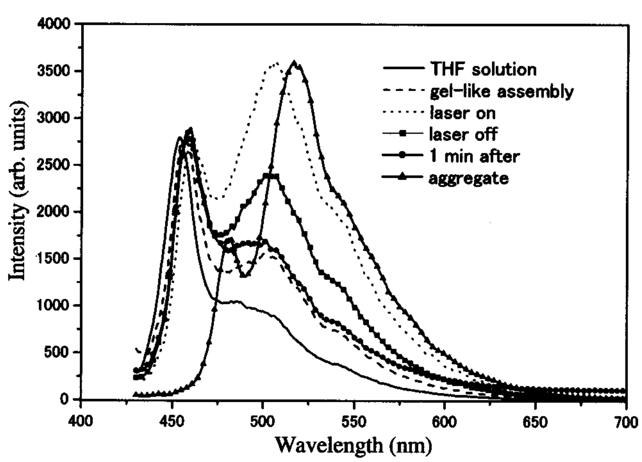

Figure 4. The fluorescence spectra from the L3PPE130 gel-like assembly. The spectrum labeled "THF solution" was detected immediately after the THF solution of dendrimer was cast on the substrate. The spectrum labeled "gel-like assembly" was detected at the gel-like assembly before trapping laser was irradiated. Spectra labeled "laser on" and "laser off" were detected immediately after the trapping laser was introduced and cut off, respectively. The spectrum labeled "aggregate" was detected after the gel-like assembly was dried completely.

owing to the increase of the dendrimer concentration as discussed later. The contribution around 500 nm was more prominent, and a further red-shifted peak at 460 nm was shown in the spectrum labeled "laser on" when the gel-like assembly was contracted due to the irradiation of the trapping laser. Subsequently, when the gel-like assembly swelled after the trapping laser was cut off, the contribution around 500 nm was decreased as shown at the spectrum labeled "laser off". After 1 min, the detected spectrum labeled "1 min after" is similar to the "gel-like assembly" spectrum. These spectral changes are induced upon the contraction and the swelling of the gel-like assembly, and eventually are attributed to the concentration change as a result of the trapping laser irradiation.

Comparing these dendrimer results with those of several other PPEs,[14,15] it is considered that the concentration change causes two influences to dendrimers as follows, and the spectral changes are induced by the two. (1) The planarization of the conjugated backbone leads to increase the conjugation length as single molecule. (2) Interpolymer electronic interaction occurs by forming an interpolymer π aggregate. However, in the case of L4PPE8, with a conjugated backbone likely be encapsulated by the bulky dendritic wedges, such spectral changes were not observed, although the contraction and swelling were observed in response to the irradiation and nonirradiation of the trapping laser. Therefore, the spectral changes observed at L3PPE130 gel-like assembly presumably attribute to the interpolymer electronic interaction as a result of increasing the concentration due to the irradiation of the trapping laser. That is to say, it is considered that the photon pressure by the focused near-infrared laser beam induced the formation molecular aggregates transiently, and it influenced the gel-like assembly volume.

Conclusions

Here we have demonstrated for the first time the focused near-infrared laser beam effect on drying process of the L3PPE130 and L4PPE8 cast THF solution on a glass substrate, and we have found interesting contraction and swelling phenomena and accompanying spectral changes of L3PPE130 and L4PPE8 gel-like assemblies, which formed during the drying process, in response to the irradiation of the near-infrared laser beam. The volume changes of polymer gel by the photon pressure were reported by the use of poly(*N*-isopropylacrylamide) (PNIPAM) in D_2O.[16] However, in the case of the PNIPAM gel, a hydrogen bond network exists in the gel, which supports the volume change. On the other hand, despite that the polymer network probably does not exist in the gel-like dendrimer assembly, contraction and swelling phenomena were observed transiently. These phenomena are attributed to the concentration increase at the focal spot by the photon pressure. This report is first step for the formation unique molecular assemblies by focused laser beam on the solid substrate surface.

Acknowledgment. The present work is partly supported by Grant-in Aid for Scientific Research on Priority Areas (B) on "Laser Chemistry of Single Nanometer Organic Particles" from The Ministry of Education, Science, Sports, and Culture of Japan.

References and Notes

(1) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658.

(2) Masuo, S.; Yoshikawa, H.; Asahi, T.; Masuhara, H.; Sato, T.; Jiang, D.-L.; Aida, T. *J. Phys. Chem. B* **2001**, *105*, 2885.

(3) (a) Latterini, L.; Blossey, R.; Hofkens, J.; Vanoppen, P.; De Schryver, F. C.; Rowan, A. E.; Nolte, R. J. M. *Langmuir* **1999**, *15*, 3582. (b) Hofkens, J.; Latterini, L.; Vanoppen, P.; Faes, H.; Jeuris, K.; De Feyter, S.; Kerimo, J.; Barbara, P. F.; De Schryver, F. C.; Rowan, A. E.; Nolte, R. J. M. *J. Phys. Chem. B* **1997**, *101*, 10588. (c) Schenning, A. P. H. J.; Benneker, F. B. G.; Geurts, H. P. M.; Liu, X. Y.; Nolte, R. J. M. *J. Am. Chem. Soc.* **1996**, *118*, 8549.

(4) Thiele, U.; Mertig, M.; Pompe, W. *Phys. Rev. Lett.* **1998**, *80*, 2869.

(5) (a) Ohara, P. C.; Gelbart, W. M. *Langmuir* **1998**, *14*, 3418. (b) Ohara, P. C.; Heath, J. R.; Gelbart, W. M.; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*(10), 1078.

(6) (a) Karthaus, O.; Gråsjö, L.; Maruyama, N.; Shimomura, M. *Chaos* **1999**, *9*, 308. (b) Reiter, G. *Science* **1998**, *282*, 888. (c) Maruyama, N.; Koito, T.; Nishida, J.; Sawadaishi, T.; Cieren, X.; Ijiro, K.; Karthaus, O.; Shimomura, M. *Thin Solid Films* **1998**, 327−329, 854. (d) Maruyama, N.; Karthaus, O.; Ijiro, K.; Shimomura, M.; Koito, T.; Nishimura, S.; Sawadaishi, T.; Nishi, N.; Tokura, S. *Supramol. Sci*. **1998**, *5*, 331. (e) Herminghaus, S.; Jacobs, K.; Mecke, K.; Bischof, J.; Fery, A.; Ibn-Elhaj, M.; Schlagowski, S. *Science* **1998**, *282*, 916. (f) Ouyang, Q.; Swinney, H. L. *Nature* **1991**, *352*, 610.

(7) (a) Smith, T. A.; Hotta, J.; Sasaki, K.; Masuhara, H.; Itoh, Y. *J. Phys. Chem. B* **1999**, *103*, 1660. (b) Borowicz, P.; Hotta, J.; Sasaki, K.; Masuhara, H. *J. Phys Chem. B* **1998**, *102*, 1896. (c) Hotta, J.; Sasaki, K.; Masuhara, H.; Morishima, Y. *J. Phys. Chem. B* **1998**, *102*, 7687. (d) Borowicz, P.; Hotta, J.; Sasaki, K.; Masuhara, H. *J. Phys Chem. B* **1997**, *101*, 5900. (e) Hofkens, J.; Hotta, J.; Sasaki, K.; Masuhara, H.; Taniguchi, T.; Miyashita, T. *J. Am. Chem. Soc*. **1997**, *119*, 2741. (f) Hofkens, J.; Hotta, J.; Sasaki, K.; Masuhara, H.; Iwai, K. *Langmuir* **1997**, *13*, 414. (g) Hofkens, J.; Hotta, J.; Sasaki, K.; Masuhara, H.; Faes, H.; De Schryver, F. C. *Mol. Cryst. Liq. Cryst*. **1996**, *283*, 165. (h) Hotta, J.; Sasaki, K.; Masuhara, H. *J. Am. Chem. Soc*. **1996**, *118*, 11968.

(8) (a) Bunz, U. H. F. *Chem. Rev*. **2000**, *100*, 1605. (b) Huang, S.; Tour, M. *J. Am. Chem. Soc*. **1999**, *121*, 4908. (c) Kloppenburg, L.; Jones, D.; Claridge, J. B.; zur Loye, H.-C.; Bunz, U. H. F. *Macromolecules* **1999**, *32*, 4460. (d) Kloppenburg, L.; Song, D.; Bunz, U. H. F. *J. Am. Chem. Soc*. **1998**, *120*, 7973. (e) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. (f) Giesa, R. *J. Macromol. Sci. Rev., Macromol. Chem. Phys*. **1996**, *C36*, 631. (g) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157. (h) Moroni, M.; Le Moigne, J.; Luzzati, S. *Macromolecules* **1996**, *29*, 5157. (i) Swager, T. M.; Gil, C. J.; Wrighton, M. S. *J. Phys. Chem*. **1995**, *99*, 4886.

(9) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem*. **1998**, *37*, 402. (b) Montali, A.; Smith, P.; Weder, C. *Synth. Met*. **1998**, *97*, 123. (c) Höger, S.; McNamara, J. J.; Schricker, S.; Wudl, F. *Chem. Mater*. **1994**, *6*, 171. (d) Zhang, C.; Höger, S.; Pakbaz, K.; Wudl, F. *J. Electron. Mater*. **1993**, *22*, 413. (e) Voss, K. F.; Foster, C. M.; Smilowitz, L.; Mihalovic, D.; Askari, S.; Srdanov, G.; Ni, Z.; Shi, S.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1991**, *43*, 5109.

(10) Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. *Acc. Chem. Res*. **1997**, *30*, 430.

(11) (a) Weder, C.; Sarwa, C.; Montali, A.; Bastiaansen, C.; Smith, P. *Science* **1998**, *279*, 835. (b) Montali, A.; Bastiaansen, C.; Smith, P.; Weder, C. *Nature* **1998**, 392, 261. (c) Montali, A.; Smith, P.; Weder, C. *Synth. Met*. **1998**, *97*, 123.

(12) (a) Dol, G. C.; Tsuda, K.; Weener, J.-W.; Bartels, M. J.; Asavei, T, Gensch, T.; Hofkens, J.; Latterini, L.; Schenning, A. P. H. J.; Meijer, B. W.; De Schryver, F. C. *Angew. Chem., Int. Ed. Engl.* **2001**, *40*, 1710. (b) Gensch, T.; Tsuda, K.; Dol, G. C.; Latterini, L.; Weener, J. W.; Schenning, A. P. H. J.; Hofkens, J.; Meijer, E. W.; De Schryver, F. C. *Pure Appl. Chem*. **2001**, *73*, 435.

(13) Wurlitzer, S.; Lautz, C.; Liley, M.; Duschl, C.; Fischer, T. M. *J. Phys. Chem. B* **2001**, *105*, 182.

(14) (a) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652. (b) Fiesel, R.; Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Scherf, U.; Bunz, U. H. F. *Macromol. Rapid Commun*. **1999**, *20*, 107.

(15) (a) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030. (b) McQuade, D. T.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 5885. (c) Kim, J.; McQuade, D. T, McHugh, S. K.; Swager, T. M. *Polym. Prepr*. **2000**, *41*, 32. (d) Levitsky, I. A.; Kim, J.; Swager, T. M. *J. Am. Chem. Soc*. **1999**, *121*, 1466.

(16) Juodkazis, S.; Mukai, N.; Wakaki, R.; Yamaguchi, A.; Matsuo, S.; Misawa, H. *Nature* **2000**, *408*, 178.