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Laser-induced polymeric film formation from gaseous methyl acrylate

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Abstract

Upon exposure to N_2 laser light, gaseous methyl acrylate at a pressure of 10–65 Torr produced a solid polymeric material as a thin film on the surface of an optical quartz window. The product yield measured by weighing was proportional to the irradiation time of laser light, and was roughly proportional to the second power of the laser intensity. From the fact that the IR spectrum of the deposited film has bands characteristic of poly(methyl acrylate), it is suggested that two-photon excitation of methyl acrylate under N_2 laser light irradiation initiates polymerization of gaseous methyl acrylate. The mechanism resulting in the formation of the polymer film from gaseous methyl acrylate is briefly discussed.

Keywords: Polymeric films; Methyl acrylate

1. Introduction

By multiphoton excitation and ionization of gaseous organic molecules under the irradiation of UV laser light, chemically reactive species can be easily produced in the vapor phase. Through intermolecular reactions of these species in the vapor phase and in the adsorbed layer on the substrate and/or on the wall of an irradiation vessel, aerosol particles and solid materials can be deposited directly from gaseous molecules. From gaseous acrolein [1] and methyl methacrylate (2-methylpropenoic acid methyl ester) (MMA) [2], polymerization reaction was induced under light irradiation. Polymerization of acrolein resulted in the formation of a white powder on the wall of an irradiation vessel [1], while polymerization of MMA resulted in the formation of an aerosol [2]. Photopolymerization of monomer vapor in contact with a metal surface was initially reported with butadiene, resulting in the selective poly-1,3-butadiene deposition on lead and tin films [3]. Surface photopolymerization of several vinyl monomers such as acrylonitrile, MMA, and acrolein on evaporated aluminum and nickel films was studied in detail upon the exposure to a medium pressure mercury lamp [4,5]. UV laser photopolymerization of surface-adsorbed MMA was used to deposit poly(methyl methacrylate) for direct patterning in the negative resist process by using a frequency-doubled Ar-ion laser [6]. As to aerosol formation from gaseous molecules, CS_2 was recently studied upon the exposure to N_2 laser light [7–10], and it was found that the sedimental particle was neither carbon monosulfide polymer nor carbon disulfide polymer, but an amorphous mixture of sulfur polymer and carbon polymer hitherto unknown [11]. In an attempt to synthesize new solid materials by multiphoton excitation of gaseous organic molecules, we have irradiated pulsed laser light of 337.1 nm upon methyl acrylate (2-propenoic acid methyl ester) (MA), ethyl acrylate (2-propenoic acid ethyl ester) (EA), and MMA vapors, and have recently succeeded to synthesize a polymeric substance as a thin film on a quartz optical window of an irradiation vessel. In this paper, we report the formation process and some physical and chemical properties of the film synthesized from gaseous methyl acrylate under the irradiation of pulsed N_2 laser light.

2. Experimental details

MA (Wako Pure Chemical Industries, 98%, stabilized with hydroquinone monomethyl ether of 0.03%), EA (Wako, 97%, stabilized with hydroquinone monomethyl ether of 0.01%) and MMA (Wako, 98%, stabilized with hydroquinone of 0.005%) were stored in a refrigerator

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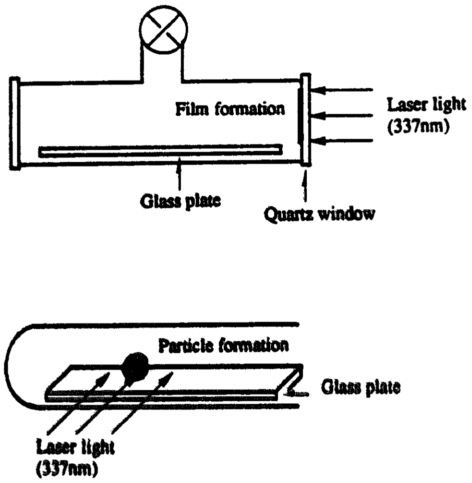

Fig. 1. Schematic diagram illustrating the experimental set-up of an irradiation cell with quartz windows on both ends (the top) and of a pyrex tube (the bottom).

under 10 °C to prevent polymerization. The acrylate monomer liquids were distilled under vacuum and degassed by freeze–pump–thaw cycles immediately before use. Vapor of each acrylate at a pressure of 10–70 Torr (1 Torr = 133.3 Pa) was introduced through a vacuum line into a cylindrical cell (inner diameter: 36 mm, cell length: 200 mm) with quartz optical windows on both ends. The background pressure of the vacuum system was 5×10^{-5} Torr, and the leakage of the cell from atmosphere was carefully controlled to be less than 1 Torr in a day. Nitrogen gas laser light (Lumonics HE-440, 337.1 nm) was irradiated on the gas samples through the quartz window with a repetition rate of 10 Hz for 0.5–10 h (Fig. 1). Laser power was measured with a pyroelectric joulemeter (Gentec ED-500) combined with a synchroscope (Iwatsu SS-5121B). Solid material deposited on the quartz window as a film. The yield of the deposited material was measured by weighing. Thick films obtained under prolonged irradiation could be stripped off from the quartz window surface, and were used to measure IR and FT-IR spectra by a Hitachi 260-10 IR spectrophotometer and a Nicolet 740 FT-IR spectrometer. Thermal stability of the film was checked by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Rigaku Denki CN-8085EI).

3. Results and discussion

3.1. Film formation process from gaseous MA

Upon the exposure to N_2 laser light, gaseous MA, EA and MMA deposited solid materials on the surface of a quartz window. In preliminary experiments, MA at a pressure of 20 Torr produced a solid material of ca. 20 mg, whereas EA and MMA at a pressure of 30 Torr produced solid materials only of 1 mg under the laser light irradiation for 8 h. Because the product yield from MA vapor was much higher than the yield from EA and MMA under the irradiation of 337.1 nm light as was the case when irradiated with a medium pressure mercury lamp [5], further experiments were done mainly for MA vapor. Under the irradiation of N_2 laser light, MA vapor produced a thin solid film on the entire surface of a quartz window followed by the thick film formation in the area directly exposed to the incident laser light as is schematically shown in Fig. 1. When irradiation time of laser light was fixed to 8 h, the yield of the deposited material from MA vapor increased with increasing sample pressure of MA, and also depended on the laser intensity. The laser intensity dependence (1.5–3.0 mJ pulse^{-1}) of the yield was measured for MA vapor at a pressure of 40 Torr under the irradiation for 8 h. The result is shown in Fig. 2. The yield is roughly proportional to the second power of the laser intensity. UV absorption spectrum [12] and electron-energy-loss spectrum [13] of MA vapor show that the lowest excited singlet state, $S_1(^1n\text{-}\pi^*)$ and the second excited singlet state, $S_2(^1\pi\text{-}\pi^*)$ appear at 5.08 eV (244 nm) and 6.6 eV (188 nm), respectively, and the optically forbidden lowest triplet state, T_1 ($^3\pi\text{-}\pi^*$) lies at 3.85 eV (322 nm). Moreover, a semiempirical calculation of acrylic acid suggests that $^1\sigma\text{-}\pi^*$ state lies at $\approx$6.9 eV [14]. To measure the absorbance at 337.1 nm, UV absorption spectrum of MA vapor at a pressure of 40 Torr was measured by using a cell with a light path length of 10 cm; the absorbance at 240 nm was 1.35, but the absorbance in the wavelength region longer than 290 nm was negligibly small. Considering the fact that the ionization potential of MA is 10.5 eV [15] and exceeds two photon energy of 337.1 nm laser light (7.4 eV), the result in Fig. 2 indicates that MA molecules are excited to $^1\pi\text{-}\pi^*$ and/or $^1\sigma\text{-}\pi^*$ state(s) by two photon absorption as a major excitation process, and to the highly excited triplet state (plausibly $^3\pi\text{-}\pi^*$ state) by two step excitation (T_n–T_1 absorption following T_1–S_0

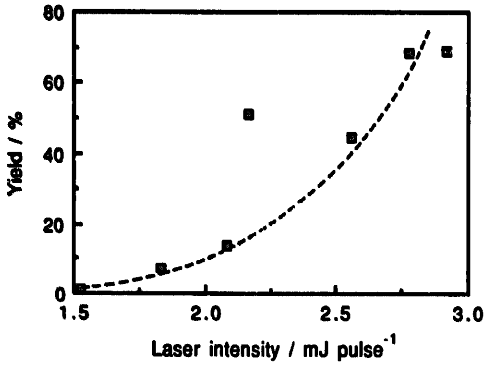

Fig. 2. Laser intensity dependence of the yield of polymer film deposited from MA vapor at a pressure of 40 Torr upon the exposure to N_2 laser light for 8 h.

absorption) as a minor process. The excited molecules initiate chemical reaction resulting in film deposition from gaseous molecules.

Dependence of the yield on laser irradiation time was measured for MA vapor at a pressure of 40 Torr upon the exposure to N_2 laser light at an energy of 2.2 mJ pulse^{-1}. The results are shown in Fig. 3. After irradiation for 30 min, we could observe the formation of deposited film on the window. After an induction period of ca. 1 h, the yield increased linearly with irradiation time up to 8 h. Considering the fact that the laser light was effectively scattered on the quartz window by the deposited polymeric material, this result suggests that the laser light excites the polymer film, and propagation in film formation proceeds via surface photochemistry of the polymer film.

Film formation process from MA vapor at a pressure of 40 Torr was monitored by SEM images (Fig. 4). Upon the exposure to laser light at an energy of 1.9 mJ pulse^{-1} for 20 min (Fig. 4(a)), a thin film with a rather uniform and smooth surface has already deposited on which small particles (1–2 μm in diameter) started to grow. Upon the exposure for 90 min (Fig. 4(b)), a thick film was formed, and the film surface was entirely covered by polymer particles (5–10 μm in diameter) which accumulated randomly and were bound in each other. The SEM images indicate that polymerization in propagating process occurs at many photogenerated active sites on the film surface. Polymer film with granular surface effectively scatters the incident laser light, and polymerization reaction at the surface of the deposited film rather than in gaseous phase dominates the propagation process.

3.2. Characterization of the film deposited from gaseous MA

To characterize properties of the deposited material, elemental analysis was carried out, and IR and FT-IR spectra were measured. From the elemental analysis of the film (Found: C, 55.9; H, 6.9%), number ratio of C, H, and O atoms was 4.0:5.9:2.0, if all the residual weight (37.2%) was assigned to O atom. This result is very close to the chemical composition of MA monomer and poly(methyl acrylate) $(C_4H_6O_2)_n$. The IR spectrum was measured with the film deposited from MA vapor at a pressure of 65 Torr (Fig. 5). The IR spectrum in the 1100–1800 cm^{-1} region coincides with the spectrum of MA polymer, but not with the one of MA monomer [16]. This result together with the one of elemental analysis clearly shows that the chemical component of the film is MA monomer unit, and upon the exposure to laser light of 337.1 nm, MA molecules are polymerized without decomposing into such fragments as C_3H_3O

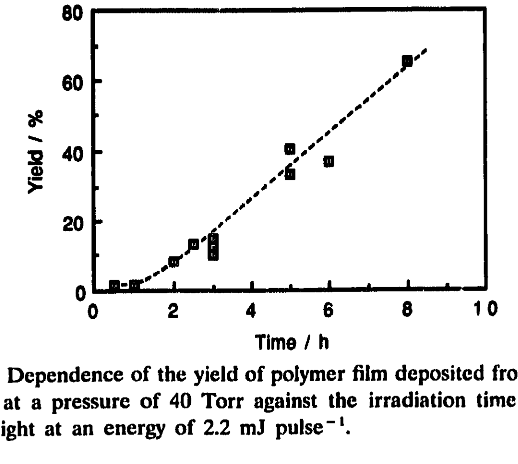

Fig. 3. Dependence of the yield of polymer film deposited from MA vapor at a pressure of 40 Torr against the irradiation time of N_2 laser light at an energy of 2.2 mJ pulse^{-1}.

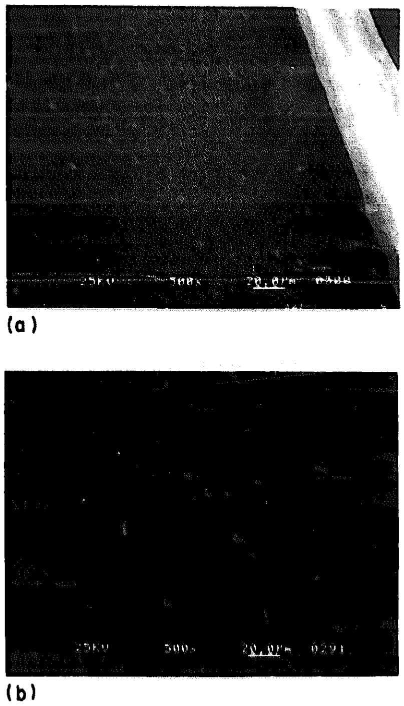

Fig. 4. Scanning electron micrographs of the polymer film deposited on a quartz window upon the exposure to N_2 laser light at an energy of 1.9 mJ pulse^{-1} for (a) 20 min and (b) 90 min.

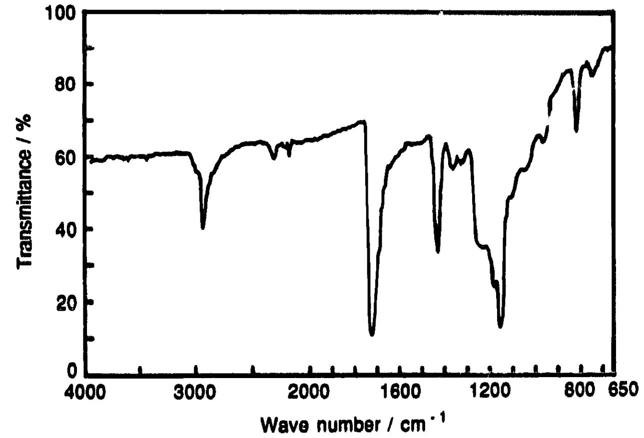

Fig. 5. IR spectrum measured with the polymer film deposited from MA vapor at a pressure of 65 Torr on a quartz window.

observed in multiphoton ionization by an ArF excimer laser light [17] and as CH and C_2 observed in electron-beam irradiation [18].

Thermal stability of the film was measured by using thermogravimetric analysis (TGA). The film deposited from MA vapor was stable up to 330 °C, and thermal stability was a little (~10 °C) better than poly(methyl methacrylate) (PMMA) commercially available (molecular weight: 12 000).

Solubility in organic solvents of the film deposited from MA vapor was measured qualitatively. The film was insoluble in methylethylketone, acetone, chloroform, and dioxane to which poly(methyl acrylate) commercially available and PMMA dissolve. In tetrahydrofuran and *p*-xylene, the film swelled slightly, and dissolved component was detected by a gel permeation chromatography (GPC). Molecular weight of the component dissolved into *p*-xylene was 2.7×10^6. Hence, the molecular weight of the main component of the film which was insoluble in *p*-xylene is much larger than 2.7×10^6, suggesting that polymer chains crosslink together.

3.3. *Mechanism of polymerization by two photon absorption*

MMA and acrolein vapors increased the rate in polymer growth on metal surfaces such as lead, tin, and nickel under the irradiation of UV laser light [5]. MMA adsorbed on the surfaces of SiO_2 and of PMMA also increased the rate of polymerization [6]. Under the irradiation of N_2 laser light, MA is excited to the highly excited $^1\pi$-π^* and/or $^1\sigma$-π^* state(s) by two photon absorption, and dissociates into fragments [17,19].

$$CH_2{=}CH{-}COOCH_3 \longrightarrow \cdot C_2H_3 + \cdot COOCH_3 \longrightarrow \cdot C_2H_3 + CO_2 + \cdot CH_3 \quad (1)$$

Both CH_3 and C_2H_3 radicals (hereafter, denoted by I) can initiate radical polymerization of MA (abbreviated by $CH_2{=}CHR$) in the vapor phase.

$$I + CH_2{=}CHR \longrightarrow I{-}CH_2{-}\cdot CHR \quad (2)$$

$$I{-}CH_2{-}\cdot CHR + n(CH_2{=}CHR) \longrightarrow I{-}(CH_2{-}CHR)_n{-}CH_2{-}\cdot CHR \quad (3)$$

Diffusion of photogenerated initiating radicals to the surface of the quartz window is followed by more rapid polymer growth than in the vapor phase. Once the polymer is formed on the quartz window, the formation of adsorbed layer of MA on the polymer surface further increases the rate in polymer growth.

Radical polymerization on the quartz window terminates by the recombination of the propagating polymer radical with either another polymer radical or initiating radical (I').

$$I{-}(CH_2{-}CHR)_n{-}CH_2{-}\cdot CHR + I' \longrightarrow I{-}(CH_2{-}CHR)_{n+1}{-}I' \quad (4)$$

$$I{-}(CH_2{-}CHR)_n{-}CH_2{-}\cdot CHR + \cdot CHR{-}CH_2{-}(CHR{-}CH_2)_m{-}I' \longrightarrow I{-}(CH_2{-}CHR)_{n+1}{-}(CHR{-}CH_2)_{m+1}{-}I' \quad (5)$$

By multiphoton absorption of UV laser light, poly(methyl acrylate) dissociates the pendent group, R (i.e., $COOCH_3$ group) as was suggested from the photolysis of PMMA [20].

$$I{-}(CH_2{-}CHR)_{n+m+1}{-}I' \longrightarrow I{-}(CH_2{-}CHR)_n{-}CH_2{-}\cdot CH{-}(CH_2{-}CHR)_m{-}I' + \cdot R \quad (6)$$

This polymer radical (P_0) can again initiate radical polymerization with MA monomer to result in the formation of a long side polymer chain as in the case of graft copolymerization. Propagation of long side polymer chains occurs at many photogenerated active sites in the area of the polymer film directly exposed to the laser light, and forms granules on the polymer surface as was observed in the SEM images (Fig. 4). Furthermore, recombination between the two polymer radicals, P_0s (i.e., P_0–P_0) results in crosslinking between the polymer chains to make the polymer film insoluble into organic solvents.

It is noteworthy that irradiation of 337.1 nm laser light upon gaseous MA in a pyrex tube produced a large particle (size of which is ca. 8 mm) composed of small polymer particles of ca. 1 mm. The morphology of solid material produced in a pyrex glass tube is different from the one produced in a quartz cell mentioned above. The different morphology in a pyrex tube may be ascribed to the fact that only negligibly small numbers of the initiating radicals were formed in a pyrex tube because the laser light was effectively attenuated and scattered by the pyrex tube. Under these experimental conditions, one of the initiating radicals happens to be formed by two photon absorption (Eq. (1)), radical polymerization (Eqs. (2) and (3)) propagates almost infinitely owing to the negligibly small efficiency of termination processes (Eqs. (4) and (5)). Basically, single polymer chain with infinite molecular weight was formed in a pyrex tube, resulting in the formation of a large particle. This is in accord with the observation that the polymer growth continued for several hours after the laser light irradiation was terminated.

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References

[1] F.E. Blacet, G.H. Fielding and J.G. Root, *J. Am. Chem. Soc., 59* (1937) 2375.

[2] H.W. Melville, *Proc. Roy. Soc., A163* (1937) 511.

[3] P. White, *Proc. Chem. Soc.*, (1961) 337.

[4] A.N. Wright, *Nature, 215* (1967) 953.

[5] F.D. Lewis, M.J. Nepras and H.L. Hampsch, *Tetrahedron, 43* (1987) 1635.

[6] J.Y. Tsao and D.J. Ehrlich, *Appl. Phys. Lett., 42* (1983) 997.

[7] K. Ernst and J.J. Hoffman, *Chem. Phys. Lett., 68* (1979) 40; K. Ernst and J.J. Hoffman, *Chem. Phys. Lett., 75* (1980) 388.

[8] F.C. Wen, T. McLaughlin and J.L. Katz, *Phys. Rev., A26* (1982) 2235.

[9] Y.P. Vlahoyannis, E. Patsilinakou, C. Fotakis and J.A.D. Stockdale, *Radiat. Phys. Chem., 36* (1990) 523.

[10] A. Matsuzaki, H. Morita and Y. Hamada, *Chem. Phys. Lett., 190* (1992) 331.

[11] A. Matsuzaki, Y. Hamada, H. Morita and T. Matsuzaki, *Chem. Phys. Lett., 190* (1992) 337.

[12] J. Brunn, F. Peters and M. Dethloff, *J. Prakt. Chem., 318* (1976) 745.

[13] O. Schafer, M. Allan, E. Haselbach and R.S. Davidson, *Photochem. Photobiol., 50* (1989) 717.

[14] H. Morita, K. Fuke and S. Nagakura, *Bull. Chem. Soc. Jpn., 49* (1976) 922.

[15] M.A.M. Meester, H. van Dam, D.J. Stufkens and A. Oskam, *Inorg. Chim. Acta, 20* (1976) 155; H. van Dam and A. Oskam, *J. Electron Spectrosc. Relat. Phenom., 13* (1978) 273.

[16] L.H. Briggs and L.D. Colebrook, *Anal. Chem.*, 29 (1957) 904.

[17] H. Morita, J.E. Freitas and M.A. El-Sayed, *J. Phys. Chem., 95* (1991) 1664.

[18] H. Morita and T. Sawada, *J. Photopolym. Sci. Technol., 6* (1993) 87.

[19] R.N. Rosenfeld and B.R. Weiner, *J. Am. Chem. Soc., 105* (1983) 6233.

[20] J.B. Pallix, U. Schuhle, C.H. Becker and D.L. Huestis, *Anal. Chem., 61* (1989) 805.