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Chemical reactivity of two-photon excited trimethylsilylacetylene in aerosol particle formation with acrolein

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Abstract

Under irradiation with N_2 laser light, a gaseous mixture of trimethylsilylacetylene (ethynyltrimethylsilane) (TMeSiA) and acrolein (AC) produced sedimentary aerosol particles with a mean diameter of 1.0 μm. Nucleation process of the aerosol particles was studied by measuring monitor (He–Ne laser) light intensity scattered by the aerosol particles as formed under N_2 laser light irradiation. With increasing partial pressure of TMeSiA, the nucleation reaction of aerosol particles was accelerated due to additional generation of reactive species from TMeSiA molecules by a two-photon process. FT-IR spectra of the sedimentary particles showed that TMeSiA molecules were incorporated into polymerization reaction of AC by forming –Si–O–C– bond from $R(CH_3)_2Si$ radicals. Two-photon processes of both AC and TMeSiA molecules under N_2 laser light irradiation were briefly discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aerosol particle formation; Two-photon excitation; Trimethylsilylacetylene; Acrolein

1. Introduction

Synthesis and functionalization of polymeric fine and ultrafine particles have attracted great interest due to their wide applicability in chemical industry [1–3]. Many kinds of composite particles have been prepared by polymerization reaction in solution and only seldom in vapor phase. As a unique technique to produce polymeric particles, photochemical reaction of acrolein (2-propenal) (AC) vapor was used to synthesize sedimentary aerosol particles through a two-photon process of AC molecules under N_2 laser light irradiation [4]. It was found that AC molecules could initiate chemical reactions with foreign gases and produce composite particles from some gaseous mixtures [5–7]. This technique was extended to synthesize aerosol particles involving some organosilicon compounds such as trimethyl(2-propynyloxy)silane [8], allyltrimethylsilane [9] and vinyltrimethoxysilane (VTMSi) [4,10]. Chemical analysis from FT-IR and XPS spectra of sedimentary particles produced from a gaseous mixture of VTMSi and AC revealed that the chemical structure of the products depended on intensity and wavelength of exciting light and VTMSi was involved in the aerosol particles as polysiloxane through photochemical reaction of silanones which were produced from VTMSi by two-photon decomposition of N_2 laser light [10].

Trimethylsilylacetylene (ethynyltrimethylsilane) (TMeSiA) has the longest wavelength absorption band at shorter than 230 nm. Pure gaseous TMeSiA produced polymeric thin film by a one-photon process of ArF laser light (193 nm) [11,12], and by a two-photon process of N_2 laser light (337.1 nm) [13]. Chemical structures of the deposited film were different depending on excitation wavelengths, showing different chemical processes taking place. TMeSiA was also shown to chemically interact with methyl acrylate (MA) to form both aerosol particles and composite film under light irradiation [13].

In this paper, in order to prepare novel aerosol particles and to investigate the chemical reactivity of TMeSiA, we have undertaken to produce aerosol particles from a gaseous mixture of TMeSiA and AC under N_2 laser light irradiation. Nucleation processes of aerosol particles have been studied by measuring FT-IR spectra of the gaseous samples and by measuring monitor (He–Ne laser) light intensity scattered by the aerosol particles as formed under light irradiation with N_2 laser and with a medium pressure mercury lamp. From the analysis of chemical structure of the sedimentary aerosol particles, chemical processes in aerosol particle formation have been briefly discussed.

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2. Experimental

AC (Merck, 95%, stabilized with 0.2% hydroquinone) and TMeSiA (Tokyo Kasei, 98%, G.R. grade) were stored in a refrigerator below 10 °C to prevent polymerization. TMeSiA and AC were purified by vacuum distillation and degassed by freeze–pump–thaw cycles. TMeSiA and AC vapors were introduced into a cross-shaped irradiation cell with four optical quartz windows (inner diameter and length of long arm, 35 mm and 155 mm inner diameter and length of short arm, 20 mm and 80 mm) through a vacuum line at a background pressure of below 8×10^{-5} Torr (1 Torr = 133.3 Pa). Partial pressures of gaseous samples were measured with a capacitance manometer (Edwards Barocel Type 600), and the leakage into the evacuated cell from the atmosphere was carefully controlled to result in pressure increase lower than 1 Torr in a day. A gaseous sample in the cell was irradiated with collimated light of a medium pressure mercury lamp (Ushio UM-452, 450 W) through UVD33S and UV-29 filters or with nitrogen gas laser light (Lumonics HE-440, 337.1 nm, 1.8 mJ per pulse) with a repetition rate of 12 Hz. Laser power was measured with a pyroelectric joulemeter (Gentec ED-500) combined with a synchroscope (Iwatsu SS-5121). FT-IR spectra of the gaseous samples and the deposited products were measured with a Nicolet NEXAS 670 FT-IR spectrometer. He–Ne laser light intensity scattered by the aerosol particles as formed in the irradiation 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. Scanning electron microscope (SEM) images of the sedimentary aerosol particles were taken with a Topcon ABT-32.

3. Results and discussion

Under irradiation with N_2 laser light at an energy of 0.3 mJ cm^{-2} per pulse for 3 h, a gaseous mixture of TMeSiA (37 Torr) and AC (41 Torr) produced sedimentary aerosol particles (yield: less than 0.05 mg) which were deposited on a glass plate placed at the bottom of the irradiation cell with a reproducible sedimentation pattern due to the convection of the gaseous mixture. The sedimentary particles were spherical with a mean diameter of 1.0 μm as shown in Fig. 1.

Nucleation process of the aerosol particles produced from gaseous mixtures of TMeSiA and AC (41 Torr) with different partial pressures of TMeSiA was studied by measuring monitor (He–Ne laser) light intensity scattered by the aerosol particles as formed in the irradiation cell; the results are shown in Fig. 2. During induction period to detect scattered light, nucleation reaction followed by particle growth proceeded. Hence, the induction period is a measure of relative rate of nucleation and propagation reactions in aerosol particle formation. Scattered light intensity after reaching its maximum value is proportional to the number of aerosol particles with various particle size in cases where the particle size distribution is not dependent on irradiation time of exciting light as in the present experimental conditions [9]. Under N_2 laser light irradiation at an energy of 0.3 mJ cm^{-2} per pulse (Fig. 2A), the induction period became shorter (from 14 min at 0 Torr to 4 min at 22 Torr of TMeSiA) and the scattered light intensity became larger with increasing partial pressure of TMeSiA, indicating that TMeSiA contributed to the nucleation process of the aerosol particles and to the propagation reaction in particle growth.

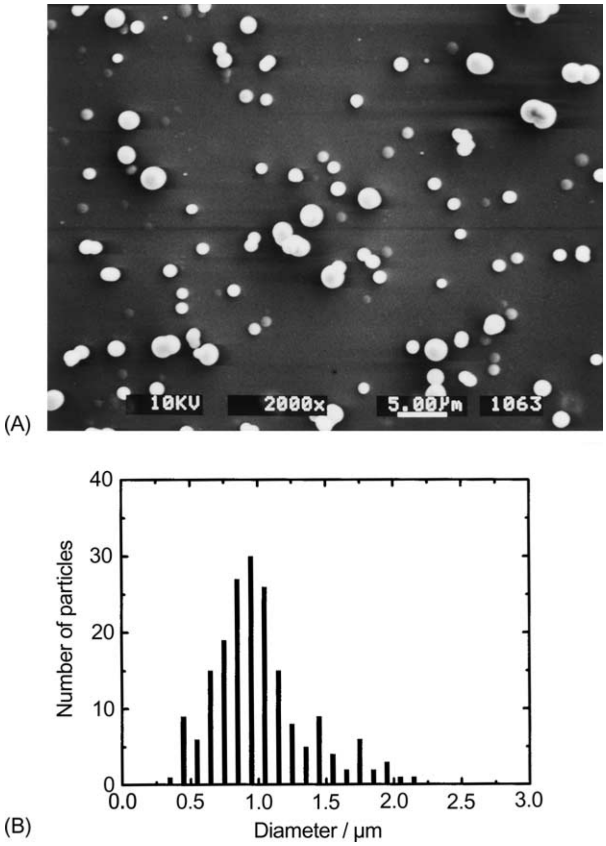

Fig. 1. (A) SEM image of sedimentary aerosol particles deposited from a gaseous mixture of TMeSiA (37 Torr) and AC (41 Torr) under irradiation with N_2 laser light for 3 h, and (B) particle size distribution therefrom. Original magnification of SEM, 2000×.

Under light irradiation with a medium pressure mercury lamp through a UV-29 and a UVD33S filters (Fig. 2B), the induction period did not depend on the partial pressure of TMeSiA, although the scattered light intensity became stronger with increasing partial pressure of TMeSiA. These results indicated that nucleation reaction of aerosol particle formation was initiated by photochemical reaction of only AC molecules by a one-photon process [9,14], and TMeSiA molecules were incorporated into propagation reaction in particle growth.

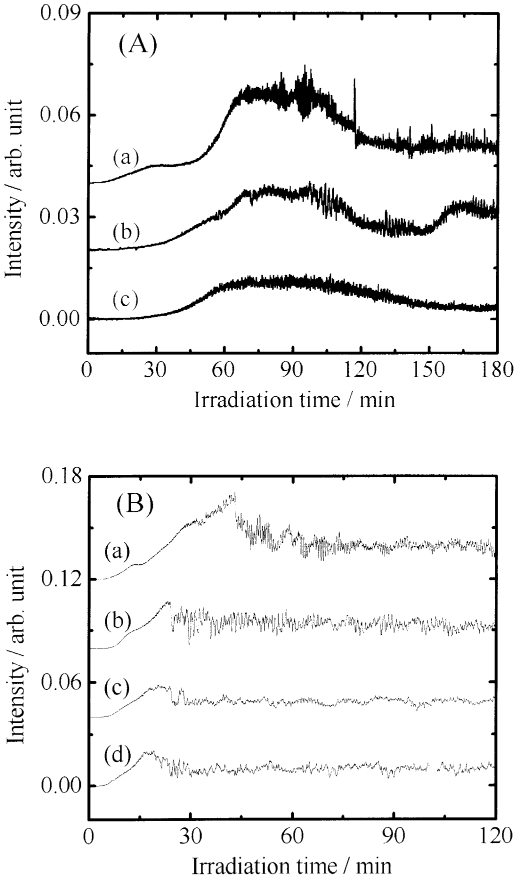

Fig. 2. He–Ne laser light intensity scattered by the aerosol particles produced from a gaseous mixture of TMeSiA and AC (41 Torr) (A) under irradiation with N_2 laser light at an energy of 0.3 mJ cm^{-2} per pulse, and (B) under light irradiation with a mercury lamp at an energy of 6.1 mJ cm^{-2} s^{-1}. The partial pressure of TMeSiA in (A) was (a) 22 Torr, (b) 12 Torr and (c) 0 Torr, and the one in (B) was (a) 37 Torr, (b) 12 Torr, (c) 8 Torr and (d) 0 Torr. The ordinates are shifted consecutively by 0.02 from (c) to (b) and (a) in (A) and by 0.04 from (d) to (c), (b) and (a) in (B).

As reported previously [13], TMeSiA molecule which has no absorption longer than 230 nm could produce thin film on an optical quartz window by a two-photon process of N_2 laser light. Photodecomposition of pure TMeSiA vapor (41 Torr) was investigated under irradiation with N_2 laser light at an energy of 0.3 mJ cm^{-2} per pulse by measuring FT-IR spectrum. Although the depletion of TMeSiA vapor was little and FT-IR band of volatile products was not detected under the present experimental conditions, photodecomposition rate of TMeSiA vapor was evaluated based on the following chemical processes:

$$\mathrm{TMeSiA} + 2h\nu\ (\lambda = 337.1\,\mathrm{nm}) \xrightarrow{I_a} \mathrm{TMeSiA}^* \tag{1}$$

$$\mathrm{TMeSiA}^* \xrightarrow{k_1} {}^\bullet\mathrm{Si(CH_3)_3} + {}^\bullet\mathrm{C} \equiv \mathrm{CH} \tag{2}$$

$$\mathrm{TMeSiA}^* \xrightarrow{k_2} {}^\bullet\mathrm{Si(CH_3)_2C} \equiv \mathrm{CH} + {}^\bullet\mathrm{CH_3} \tag{3}$$

$$\mathrm{TMeSiA}^* \xrightarrow{k_3} \mathrm{TMeSiA} \tag{4}$$

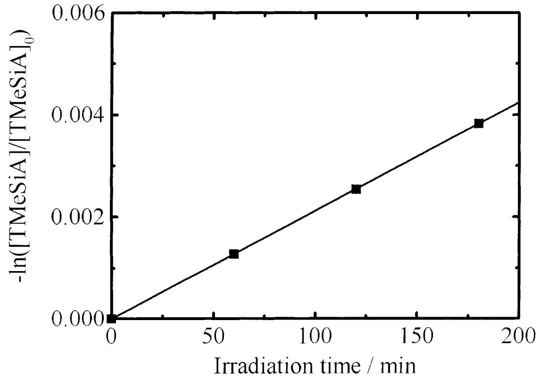

Fig. 3. Irradiation time dependence of $-\ln([\mathrm{TMeSiA}]/[\mathrm{TMeSiA}]_0)$ for pure TMeSiA (41 Torr) under N_2 laser light at an energy of 0.3 mJ cm^{-2} per pulse.

From the intensity change of 2046 cm^{-1} band ascribed to C≡C stretching vibration [15], photodecomposition rate of TMeSiA molecules, k_{TMeSiA}, was evaluated according to the following equation.

$$-\frac{\mathrm{d[TMeSiA]}}{\mathrm{d}t} = k_{\mathrm{TMeSiA}}[\mathrm{TMeSiA}] \tag{5}$$

where $k_{\mathrm{TMeSiA}} = I_a(k_1 + k_2)/k_1 + k_2 + k_3$

$$-\ln\left(\frac{[\mathrm{TMeSiA}]}{[\mathrm{TMeSiA}]_0}\right) = k_{\mathrm{TMeSiA}}t \tag{6}$$

where $[\mathrm{TMeSiA}]_0$ was the initial pressure of TMeSiA vapor. The value of the left-hand side in Eq. (6), $-\ln([\mathrm{TMeSiA}]/[\mathrm{TMeSiA}]_0)$, was calculated from the FT-IR band intensity and plotted against irradiation time, t, in Fig. 3. A linear relationship holds, and the first-order rate constant, k_{TMeSiA}, was evaluated to be 2.3×10^{-5} min^{-1} from the slope of the straight line.

Photodecomposition rate of AC in a gaseous mixture of TMeSiA and AC was also evaluated from the intensity change of FT-IR bands. FT-IR spectrum of the gaseous mixture before light irradiation coincided with the superposition of the spectra of pure TMeSiA and pure AC, indicating that chemical reaction between TMeSiA and AC did not proceed in the dark. Under irradiation with N_2 laser light, all the bands decreased their intensities due to the consumption of both molecules, and weak bands ascribed to carbon monoxide appeared in 2150 cm^{-1} region, showing that dissociation into C_2H_4 and CO was a major process of AC molecules. Furthermore, AC molecules could dissociate through homolytic cleavage into C_2H_3 and CHO radicals as a minor process, and these radicals could initiate polymerization reaction leading to aerosol particle formation. Under N_2 laser light irradiation for 3 h, product yield of sedimentary aerosol particles was less than 0.5%, whereas the consumption of AC molecules was 6%, showing that the depletion of FT-IR bands of AC molecules was mainly due to the dissociation of AC into C_2H_4 and CO. The depletion rate of

AC molecules, k_{AC}, was evaluated based on the following equation [10].

$$-\ln\left(\frac{[AC]}{[AC]_0}\right) - \int_0^t \left(\frac{1}{[AC]}\, d_{AC}(t)\right) \mathrm{d}t = k_{AC}t \qquad (7)$$

where $d_{AC}(t)$ is the depletion rate by adsorption of AC vapor determined experimentally. The depletion rate constant of AC, k_{AC}, of a gaseous mixture of TMeSiA (37 Torr) and AC (41 Torr) was determined to be $3.0 \times 10^{-4}\ \mathrm{min}^{-1}$. Compared to the k_{AC} value of pure AC vapor (41 Torr), i.e., $2.9 \times 10^{-4}\ \mathrm{min}^{-1}$, k_{AC} value was not significantly influenced in the presence of TMeSiA vapor. Radicals ($R_1^{\bullet}$) produced from TMeSiA by a two-photon process (Eqs. (2) and (3)) induce chemical reactions with AC to initiate nucleation and propagation reactions of aerosol particles.

$$R_1^{\bullet} + AC \rightarrow \text{polymerization} \qquad (8)$$

Considering that consumption of AC molecules is largely due to the dissociation into C_2H_4 and CO and that depletion rate of TMeSiA is one order of magnitude smaller than that of AC, the contribution of Eq. (8) to the depletion rate of AC molecules is reasonably understood to be small in spite of its significant contribution to the nucleation and propagation reactions in aerosol particle formation. This result is compared to the case of a gaseous mixture of VTMSi and AC [10], where the depletion rate of VTMSi by a two-photon process was comparable to the rate of AC, and hence, depletion rate of AC was significantly increased by the addition of VTMSi molecules. Under light irradiation with a mercury lamp where TMeSiA did not produce any radicals ($R_1^{\bullet}$), k_{AC} value for the gaseous mixture of TMeSiA and AC was practically the same to the value for pure AC (Table 1).

In order to investigate chemical compositions of aerosol particles, XPS spectrum of sedimentary particles were measured with C 1s and Si 2s core levels. Preliminary results on stoichiometry of atoms in the sedimentary particles deposited from a gaseous mixture of TMeSiA (37 Torr) and AC (41 Torr) was $Si_{1.0}C_{25.0}O_{7.3}$ under light irradiation with a mercury lamp, and was $Si_{1.0}C_{11.9}O_{5.9}$ under N_2 laser light irradiation. These values suggested that the molar ratio of TMeSiA to AC was 1:6.7 under light irradiation with a mercury lamp and 1:2.3 under irradiation with N_2 laser light, indicating that two-photon excitation of TMeSiA molecules was effective to incorporate TMeSiA into the aerosol particle formation reaction.

Table 1
Depletion rate constant of AC vapor, k_{AC}, under light irradiation with N_2 laser and with a medium pressure mercury lamp

Sample	Light source	k_{AC} (min^{-1})
AC (41 Torr)	Hg lamp	3.1×10^{-4}
AC (41 Torr) + TMeSiA (37 Torr)	Hg lamp	3.2×10^{-4}
AC (41 Torr)	N_2 laser	2.9×10^{-4}
AC (41 Torr) + TMeSiA (37 Torr)	N_2 laser	3.0×10^{-4}

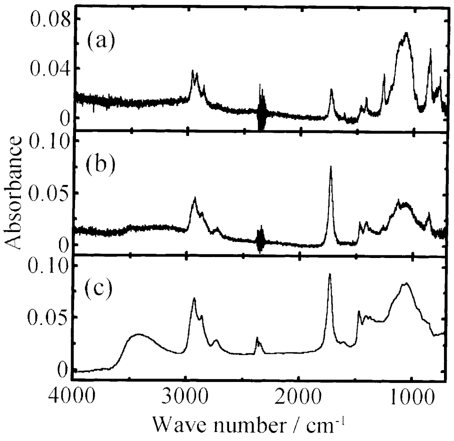

Fig. 4. FT-IR spectra of sedimentary particles produced from a gaseous mixture of TMeSiA (37 Torr) and AC (41 Torr) under light irradiation: (a) with N_2 laser at an energy of $0.3\ \mathrm{mJ\,cm^{-2}}$ per pulse for 3 h, (b) with a medium pressure mercury lamp at an energy of $6.1\ \mathrm{mJ\,cm^{-2}\,s^{-1}}$ for 4 h, and (c) FT-IR spectrum of sedimentary particles deposited from pure AC vapor (41 Torr) under irradiation with a medium pressure mercury lamp for 4 h.

Chemical structure of the sedimentary aerosol particles was studied by measuring FT-IR spectrum. Sedimentary particles produced from a gaseous mixture of TMeSiA (37 Torr) and AC (41 Torr) under irradiation with N_2 laser light at an energy of $0.3\ \mathrm{mJ\,cm^{-2}}$ per pulse for 3 h showed prominent bands at 1251, 851 and $757\ \mathrm{cm}^{-1}$ (Fig. 4a) in addition to the bands ascribed to polyacrolein (Fig. 4c). IR bands at 1251 and $851\ \mathrm{cm}^{-1}$ were assigned to CH deformation and methyl rocking vibrations of trimethylsilyl group, respectively [12,16,17]. Furthermore, the broad intense band observed in $1000–1200\ \mathrm{cm}^{-1}$ region and the $757\ \mathrm{cm}^{-1}$ band could be assigned to Si–O stretching and C–O stretching in $–Si–O–CH_2–$ group, respectively and the new band at $2956\ \mathrm{cm}^{-1}$ was ascribed to CH asymmetric stretching vibration in $SiO–CH_2–$ and $–Si–CH_3$ groups [16–18]. Observation of these bands clearly suggested that the reactive species, ${}^{\bullet}SiR(CH_3)_2$ (R: $–CH_3$, $–C{\equiv}CH$), which were produced through photodissociation of TMeSiA initiated chemical reactions with AC leading to the formation of aerosol particles.

$$\begin{aligned} {}^{\bullet}SiR(CH_3)_2 + AC &\rightarrow R(CH_3)_2Si–CH_2–\dot{C}HCHO \\ &\rightarrow \text{polymer with C=O group} \qquad (9) \end{aligned}$$

$$\begin{aligned} {}^{\bullet}SiR(CH_3)_2 + AC &\rightarrow CH_2{=}CH\dot{C}H–O–Si(CH_3)_2R \\ &\rightarrow \text{polymer with C–O–Si bond} \qquad (10) \end{aligned}$$

Under the present experimental conditions where thin film formation from pure TMeSiA vapor was not observed, disproportionation reaction between two silyl radicals which lead to the production of silylenes, $R(CH_3)Si{=}CH_2$, eventually followed by polymerization reaction to form $–Si–CH_2–Si–$ structure was not efficient [19,20]. The silyl radicals easily reacted with AC molecules to produce polymers with C=O group and C–O–Si bond. Due to the efficient contribution of Eqs. (9) and (10), the aerosol particle formation process was accelerated by the addition of TMeSiA under light irradiation with N_2 laser.

Sedimentary aerosol particles deposited under light irradiation with a mercury lamp showed moderate bands at 1251 and 846 cm^{-1} assignable to CH deformation and methyl rocking vibrations of trimethylsilyl group (Fig. 4b). C≡C stretching vibrational band of TMeSiA disappeared, and bands attributable to –CH=CR– structural unit could not be observed in the IR spectrum of sedimentary particles, indicating that photoexcited AC molecules induced chemical reaction of TMeSiA, and TMeSiA molecules were polymerized at C≡C bond with AC to form eventually $-\overset{|}{C}H-\overset{|}{C}(-Si(CH_3)_3)-$ components in the particles.

In conclusion, a gaseous mixture of TMeSiA and AC produced sedimentary aerosol particles under light irradiation with N_2 laser and with a medium pressure mercury lamp. Chemical composition of sedimentary aerosol particles depended on excitation conditions of gaseous mixtures. Under light irradiation with N_2 laser, two-photon excitations of both AC and TMeSiA molecules were effective and both the excited AC and TMeSiA molecules produced reactive species which could initiate chemical reactions to produce aerosol particles. Two-photon excitation of TMeSiA molecules resulted in the acceleration of particle formation and in high content of organosilicon components in the aerosol particles.

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