Polymerization of Methyl Methacrylate Initiated by Atmospheric Pressure Plasma Jet

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Utilization of atmospheric pressure plasma jet (AP plasma jet) was investigated for polymerization of methyl methacrylate (MMA) through the radical generation method. The AP plasma jet has a character of high-energy field at a relatively low temperature. Furthermore, this procedure can supply various types of energies to extremely restricted region of target materials irrespective of the shape and topography of the surfaces. In a liquid phase polymerization, the formation of polymethyl methacrylate (PMMA) was recovered by adding the reaction solution to an poor solvent, methanol. The amount of recovered PMMA was linearly increased with the AP plasma jet irradiation time and the formation rate of PMMA of 1.1 mg min⁻¹ was obtained. From an infrared spectrophotometric analysis, no significant change was observed between the PMMA sample formed by AP plasma jet irradiation and a reference PMMA film. It is considered that the AP plasma jet contributes to trigger for radical polymerization without imparting any considerable damage on the polymer. In addition, the polymerization of MMA was also investigated in the vapor phase. A small amount of PMMA was generated on the target glass plate surface by the irradiation of AP plasma jet through the vapor phase containing MMA. This result suggests a possibility for construction of a new formation system of a polymer film.

Keywords: polymethyl methacrylate, atmospheric pressure plasma jet, radical polymerization

1. Introduction

Many polymers are industrially synthesized by radical polymerization with an initiator, and the polymerization is initiated by radicals formed from initiator through thermolysis or photolysis. Previously, we reported the cross-linking reaction of a polymer using AP plasma jet as energy source of active species formation from a p-substituted benzene diazo compound [1]. As the result, it was found that the crosslinking reaction of diazo compound/PVA effectively progressed by plasma irradiation. Furthermore, a possibility for polymerization of PVA without any initiators was suggested using AP plasma jet irradiation. Therefore, we focused on a radical polymerization using AP plasma jet without any initiators. Recently, some approaches to the reaction using plasma have been reported by many researchers [2]. Kurowsawa et al. studied plasma-polymerization of styrene and allylalcohol using radio frequency (RF) pulse plasma, and reported the relationship between the thickness of the formed film and film resistance [3]. Choudhury et al. studied polymerization of styrene on bell metal using RF plasma, and the deposition condition was evaluated [4]. Johnson et al. investigated polymerization mechanism of methyl methacrylate (MMA) using glow discharge plasma in detail, and a substance formed in vapor phase [5]. In addition, in recent years, there are some reports on the addition of functional groups into the polymer by plasma polymerization. One of the examples, Lenka Zajičková et al. studied synthesis of amine-rich films using RF capacitively coupled plasma (RF CCP), and reported that a cyclopropylamine film of the thickness of 20 nm was successfully formed [6].

In this work, plasma polymerization of MMA in the liquid and a vapor phase was investigated using an AP...
plasma jet.

2. Experimental

2.1. AP plasma jet generator

An atmospheric pressure plasma jet (AP plasma jet) was generated in a quartz tube with the inside and outside diameters of 1.5 and 3.0 mm, respectively. The plasma generator used in this work is shown in Fig. 1. The system consists of two electrodes placed around the tube, where one electrode is set parallel to the other at the distance of 5.0 mm. The each electrode is made of copper tape, and the electrode located at the downstream side was used as working electrode, the other was as ground electrode. High voltage with low frequency (7.0 - 10.0 kV of peak voltage, 9 - 11 kHz) was generated from power supply (LHV-10AC, LOGY Electronic Co., Ltd.) toward the downstream side electrode to generate atmospheric pressure plasma in the quartz tube under argon gas flow, where the volume flow was maintained at a constant value of 500 standard cm³ per minute by a mass flow controller (Koflok mass flow controller: Model 3660, KOJIMA Instruments Inc.). Then, AP plasma jet was formed to squirt generated plasma from the nozzle.

2.2. Chemicals

MMA (99.0%) was purchased from Kanto Chemical Co., Inc. Since it contained 4-methoxyphenol (MEHQ) as inhibitor, the inhibitor was removed by washing with 10% NaOH and deionized water, and subsequently, dried with anhydrous sodium sulfate. Argon was purchased from Suzuki Shokan Co., Ltd. Methanol used as an anti-solvent was purchased from Kanto Chemical Co., Inc.

2.3. Reaction procedures

A plasma initiated polymerization of MMA using the AP plasma without any polymerization initiators was investigated under various conditions, such as the plasma irradiation time, the supplied voltage for plasma generation, and so on. Furthermore, an influence of components and of UV lights emitted from the plasma generator on polymerization was followed in order to see the initiation of polymerization. In order to estimate active and excited species formed at vapor-liquid interface, an emission spectrum was measured on a Photonic Multichannel Analyzer PMA-10 (Hamamatsu Photonics K.K.). An obtained emission spectrum was analyzed by database [7]. Infrared spectrophotometric analysis was performed by a FT/IR-4100 spectrometer (JASCO Corporation) to determine a chemical structure of the formed polymer. The size distribution of formed PMMA particles in the reaction solution was measured by a particle size distribution measuring apparatus (SALD-2300, Shimadzu Corporation).

2.3.1. Liquid phase polymerization

A diagram of reaction apparatus for liquid phase is shown in Fig. 2 (a). A glass bottle of 50.0 mL was used for the reaction vessel. MMA of 25.0 mL was poured into the bottle, and the bottle was tightly capped with a silicon stopper equipped the AP plasma jet generator. Under the initial condition, the distance from the nozzle head to a liquid level of MMA solution was fixed at ca. 10 mm in all experiments. Air in the reaction vessel was substituted with argon for 10 min without a power apply, and then a low frequency-high voltage was supplied to the AP plasma jet generator, and the reaction was started. During the reaction, the supplied voltage and conditions of
plasma torch, such as the color and the length of it, and the supplied electrical power, were observed. After the reaction, PMMA formed was recovered by pouring the reaction solution to the poor solvent, methanol. The PMMA particle deposited was filtered by a filter paper, and then dried at 358 K for 2 h. Then, the yield of the obtained PMMA particles was measured.

2.3.2. Vapor phase polymerization

A diagram of reaction apparatus for vapor phase is shown in Fig. 2 (b). In this work, two reaction conditions were changed from the experiments of liquid phase. The volume of the poured MMA was decreased from 25.0 to 10.0 mL, and the glass plate was placed over the MMA solution by four fine threads. The distance between the surface of MMA solution and the plate was fixed at ca. 20 mm. The AP plasma jet was irradiated to the plate through the vapor phase containing vapor of MMA at ambient temperature and at vapor pressure.

3. Results and Discussions

3.1. Polymerization of MMA in liquid phase

Fig. 3 shows a series of photographs taken at each stages of the experiment. During the reaction, any significant change of solution wasn't observed (Fig. 3 (a), (b), and (c)). However, when the reaction solution was added to excessive methanol as a good solvent for MMA but as a poor solvent for PMMA, white and small particles were formed, and separated out from the solution (Fig. 3 (d)). An infrared spectrophotometric analysis was performed to confirm the chemical structure of the particles. Fig. 4 shows the infrared spectrum of the particles. In the IR spectrum, strong bands at 1730 cm⁻¹ and 1260 cm⁻¹ appeared, assigning to C=O stretch and C–O–C stretches, respectively. In addition, C-H stretches in CH₂ and CH₃ emerged at 1448 cm⁻¹ and 1368 cm⁻¹, respectively. Furthermore characteristic absorption bands of PMMA emerged at 1063, 986, and 841 cm⁻¹. These absorption bands were in good agreement with the reference spectrum [8]. These results indicate that the compound was identified as PMMA, and PMMA little underwent detectable damage on PMMA by AP plasma jet irradiation.

3.2. Time course of PMMA yield using AP plasma jet in liquid phase

The relationship between the PMMA yield and the AP plasma jet irradiation time is shown in Fig. 5. The PMMA yield linearly increased with the irradiation time. From a slope of the straight line, the formation rate of PMMA was calculated to be about 1.1 mg min⁻¹. This linearity suggests that active species were continuously formed at vapor-liquid interface by the AP plasma jet irradiation. From emission spectrum analysis, some fragmentations of MMA and water were suggested at the vapor-liquid interface. Therefore, it can be considered that formed
radicals triggered the polymerization.

3. 3. Determination of a mean molecular weight and a particle size of formed PMMA

The viscosity-average molecular weight was determined to calculate the degree of polymerization. Fig. 6 shows the relationship between viscosity and the PMMA concentration. By calculation, the constants of $5.5 \times 10^3$ mL g$^{-1}$ and 0.76 was used as $K$ and $\alpha$, respectively [9]. The viscosity-average molecular weight of synthesized PMMA was calculated to be $5 \times 10^4 - 10 \times 10^5$ g mol$^{-1}$ for liquid phase polymerization at the supplied voltage of 10 kV for the irradiation time of 180 min. This supports our concept that the polymerization conditions, such as the supplied voltage and irradiation time little influence the molecular weight of PMMA.

The particle size distribution of formed PMMA was measured by a laser diffraction/scattering grain size distribution measuring apparatus under water with sodium dodecyl sulfate as a surfactant, and the particle size ranges from 100 $\mu$m to less than 1.0 $\mu$m and the mean apparent diameter of ca. 15 $\mu$m.

3. 4. Polymerization of MMA in vapor phase

Fig. 7 shows a photograph of the glass plate surface. A quite small amount of colorless and viscous deposit was obtained on it. From the infrared spectrum analysis, the deposit was identified as PMMA. The yield of PMMA formed in vapor-phase was 1.4 mg at the irradiation time of 210 min. It can be considered that the state of the PMMA was caused by a low mean molecular weight due to the polymerization under a condition of quantitative restriction of raw materials in the vapor-phase.

4. Conclusion

The PMMA sample with a low and a narrow molecular weight range was synthesized by AP plasma jet irradiation from the MMA liquid without any additional initiator. In addition, PMMA was successfully formed in the vapor-phase, but the very low viscosity-average molecular weight was estimated. As to the mechanism of polymerization, we can suggested the formation an active species by AP plasma jet irradiation to MMA, which formed in liquid or vapor phases played a very important role in the AP plasma jet initiated polymerization.

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