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Laser-induced aerosol particle formation from a gaseous mixture of acrolein and carbon disulfide

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Abstract

Upon exposure to N_2 laser light, a gaseous mixture of acrolein and carbon disulfide (CS_2) produced sedimentary spherical aerosol particles with a mean diameter of ≈ 0.6 μm. 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 3.9 mJ per pulse. The IR and Raman spectra of the sedimentary aerosol particles showed the bands characteristic of acrolein polymer and carbon polymer, respectively, indicating that acrolein is polymerized into the aerosol particles produced from CS_2. The nucleation process of the aerosol particles was briefly discussed by measuring He–Ne laser light intensity scattered by the aerosol particles which were formed under irradiation with N_2 laser light. © 1997 Elsevier Science S.A. All rights reserved.

Keywords: Aerosol particle; Acrolein; Carbon disulfide; Light scattering

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1. Introduction

By multiphoton excitation and ionization of gaseous organic molecules under irradiation of UV laser light, solid films and aerosol particles can be deposited directly from gaseous molecules. By two photon absorption of N_2 laser light, gaseous methyl acrylate (2-propenoic acid methyl ester) (MA) deposited a solid polymer film on the surface of an optical quartz window selectively in the area directly exposed to the incident laser light [1]. A gaseous mixture of MA and acrolein (2-propenal) (AC) deposited sedimentary aerosol particles in addition to a polymer film upon exposure to N_2 laser light [2]. From the measurement of IR spectrum and the elemental analysis, it was found that the film was formed by copolymerization of MA and AC, and the mole fractions of MA and AC units in the film were varied depending on the initial compositions of a gaseous mixture and on the irradiated laser intensity [2]. Aerosol particle formation from gaseous carbon disulfide (CS_2) was extensively studied upon exposure to N_2 laser light [3–6]. From the results of IR and Raman spectra, sedimentary aerosol particles deposited from CS_2 were suggested to be an amorphous mixture of sulfur polymer and carbon polymer hitherto unknown [7,8], or to be $(CS_2)_x$ polymer similar to Bridgman's black carbon disulfide [9]. This result prompted us to synthesize a new solid material from a gaseous mixture containing CS_2. Upon exposure to N_2 laser light, a gaseous mixture of MA and CS_2 was found to produce sedimentary aerosol particles which involved both components of MA and CS_2 [10]. In order to extend the study of synthesizing new composite materials from CS_2, we have irradiated N_2 laser light upon a gaseous mixture of AC and CS_2, and have succeeded to produce sedimentary aerosol particles. In the present paper, we have investigated the nucleation process of the aerosol particles produced from a gaseous mixture of AC and CS_2, in addition to morphological characteristics and some physical and chemical properties of the sedimentary particles.

2. Experimental details

AC (Merck, 98%, stabilized with 0.2% hydroquinone) and CS_2 (Kanto, 99%) were stored in a refrigerator below 10 °C to prevent polymerization. The AC and CS_2 liquids were distilled under vacuum and degassed by freeze–pump–thaw cycles immediately before use. To prepare a gaseous mixture of AC and CS_2, a fixed amount of AC vapor which was introduced into a specific region of a vacuum line with a mercury manometer was collected into a glass tube by freezing with liquid nitrogen, and then another fixed amount of

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CS_2 vapor which was introduced into the same region of the vacuum line was collected by freezing over the AC liquid already frozen in the glass tube. After thawing them into a mixed liquid, a gaseous mixture of AC and CS_2 with a fixed molar ratio was vaporized, and then introduced into a cylindrical cell (inner diameter, 35 mm; cell length, 200 mm) with quartz optical windows on both ends. From the analysis of UV absorption spectrum, the partial pressures of AC and CS_2 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 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 (He–Ne laser) light with exciting N_2 laser light pulses by using a delay and pulse generator (SRS DG535).

3. Results and discussion

Upon exposure to N_2 laser light at an energy of 1.9 mJ per pulse for 4 h, a gaseous mixture of AC (63 Torr) and CS_2 (21 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. Aerosol particles fell down on the glass plate with a reproducible sedimentary pattern due to convection of the gaseous mixture. Fig. 1 shows SEM images of the sedimentary particles deposited from the gaseous mixture of AC and CS_2. Aerosol particles were yellowish brown and spherical with a mean diameter of ≈0.6 μm. The mean diameter of the aerosol particles was not sensitive to the molar ratio of the gaseous mixture of AC and CS_2. Aerosol particles deposited from pure CS_2 vapor were brown and the mean diameter was ≈0.5 μm [6], whereas aerosol particles deposited from AC vapor were white and the diameter was ≈1.0 μm [2]. Both the color and the particle size of aerosol particles deposited from the mixture of AC and CS_2 were intermediate between the above two cases.

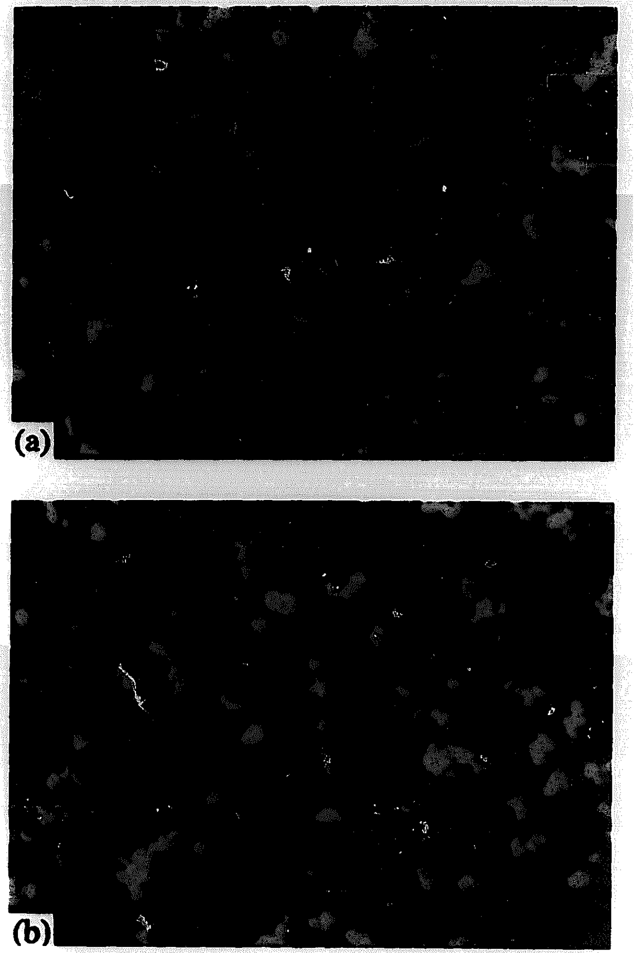

Fig. 1. SEM images of sedimentary aerosol particles deposited from a gaseous mixture of (A) AC (74 Torr) and CS_2 (20 Torr) and (B) AC (23 Torr) and CS_2 (76 Torr) under irradiation with N_2 laser light at an energy of 2.3 mJ per pulse for 3 h. Original magnification, 3000×.

The dependence of the yield of sedimentary aerosol particles on irradiation time of laser light (using Lumonics HE440) at an energy of 1.9 mJ per pulse was measured with a gaseous mixture of AC (63 Torr) and CS_2 (21 Torr). The result is shown in Fig. 2. Under irradiation for only 10 min, we could observe the formation of deposited particles on the glass plate. The yield increased linearly with irradiation time up to 8 h. Under irradiation longer than 8 h, a thin polymer

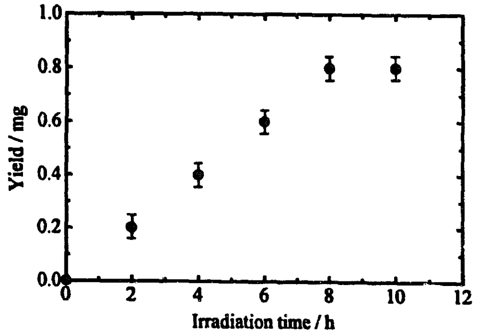

Fig. 2. Dependence of the yield of sedimentary aerosol particles deposited from a gaseous mixture of AC (63 Torr) and CS_2 (21 Torr) on irradiation time of N_2 laser light at an energy of 1.9 mJ per pulse.

film was formed on the surface of the optical quartz window. The yield of the sedimentary aerosol particles saturated at ≈ 0.8 mg. Induction period needed to visually detect the formation of sedimentary aerosol particles was ≈ 2 h for pure AC vapor and ≈ 0.5 h for pure CS_2 vapor under the present experimental conditions. The induction period for the gaseous mixture was shorter than for each pure gas.

The laser intensity dependence (1.0–3.9 mJ per pulse using a Lumonics HE440 laser) of the yield of sedimentary aerosol particles was also measured with a gaseous mixture of AC (63 Torr) and CS_2 (21 Torr) under irradiation for 4 h. The result is shown in Fig. 3. Under laser light irradiation stronger than 2.3 mJ per pulse, the gaseous mixture produced a thin polymer film on the surface of the optical quartz window in addition to the aerosol particles. In the figure, the sum of both yield is plotted. The yield increased linearly with increasing laser intensity, showing that the aerosol particle formation process was initiated by one-photon process.

In order to see which molecule is responsible for the initiation process of the aerosol particle formation, the dependence of the yield of sedimentary aerosol particles on the molar ratio of the gaseous mixture was measured under laser light irradiation for 5 h using a Molectron UV24 nitrogen gas laser at an energy of 2.2 mJ per pulse. A partial pressure of CS_2 was varied from 5 Torr to 90 Torr while the total pressure of the gaseous mixture of AC and CS_2 was kept to be constant (≈ 100 Torr). The results are shown in Fig. 4. The yield increased as the partial pressure of CS_2 increased. This result strongly suggests that the nucleation process of the aerosol particle formation is initiated through photochemical process of CS_2.

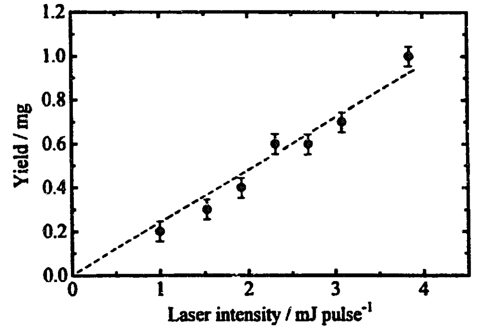

Fig. 3. Laser intensity dependence of the yield of sedimentary aerosol particles deposited from a gaseous mixture of AC (63 Torr) and CS_2 (21 Torr) under irradiation with N_2 laser light for 4 h.

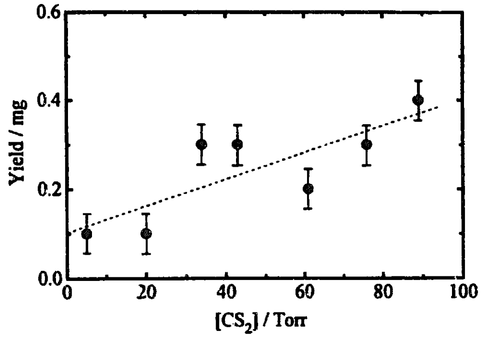

Fig. 4. Dependence of the yield of sedimentary aerosol particles on the molar ratio of a gaseous mixture of AC and CS_2 under irradiation with N_2 laser light at an energy of 2.2 mJ per pulse for 5 h. The total pressure of the gaseous mixture is 100 Torr.

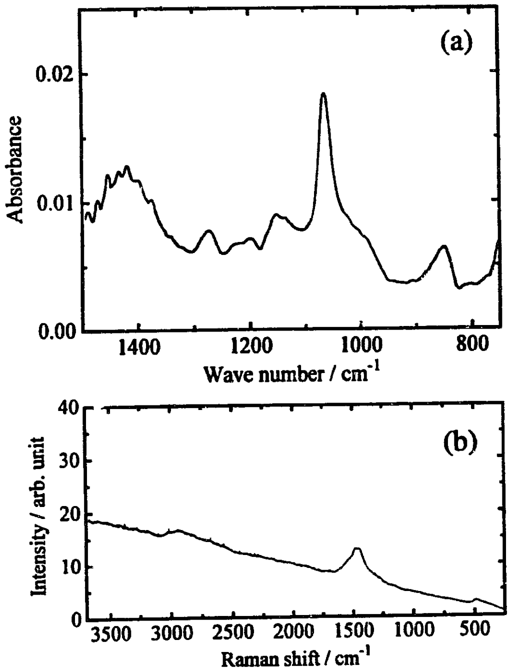

Fig. 5. (A) FT-IR RAS spectrum and (B) laser Raman spectrum of the aerosol particles deposited from a gaseous mixture of AC (54 Torr) and CS_2 (43 Torr) under irradiation with N_2 laser light at an energy of 2.3 mJ per pulse for 3 h.

To characterize properties of the aerosol particles, IR and Raman spectra were measured with the sedimentary aerosol particles deposited from a gaseous mixture of AC (54 Torr) and CS_2 (43 Torr), the results are shown in Fig. 5. In Fig. 5(A), IR bands characteristic of AC and CS_2 monomers [11,12] disappeared. Furthermore, the bands characteristic of CS polymer such as C–S and C=S stretching vibrational bands were not observed. The IR bands observed at 1063, 1155, (1275), and 1430 cm^{-1} coincided well to the spectrum of aerosol particles deposited from pure AC vapor [2] and can be assigned to polyacrolein [13,14]. The weak IR band at 850 cm^{-1} may be assigned to sulfur polymer, S_8 [15,16]. Raman spectrum in Fig. 5(B) showed strong bands at 1470 and 485 cm^{-1}. The corresponding bands were also observed with aerosol particles deposited from pure CS_2 vapor [7]. Spectral features of these bands partly agreed with the Raman bands observed with graphite [17,18] and C_{60} [19], but did not coincide with both of them. As discussed in a previous paper [7], we tentatively assign these bands to a carbon polymer hitherto unknown. As to the structure of sedimentary particles deposited from CS_2 vapor, Colman and Trogler noticed that the IR spectrum of sedimentary particles deposited from pure CS_2 was nearly identical to the spectrum of Bridgman's black carbon disulfide when the CS_2 vapor was irradiated at 313 nm with a Hg–Xe lamp [9]. In the present experiment where a gaseous mixture of AC and CS_2 was irradiated with N_2 laser light (337.1 nm), IR bands due to CS_2 was covered with strong IR bands of polyacrolein, and

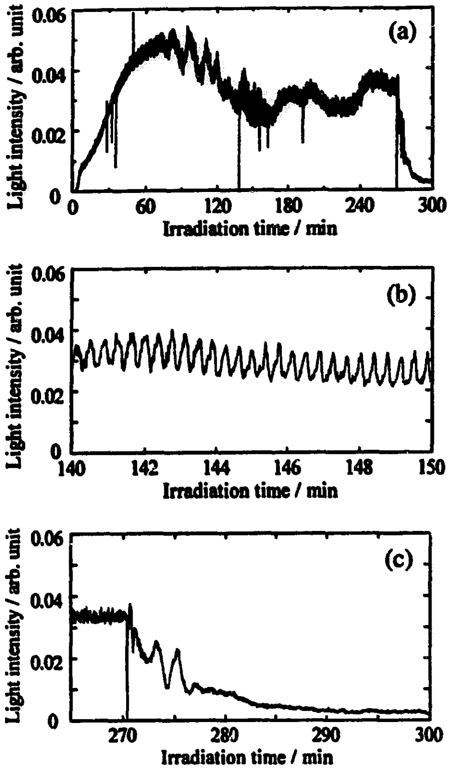

Fig. 6. Light intensity scattered by the aerosol particles produced from a gaseous mixture of AC (50 Torr) and CS_2 (50 Torr) under irradiation with N_2 laser light at an energy of 3.1 mJ per pulse. Scattered light intensity of He–Ne laser light used as a monitor was measured between (A) 0 and 300 min, (B) 140 and 150 min, and (C) 265 and 300 min.

we could not get information on polymerization of CS_2 molecule. S_8 shows a strong Raman band at 474 cm^{-1} [20–22]. Judging from an asymmetrical shape of the 485 cm^{-1} band in Fig. 5(B), we may say that the S_8 band is overlapped with the band of the carbon polymer. From the assignment of the IR and Raman spectra, it is strongly suggested that AC is polymerized into the aerosol particles produced from CS_2.

The nucleation process of a gaseous mixture of AC and CS_2 was studied by measuring the intensity of He–Ne laser light scattered by the aerosol particles being formed under irradiation with N_2 laser (Molectron UV24) light. The result for a gaseous mixture of AC (50 Torr) and CS_2 (50 Torr) under irradiation at an energy of 3.1 mJ per pulse is shown in Fig. 6. Under irradiation for 3 min, scattered light intensity began to increase, and reached to its maximum at ≈90 min (Fig. 6(A)). Between 70 and 120 min, scattered light intensity significantly fluctuated at intervals of 10–15 min, and reached to a minimum at ≈155 min. Between 140 and 180 min, we could observe an oscillatory behavior of the scattered light intensity at intervals of ≈22 s (Fig. 6(B)). Oscillatory behavior of the scattered light intensity was reported for nucleation of CS_2 [3,5,23,24], and was qualitatively interpreted on the basis of propagation of nucleation, sedimentation of large aerosol particles and convection of gaseous molecules. In this experiment, N_2 laser light was shut down at 270 min. Without the exciting laser light, scattered light intensity almost decayed after ≈15 min, accompanied with intensity fluctuation due to continued propagation and sedimentation of the aerosol particles (Fig. 6(C)). Although the light intensity scattered by the aerosol particles depends on the size distribution and the number of the aerosol particles, relative intensity is a measure of the degree of nucleation.

To investigate the efficiency of nucleation of AC and CS_2 in a gaseous mixture, scattered light intensity was measured by varying the partial pressure of AC and CS_2, the total pressure of them being kept to be constant (≈100 Torr). The results under irradiation with N_2 laser light (using Molectron UV24) at an energy of 3.1 mJ per pulse are shown in Fig. 7. Scattered light intensity measured with pure CS_2 vapor (100 Torr) increased most rapidly. With increasing the partial pressure of AC, induction period (during which the nucleation propagates to form aerosol particles) became longer, and the scattered light intensity increased more slowly. This clearly shows that the nucleation of CS_2 is more efficient than that of AC. It is noteworthy that the first peak of the scattered light intensity continued for longer time when AC molecules were added (see curves a and b in Fig. 7). This result indicated that the nucleation reaction of AC was induced through the reaction of CS_2, and the aerosol particles were produced efficiently from both molecules.

The AC molecule has the lowest excited singlet state ($^1n,\pi^*$) at 330 nm [25–27]. CS_2 molecule has an allowed electronic transition to the $^1B_2$ state (V system) and a forbidden transition to the $^1A_2$ state in the 330 nm region [28,29]. N_2 laser light can excite the CS_2 molecule to $v'_2=3$ and 5 levels of the $^1A_2$ state from $v''_2=1$ and 2 levels, respectively. Absorbance at 337.1 nm was measured with CS_2 at a pressure of 30 Torr and with AC at a pressure of 40 Torr by using a cell with a light path length of 10 cm; absorbance is 0.04 for CS_2, and 0.33 for AC. Although AC molecule absorbs N_2 laser light more efficiently than CS_2 molecule, nucleation process is more efficient for CS_2 than for AC as revealed from the shorter induction period and larger scattered light intensity in Fig. 7. Under light irradiation at 313 nm, the quantum

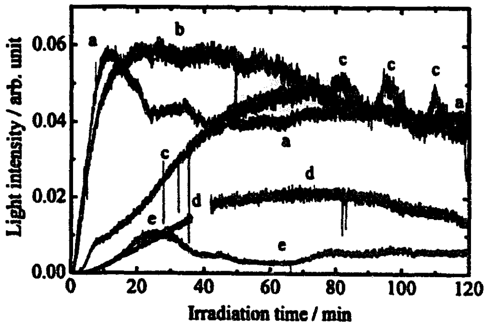

Fig. 7. Light intensity scattered by the aerosol particles produced from pure AC and CS_2 vapors and from a gaseous mixture of AC and CS_2 under irradiation with N_2 laser light at an energy of 3.1 mJ per pulse. The partial pressures of the gaseous sample of AC and CS_2 are (a) 0 and 100 Torr, (b) 20 and 80 Torr, (c) 50 and 50 Torr, (d) 80 and 20 Torr, and (e) 100 and 0 Torr.

efficiency of polymerization of AC vapor through the initiating photodecomposition reaction,

$$CH_2{=}CH{-}CHO \rightarrow C_2H_3 + HCO \qquad (1)$$

was estimated to be very low (6.2×10^{-3}) [30]. This suggests that efficient photodecomposition of AC to initiate polymerization at 337.1 nm needs two-photon energy [31]. In the gaseous mixture of AC and CS_2, initiating radicals produced from CS_2 efficiently initiate polymerization and nucleation reactions. It was proposed that CS_2 molecules excited by N_2 laser light generate C_2S_2 instead of CS radical.

$$CS_2^* + CS_2 \rightarrow S{=}C{=}C{=}S + S_2 \qquad (2)$$

C_2S_2 can propagate into C_nS_2 through successive collisions with other CS_2 molecules eventually to produce linear and cyclic carbon polymers [8]. AC molecule may react with an intermediate carbon polymer C_mS_2 so as to produce a radical species and initiate polymerization of AC. Thus, polymerization of AC and polymerization of CS_2 may independently propagate within an aerosol particle. We can not exclude the possibility that CS_2 and AC molecules copolymerize in an aerosol particle.

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