Fluorescent Spherical Particle Formation from Poly(dimethylsilane) by the Aid of Laser Ablation and Photochemical Reaction

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With the aid of laser ablation using the third harmonic of Nd:YAG laser light, poly(dimethylsilane) (PDMS) powder produced crystalline deposits as the major product together with a small amount of spherical particles with a diameter of 1 \( \mu \)m. In order to produce the spherical fine particles predominantly, photochemical reactivity of carbon disulfide (CS\(_2\)) and trimethylsilyl azide (TMSAz) was used during the laser ablation process. In the presence of CS\(_2\) vapor, laser-ablated PDMS produced spherical particles with a diameter of \(~1\) \( \mu \)m and aggregated small particles originating from CS\(_2\). To escape from producing aerosol particles from the gaseous molecules, TMSAz vapor which itself did not produce any solid product was introduced onto PDMS powder. Laser-ablated PDMS produced only morphologically identical particles on the whole glass plate with a mean diameter of 1.3 \( \mu \)m. The PDMS/TMSAz particles thus obtained showed a fluorescence peak at 344 nm, being shifted to shorter wavelength by 18 nm than that of PDMS powder.

Keywords: laser ablation, photochemical reaction, fine particles, trimethylsilyl azide, poly(dimethylsilane), carbon disulfide

1. Introduction

Using photochemical reactions of gaseous molecules, ultrafine and fine particles can be synthesized from some gaseous molecules such as acrolein (2-propenal) and carbon disulfide (CS\(_2\)) [1-3]. This method, i.e., the photochemical method [4, 5] was applied to other gaseous molecules such as organosilicon compounds and organometal compounds [6-13], and succeeded in producing spherical ultrafine and fine particles involving Si, Fe, and Co species. Based on the experimental results so far obtained, the photochemical method is suitable to synthesize composite spherical particles.

Synthesis of ultrafine and fine particles from solid materials needs the melting and/or vaporization of solid materials. For this purpose, laser ablation of solid materials has frequently been used as a convenient and powerful method [14-19]. It is well known that depending on the laser light intensity and laser pulse duration, chemical and physical phenomena of laser ablation change dramatically [20]. Hence, in actual application of laser ablation to a specific purpose, determination of the experimental conditions is essential.

In this paper, we have undertaken to produce spherical ultrafine and fine particles from solid material by the aid of laser ablation and photochemical reaction. Poly(dimethylsilane) (PDMS) has been chosen as a solid target in laser ablation expecting to take place any chemical reactions with ambient gaseous molecules during the laser ablation process. In the present study, chemical reactivity of CS\(_2\) [21, 22] and trimethylsilyl azide (TMSAz) [9] towards PDMS were utilized to produce spherical fine particles. Polysilanes emit fluorescence [23]. Characteristics of fluorescence spectrum of fine particles of PDMS were discussed briefly.
2. Experimental

PDMS (Wako, E.P. grade) was used as supplied. CS$_2$ (Kanto, 98%) and TMSAz (Tokyo Kasei, 96%, E.P. grade) were stored in a refrigerator below 10°C to prevent polymerization and/or photodecomposition. CS$_2$ and TMSAz were degassed by freeze-pump-thaw cycles in the dark and purified by vacuum distillation immediately before use. A small amount (40 - 60 mg) of PDMS powder was put into a small aluminum chamber placed on a glass plate accommodated at the bottom of a cross-shaped irradiation cell (both arms, inner diameter 35 mm, length 130 mm) (Fig. 1) followed by the introduction of vapor of CS$_2$ or TMSAz through a vacuum line equipped with a capacitance manometer (Edwards Barocel Type 600). The background pressure of the irradiation cell was less than 8 × 10$^{-5}$ Torr (1 Torr = 133.3 Pa). The small chamber (8 × 8 mm, H = 15 mm) has an aperture (5.9 φ) on the top surface, and the third harmonic (355 nm) of pulsed Nd:YAG laser light (Continuum Surelite I-10, pulse width 6 ns, repetition rate 10 Hz) was irradiated on the PDMS powder vertically across the aperture. The laser-ablated materials escaped from the chamber across the aperture and scattered on the glass plate. Scanning electron microscope (SEM) images of the laser-ablated materials were recorded with a JEOL JSM 6060 scanning electron microscope, and SEM-EDS analyses were performed using a Philips XL30 CP scanning electron microscope. The laser-ablated materials were mixed with KBr powder to prepare KBr pellets and FT-IR spectra of the laser-ablated materials embedded in the pellets were measured with a Nicolet NEXUS 470 FT-IR spectrometer. Fluorescence spectrum of particles deposited on the glass plate was measured at room temperature with the combination of a monochromator (JASCO CT-50) and a photomultiplier tube (EMI 6256S), exciting light from a 150 W xenon arc lamp (Ushio UXL 150D) being monochromatized with a monochromator (Nikon G250).

3. Results and discussion

3.1. Particle formation in the atmosphere of CS$_2$ vapor

The third harmonic (355 nm) of pulsed Nd:YAG laser light (energy 32 mJ/pulse) was irradiated on PDMS powder as a preliminary experiment. A small amount of spherical particles with a diameter of ~1 µm was produced as a minor product in addition to crystalline deposits as the major product (Fig. 2). In the presence of CS$_2$ vapor (50 Torr), PDMS powder was irradiated with the laser light at an energy of 31 mJ/pulse. Spherical particles with a diameter of ~1 µm and aggregated smaller particles with a diameter of ~0.2 µm were detected on the glass plate (Fig. 3).
deposits detected in the laser ablation without CS$_2$ vapor (Fig. 2(a)) were hardly detected. Based on the fact that CS$_2$ molecules slightly absorb light at 355 nm [24-26] and produce the sedimentary aerosol particles [27], the aggregated particles may be the sedimentary aerosol particles produced from CS$_2$ molecules. To support for this, with decreasing pressure of CS$_2$ molecules from 50 to 20 Torr, the yield of the aggregated particles decreased.

The particle size distribution was measured for both kinds of the particles. The results are shown in Fig. 4. The size distribution of the aggregated particles is in the 0.1 - 0.5 µm range with a mean diameter of 0.23 µm. Rather narrow size distribution is characteristic of aerosol particles synthesized in the gas phase under photochemical reaction [8, 21]. On the other hand, the size of the larger particles is widely distributed with a mean diameter of 1.4 µm, suggesting that these are laser-ablated product of PDMS.

The chemical composition of a large particle was analyzed by SEM-EDS measurement. The population of Si, S, C, and O atoms in a particle with a diameter of 3.7 µm is 25.6, 2.2, 67.9, and 4.3 At%, respectively, and the atomic ratio of Si atom to C and S atoms is 1: 2.6 : 0.09, showing that PDMS reacted with CS$_2$ molecules to produce spherical particles. Because the aggregated particles originating from CS$_2$ deposited entirely on the whole glass plate, it was difficult to separate the PDMS/CS$_2$ composite particles from the aggregated particles.

3.2. Particle formation in the atmosphere of TMSAz vapor

Although TMSAz is a reactive molecule, it does not absorb light at 355 nm. Under light irradiation at 355 nm (energy 36 mJ/pulse) for 5 min with the YAG laser, TMSAz vapor (20 Torr) did not produce any solid material. Taking this into account, PDMS powder in the presence of TMSAz vapor (20 Torr) was irradiated with 355 nm laser light (energy 36 mJ/pulse) for 5 min. Laser-ablated PDMS produced only morphologically identical particles on the whole glass plate with a mean diameter of 1.3 µm as is shown in Fig. 5. FT-IR spectrum of the particles is shown in Fig. 6, together with the spectra of PDMS powder without laser ablation and TMSAz vapor. In addition to the bands at 1250, 832, 743, 691, and 630 cm$^{-1}$ ascribed to PDMS and the bands at 1259 and 834 cm$^{-1}$ ascribed to TMSAz [28], a new band was observed at 1036 cm$^{-1}$, assignable to ν(C-N). Considering that antisymmetric stretching band of the azido group, ν$_a$(N$_3$) at 2153 cm$^{-1}$ became very
weak, it is strongly suggested that TMSAz reacted with PDMS accompanying the decomposition of

the azido group to produce the trimethylsilyl nitrene intermediate. Through chemical reactions between the nitrene and laser-ablated PDMS, spherical particles were successfully formed.

3.3. Fluorescence spectrum of PDMS/TMSAz particles

Fluorescence spectrum of PDMS/TMSAz particles as deposited on the glass plate was measured at room temperature with an excitation wavelength at 320 nm. The spectrum is shown in Fig. 7, compared with the spectrum of PDMS powder without laser ablation. Narrow and structureless emission spectra in Fig. 7 are characteristic of polysilanes [23]. PDMS/TMSAz particles have a fluorescence peak at 344 nm, which is at shorter wavelength by 18 nm than that of PDMS powder at 362 nm. This may be due to Si-Si bond breakage to reduce the
polymerization degree and bond formation such as Si-N-C and/or Si-C-N during laser ablation. Detailed study on fluorescence characteristics is now in progress.

4. Conclusions

By the aid of laser ablation and photochemical reaction, spherical fine particles were successfully produced from PDMS powder and TMSAz vapor. Morphological change of laser-ablated materials of PDMS in the atmosphere of CS$_2$ and TMSAz vapors strongly suggested that chemical reactions between laser-ablated materials and gaseous molecules played an important role in producing spherical fine particles.

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References