

Laser-induced nucleation process in aerosol particle formation from a gaseous mixture of methyl acrylate and carbon disulfide

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Abstract

Upon exposure to N_2 laser light, a gaseous mixture of methyl acrylate (MA) and carbon disulfide (CS_2) produced sedimentary spherical aerosol particles with a mean diameter of $\approx 0.8 \mu m$. The product yield of the sedimentary aerosol particles deposited on a glass plate at the bottom of the cylindrical irradiation cell increased with increasing irradiation time of N_2 laser light, and with increasing laser intensity up to 3.5 mJ/pulse. The IR and Raman spectra of the sedimentary aerosol particles showed the bands characteristic of poly(methyl acrylate) and carbon polymer, respectively, indicating that MA is polymerized into the aerosol particles produced from CS_2 . The nucleation process of aerosol particles are briefly discussed by measuring He–Ne laser light intensity scattered by the aerosol particles and by observing the fluorescence spectrum of CS_2 . © 1998 Elsevier Science S.A.

Keywords: N_2 laser-induced nucleation; Sedimentary aerosol particles; Methyl acrylate; Carbon disulfide

1. Introduction

Through multiphoton excitation and ionization, gaseous organic molecules can initiate chemical reactions from a highly excited (or ionic) state, and produce noble materials in the vapor phase. In an attempt to synthesize noble fine particles and thin films from gaseous organic molecules, we have irradiated N_2 laser light on gaseous methyl acrylate (2-propenoic acid methyl ester) (MA) and gaseous acrolein (2-propenal) (AC). These molecules initiated chemical reactions by two photon process, and gaseous MA deposited a solid polymer film of poly(methyl acrylate) on the surface of an optical quartz window [1], and gaseous AC produced sedimentary aerosol particles of polyacrolein [2,3]. Furthermore, a gaseous mixture of MA and AC produced both a polymer film and aerosol particles in which MA and AC were copolymerized in each other [4].

Photochemical process of carbon disulfide (CS_2) clusters and nucleation process of CS_2 vapor have been studied extensively [5–13], and CS_2 produced sedimentary aerosol particles under irradiation with N_2 laser light [8–13]. Chemical structure of the aerosol particles was suggested to be an amorphous mixture of sulfur polymer and carbon polymer hitherto unknown [14–16] or to be $(CS_2)_x$ polymer similar to Bridg-

man's black carbon disulfide which was synthesized at high pressures [17]. These results suggested a possibility in producing noble solid materials from a gaseous mixture of CS_2 under UV laser light irradiation. Hence, in a preliminary experiment we have irradiated N_2 laser light upon a gaseous mixture of MA and CS_2 [18] and found that the gaseous mixture predominantly produced aerosol particles, suggesting that photochemical process of CS_2 is more efficient than that of MA. In the present paper, in order to understand the nucleation process in aerosol particle formation from a gaseous mixture of MA and CS_2 , we have investigated some physical and chemical properties of the aerosol particles and measured He–Ne laser light intensity scattered by the aerosol particles which were formed under irradiation with N_2 laser light.

2. Experimental details

MA (Wako, 98%, stabilized with 0.03% hydroquinone monomethyl ether) and CS_2 (Kanto, 99%) were stored in a refrigerator below $10^\circ C$ to prevent polymerization. The MA and CS_2 liquids were distilled under vacuum and degassed by freeze-pump-thaw cycles immediately before use. To prepare a gaseous mixture of MA and CS_2 , a fixed amount of MA vapor which was introduced into a specific region of a

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vacuum line with a mercury manometer was collected into a glass tube by freezing with liquid nitrogen, and then another fixed amount of CS₂ vapor which was introduced into the same region of the vacuum line was collected by freezing over the MA liquid already frozen in the glass tube. After thawing them into a mixed liquid, a gaseous mixture of MA and CS₂ with a fixed molar ratio was vaporized, and then introduced into a cylindrical cell (inner diameter: 35 mm, cell length: 165 mm) with quartz optical windows on both ends. From the analysis of UV absorption spectrum, the partial pressures of MA and CS₂ vapors in the cell were determined. The result agreed well with the initial pressure of each component measured with the mercury manometer. The background pressure of the vacuum system was 5×10^{-5} Torr (1 Torr = 133.3 Pa). The leakage into the evacuated cell from the atmosphere was carefully controlled to be less than 0.5 Torr in a day. The gaseous samples were irradiated with nitrogen gas laser light (Lumonics HE-440 or Molectron UV24, 337.1 nm) through an optical quartz window with a repetition rate of 12 Hz for 0.5–10 h. Laser power was measured with a pyroelectric joulemeter (Gentec ED-500) combined with a synchroscope (Iwatsu SS-5121B). IR and FT-IR spectra of the sedimentary aerosol particles were measured with a Hitachi 260-10 IR spectrophotometer and a Herschel FT/IR-350 FT-IR spectrophotometer equipped with a microscope M-20, and Raman spectra, with a JASCO NR-1800 laser-Raman spectrophotometer. Scanning electron microscope (SEM) images were taken with a Topcon ABT-32 scanning electron microscope. Light intensity scattered perpendicularly to the incident monitor (He–Ne laser) light by the aerosol particles floating in the cell was measured with a combination of a photomultiplier tube (EMI 6256S) and a lock-in amplifier (SRS SR-530) by chopping and synchronizing monitor light with exciting N₂ laser light pulses by using a delay and pulse generator (SRS DG535). Fluorescence spectrum was measured with a gaseous mixture of MA and CS₂ by using N₂ laser light as an exciting source.

3. Results and discussion

Upon exposure to N₂ laser light at an energy of 1.2 mJ/pulse for 4 h, a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) deposited sedimentary aerosol particles on a glass plate which was placed at the bottom of the irradiation cell in order not to be directly exposed to the incident laser light. Absorbance of CS₂ at a pressure of 53 Torr in the light path length of 165 mm was measured to be 0.1 at 337.1 nm, and the one of MA at a pressure of 25 Torr was negligibly small [1]. Because of the low absorbance of the gaseous mixture, a number of excited molecules were generated uniformly along the axis of the cylindrical cell and hence, the nucleation process proceeded homogeneously along this axis under the present experimental conditions. Aerosol particles fell down on the glass plate with a reproducible sedimentary pattern due to convection of the gaseous mixture. Fig. 1 shows SEM

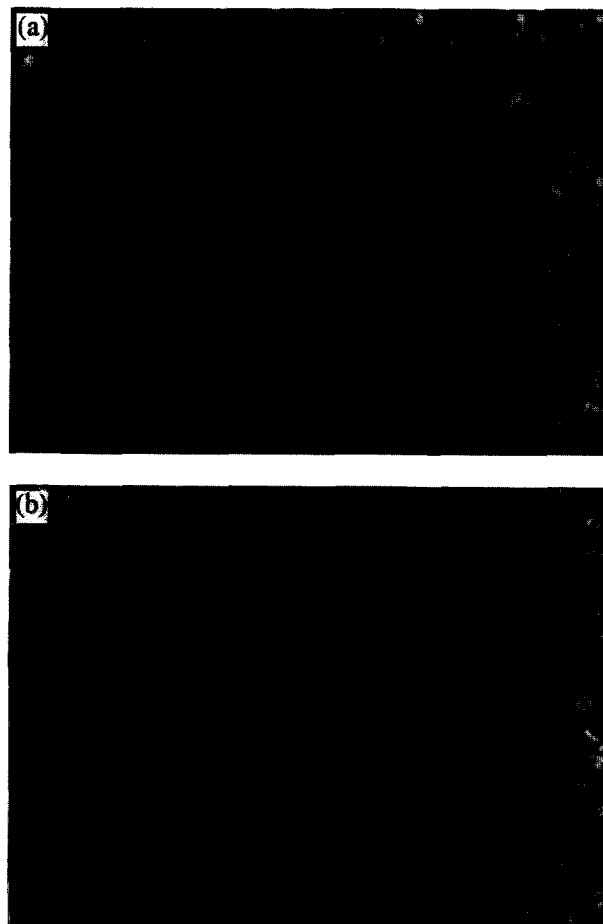


Fig. 1. SEM images of sedimentary aerosol particles deposited from a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) under irradiation with N₂ laser light at an energy of (a) 1.2 mJ/pulse and (b) 3.5 mJ/pulse for 4 h. Original magnification, 2000 \times .

images of the sedimentary aerosol particles deposited from the gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) under irradiation with N₂ laser light at an energy of 1.2 and 3.5 mJ/pulse. Aerosol particles were brown and spherical with a mean diameter of $\approx 0.72 \mu\text{m}$ and $\approx 0.88 \mu\text{m}$ at energies of 1.2 and 3.5 mJ/pulse, respectively. The mean diameter of the aerosol particles was slightly dependent on the exciting laser intensity, and was larger than the corresponding value ($\approx 0.5 \mu\text{m}$) produced from pure CS₂ [14]. Considering the fact that the size distribution of the deposited particles from the gaseous mixture showed only one maximum and that pure MA did not produce any aerosol particles [1], this result suggested that the sedimentary aerosol particles were not a mixture of the solid products produced separately from pure MA and from pure CS₂, but that MA was incorporated into the nucleation reaction of CS₂.

The dependence of the yield of sedimentary aerosol particles on the irradiation time of laser light (using Lumonics HE440) at an energy of 1.9 mJ/pulse was measured with the gaseous mixture of MA (25 Torr) and CS₂ (53 Torr). The result is shown in Fig. 2. The yield increased linearly with irradiation time up to 10 h as in the case of a gaseous mixture

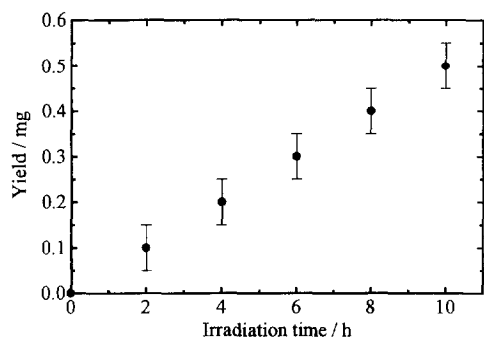


Fig. 2. Dependence of the yield of sedimentary aerosol particles deposited from a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) on irradiation time of N₂ laser light at an energy of 1.9 mJ/pulse.

of AC and CS₂ [2]. With irradiation longer than 2 h, a very thin polymer film was formed on the surface of the optical quartz window. The yield of the thin film increased to 0.3 mg under irradiation for 10 h. Induction period needed to visually detect the formation of sedimentary aerosol particles was \approx 10 min, being shorter than the one for pure CS₂ vapor.

The laser intensity dependence (1.2–3.5 mJ/pulse using a Lumonics HE440 laser) of the yield of the sedimentary aerosol particles was also measured with the gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) under irradiation for 4 h. The result is shown in Fig. 3. Under laser irradiation at energies of 2.6 and 3.5 mJ/pulse, a thin polymer film was deposited (\approx 0.1 mg) on the surface of the optical quartz window in addition to the aerosol particles. The yield of the sedimentary aerosol particles increased linearly with increasing laser intensity, showing that the aerosol particle formation process was initiated by one-photon process. Because the MA molecules needed two photons to generate the radicals which could initiate polymerization [1], the result indicated that one-photon process of CS₂ initiated the nucleation process of the aerosol particle formation.

To characterize properties of the aerosol particles, IR and Raman spectra were measured with the sedimentary aerosol particles deposited from a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr); the results are shown in Fig. 4. In Fig. 4A, IR bands observed in 1100–1800 cm⁻¹ region (i.e., at 1170, 1196, 1262, 1372, 1434, and 1730 cm⁻¹) can clearly be assigned to poly(methyl acrylate) [1,19], showing that MA was involved in the sedimentary aerosol particles as polymeric species. In Fig. 4A, a strong band at 1068 cm⁻¹ and a weak band at 1010 cm⁻¹ were observed in addition to the bands assigned to poly(methyl acrylate). Because the corresponding bands were also observed with the aerosol particles deposited from pure CS₂ vapor under irradiation with N₂ laser light [15], these bands observed at 1068 and 1010 cm⁻¹ can be ascribed to the chemical species originated from CS₂. Raman spectrum of the sedimentary particles in Fig. 4B is almost identical to the spectrum observed with the aerosol particles deposited from a gaseous mixture of AC and CS₂ [2], except that the intensity of 1445 cm⁻¹ band in Fig. 4B is more prominent than the one of 1485 cm⁻¹ band (see

Fig. 5B in Ref. [2]). The bands at 1445 and 1485 cm⁻¹ can be assigned to polymeric species of CS₂. As was discussed in previous papers [2,15], spectral features of these bands partly agreed with the Raman bands observed with graphite [20–22] and C₆₀ [23], but did not coincide with both of them. On the other hand, the IR bands observed at 1068 and 1010 cm⁻¹ may be assigned to Bridgman's black carbon disulfide which was synthesized from CS₂ under irradiation at 313 nm with a Hg–Xe lamp [17], but a strong IR band at 1420 cm⁻¹ of Bridgman's black carbon disulfide was not observed in Fig. 4A. Although the chemical structure of the aerosol particles deposited from CS₂ vapor is still open to discussion [15–17], the IR and Raman spectra in Fig. 4 clearly showed that the sedimentary aerosol particles deposited from the gaseous mixture of MA and CS₂ involved two components in each particle, i.e., poly(methyl acrylate) and the polymeric species originated from CS₂. Considering that

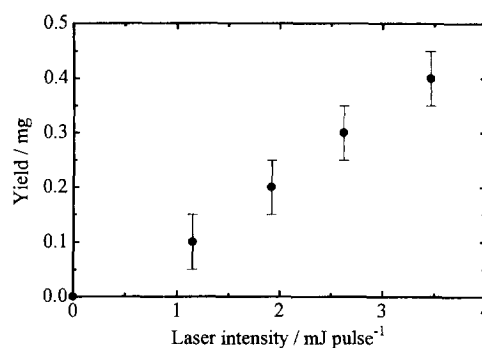


Fig. 3. Laser intensity dependence of the yield of sedimentary aerosol particles deposited from a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) under irradiation with N₂ laser light for 4 h.

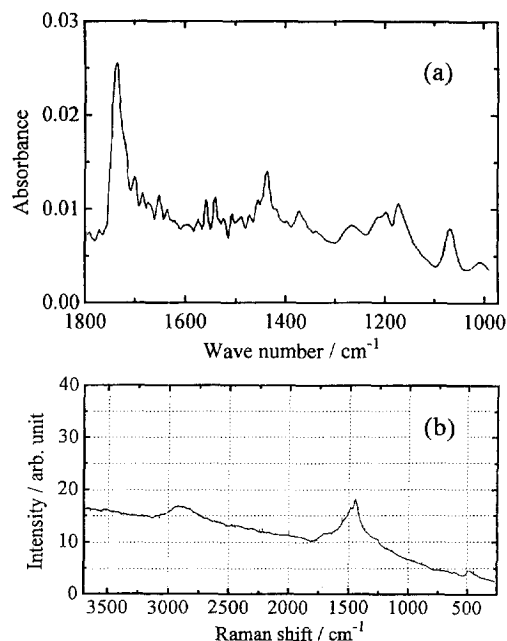


Fig. 4. (a) FT-IR RAS spectrum and (b) laser Raman spectrum of the aerosol particles deposited from a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) under irradiation with N₂ laser light at an energy of 4.6 mJ/pulse for 3.5 h.

the CS₂ molecules initiated the nucleation process of the aerosol particles, this result strongly suggested that MA was polymerized into the aerosol particles produced from CS₂.

Nucleation processes of a gaseous mixture of MA and CS₂ and of pure CS₂ were studied by measuring the intensity of He–Ne laser light scattered by the aerosol particles being formed under irradiation with N₂ laser (Molelectron UV24) light. Because the experimental results on the light intensity scattered in nucleation process of CS₂ depended on the sample pressure and upon the geometry of the reaction cell [24], the experiment for pure CS₂ was done for the purpose of comparison with the result of the gaseous mixture. The results for pure CS₂ (50 Torr) are shown in Fig. 5. Under irradiation with N₂ laser light at an energy of 1.5 mJ/pulse, scattered light intensity began to increase at ≈ 12 min, and reached to its maximum at ≈ 21 min. Between 30 min and 75 min (at which N₂ laser light was shut down), scattered light intensity became almost constant with large fluctuation around a constant value at intervals of ≈ 20 min. Under irradiation with N₂ laser light at an energy of 3.1 mJ/pulse, scattered light intensity began to increase at ≈ 5 min, and reached to its maximum at ≈ 10 min. After a large fluctuation, scattered light intensity became almost constant for longer irradiation time than 50 min. With increasing laser intensity, the induction period for detecting the scattered light became shorter and the scattered light intensity became stronger. Under irradiation with low laser power (curve c in Fig. 5), scattered light intensity fluctuated irregularly with relatively short intervals (≈ 2 min) mainly due to the convection of the aerosol particles in the irradiation cell.

Light intensity scattered by the aerosol particles formed from a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) was measured under irradiation with N₂ laser light at energies of 2.1–3.3 mJ/pulse. The results are shown in Fig. 6. The scattered light intensity began to increase under irradiation for 2–3 min. This induction period is shorter than the one of pure CS₂ in Fig. 5 (curve a). It is noteworthy that for the gaseous mixture the first peak of the scattered light intensity appeared at longer irradiation time (i.e., at 20–30 min) and the first band continued for longer time (at least 30 min) compared to the case of pure CS₂. This result clearly indicated that polymerization reaction of MA was induced through the nucleation reaction of CS₂ and contributed significantly to grow up the aerosol particles. Polymerization of MA and polymerization of CS₂ may independently propagate at the surface of an aerosol particle. In Fig. 6, N₂ laser light was shut down at 75 min. Immediately after the last laser pulse was shot, scattered light intensity increased very sharply and quickly dropped down, reflecting the formation process of nucleation after the shot of laser pulse. After this intensity change, scattered light intensity fluctuated irregularly due to continued propagation and sedimentation of the aerosol particles without irradiation of light as in the case of AC/CS₂ system [2]. Scattered light intensity almost decayed after 20 min.

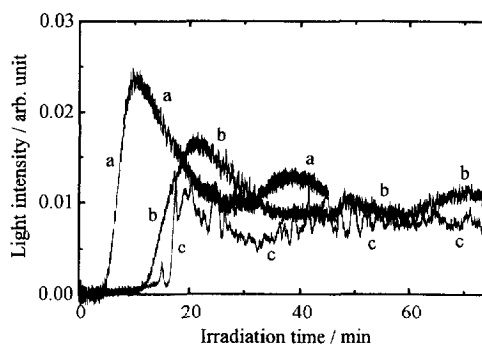


Fig. 5. Light intensity scattered by the aerosol particles produced from pure CS₂ (50 Torr) under irradiation with N₂ laser light at an energy of (a) 3.1, (b) 1.5, and (c) 0.8 mJ/pulse. Curve a overlapped with curve b at 48–55 min. For the clarity of the figure, curve a was cut at 45 min.

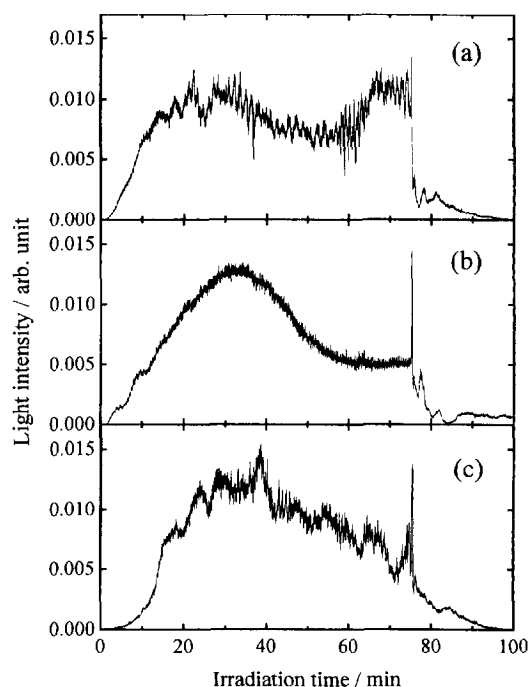


Fig. 6. Light intensity scattered by the aerosol particles produced from a gaseous mixture of MA (25 Torr) and CS₂ (53 Torr) under irradiation with N₂ laser light at an energy of (a) 3.3, (b) 2.9, and (c) 2.1 mJ/pulse.

Fluorescence spectrum of a gaseous mixture of MA and CS₂ was measured under irradiation with N₂ laser light. N₂ laser light can excite CS₂ molecule to $v'_2 = 3$ and 5 levels of the ¹A₂ state from $v''_2 = 1$ and 2 levels, respectively [25,26], and can be used as an exciting light source for detecting the emission in addition to the light source for inducing the nucleation of the aerosol particles. The fluorescence spectrum of CS₂ which was composed of sharp bands and broad continuous band [27–32] was quenched considerably by the addition of MA, and the spectrum observed did not show any shift of the emitting bands of CS₂ nor any new emitting band in the 340–600 nm region during irradiation with N₂ laser light for 3 h, showing that CS₂ did not form any complex with MA in its excited state during the nucleation reaction. Indeed, we have observed the increase of the scattered light

intensity due to nucleation at 337.1 nm in accordance with the result of light scattering of He–Ne laser light shown in Fig. 6.

In conclusion, in spite of the collisional deactivation with MA, CS₂ molecules in the excited state initiated the nucleation reaction [2,16] and induced the polymerization reaction of MA to efficiently form the aerosol particles which were composed of two main components, i.e., poly(methyl acrylate) and the polymeric species originated from CS₂.

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