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RAPID COMMUNICATION

On-line measurement of monomer concentration in UV photopolymerization using a quartz crystal resonator

Young Han Kim†

Department of Chemical Engineering, Dong-A University, 840 Hadan-dong, Saha-gu, Busan 604-714, Korea
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Abstract–In spite of the importance of monomer concentration measurement in polymerization, it is difficult to measure the concentration in thin film polymerization, such as the UV photopolymerization of acrylates. A small device, a quartz crystal resonator, has been applied to the measurement of monomer amount in the UV photopolymerization of trimethylolpropane triacrylate with an initiator of 2-ethylanthraquinone. The resonant resistance of the resonator is converted to the monomer concentration using an empirical relationship. The measurement results indicate that the proposed technique is effective for determining the monomer concentration. The simplicity and ready availability of the proposed application have been proven experimentally.

Key words: UV Photopolymerization, On-line Monitoring, Quartz Crystal Resonator

INTRODUCTION

In various thin film applications UV photopolymerization is widely used due to its simplicity and wide applicability. However, monitoring the process is very difficult, because the photopolymerization is done in a range of seconds. Photorheometry has been used in monitoring the UV photopolymerization [1-3]. As the polymerization proceeds, the viscosity increase in the reactants is determined with a rheometer to calculate the polymerization degree. The variation of rheological property was detected from the microscopic observation of trace particles, and the polymerization process was monitored [4]. Spectroscopy has been widely employed in monitoring the reduction of carbon-carbon double bonds for the determination of polymerization degree. According to the wavelength of detecting light source, UV-VIS spectrometry [5,6], FTIR [7-9], and NIR [10-12] have been applied for measuring the double bonds.

A quartz crystal resonator-9 mm in diameter and 0.1 mm thick-comprised a thin quartz crystal sandwiched between two metal electrodes that establish an alternating electric field across the crystal, causing vibrational motion of the crystal at its resonant frequency. This frequency is sensitive to mass changes due to the loading on one of the electrodes and viscoelastic property at the interface of the crystal and its electrode. The quartz crystal resonator has been used in various applications by monitoring mass changes in nanogram scale and microrheological variation on its electrode surface. Its characteristics and applications are explained in the literature [13,14]. In a polymerization study, a stereocomplex assembly of poly(methyl methacrylate) was developed on the resonator surface to investigate the assembling mechanism [15]. A thickness shear mode resonator was utilized in the characterization of an epoxy resin film [16]. While a contacting phase changes on the resonator surface, the resonant frequency and resistance of the resonator vary due to mass load change and rheological alteration on the surface. For example, the resonator was applied to monitor gas-phase polymerization [17], crystallization [18-20] and condensation process involving phase change [21]. In photopolymerization, the resonator was employed in an on-line monitoring the UV photopolymerization [22] and in measuring the surface adsorption of surfactant used for the surface modification of glycidyl methacrylate [23].

In this study, the quartz crystal resonator is implemented in measuring the amount of acrylate monomer to examine the UV photopolymerization. A monomer of trimethylolpropane triacrylate is used in the monomer measurement. The resonant resistance of the resonator is used to determine the monomer amount. The relationship between the monomer amount and the resonant resistance is found from the experimental result, and the measuring technique is applied to a photopolymerization for the performance evaluation of the proposed measurement technique.

EXPERIMENTAL

1. Chemical

A monomer of trimethylolpropane triacrylate (TMPTA, Sigma-Aldrich Co., U.S.A., Code No. 246808) was used as received.

2. Resonator and UV Source

The quartz crystal resonator has a thin quartz plate of 9 mm in diameter, and either side of the quartz plate has a circular electrode of 5 mm in diameter at the plate center. When the UV photopolymerization was performed, the resonator was placed at the distance of 6 mm from the tip of the optical fiber. The resonant frequency and resistance were measured using home-made devices, and an A/D converter was employed for signal processing. The digital signals of the resonant frequency and resistance were provided to a PC for data analysis. An AT-cut quartz crystal resonator having a base frequency of 8 MHz (Sunny Electronics Co., Korea) was used in this experiment. A spot UV light source (Lichtzen Co., Korea, Model Inno-Cure 100N) was used, and its light intensity is 3 W/cm^2 with UV wavelengths between 250 nm and 450 nm. Fig. 1 shows the experimental setup for the monomer measurement in the UV

†To whom correspondence should be addressed.
E-mail: yhkim@mail.donga.ac.kr

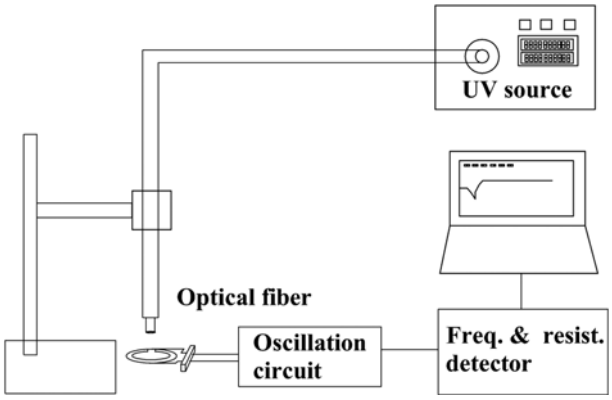

Fig. 1. A schematic diagram of experimental setup for UV irradiation.

photopolymerization.

3. Measurement Theory

The frequency variation due to the mass load change of the polymer sample placed on the electrode surface of a quartz crystal resonator is computed from the following equation [24].

$$\Delta f = \frac{-2f_0^2 \Delta m}{A(\mu_0 \rho_0)^{1/2}} \quad (1)$$

where f is the resonant frequency, m is the mass load, A is the piezoelectrically active area, μ is the elastic constant, ρ is the density, and the subscript 0 denotes the quartz plate. When the monomer is applied on the resonator surface, the sample amount is determined from the frequency decrease. At the same time, the resonant resistance of the resonator can be used to monitor the polymerization. The resistance is given as [25]

$$R = \frac{2\omega_f L_0}{\pi\sqrt{\mu_0 \rho_0}}\left[\frac{\omega}{\sqrt{2}}\sqrt{\rho\eta}\right] \quad (2)$$

where ω is the angular velocity, L is the inductance, ρ is the density, η is the viscosity, and μ is the elastic constant of the quartz plate. The subscript 0 denotes the properties of quartz plate, and the properties of polymerization material are represented without the subscript. The subscript f in the frequency means a base frequency. The resistance is proportional to the square root of viscosity of polymerization material, and therefore tracing the resistance gives the viscosity variation, namely, the polymerization process.

4. Experimental Procedure

The monomer of TMPTA 0.1 g was dissolved in 10 g toluene, and various amounts of sample were applied on the electrode surface of a quartz crystal resonator with a micropipette. Without UV illumination the resonant resistance was measured for the different amounts of monomer, and the relationship between the monomer amount and resonant resistance of the quartz crystal resonator was obtained from the measured resistance and the known amount of monomer determined from the frequency change.

For the evaluation of the relationship found from the experimental results, the proposed measuring technique was applied to the UV photopolymerization. A 1 g mixture of TMPTA and a photoinitiator of 2-ethylanthraquinone at the weight ratio of 35 to 1 were dissolved in 10 g toluene, and 0.8 μL of the solution was spread on the resonator surface. The variations of resonant frequency and resistance were measured with the irradiation of UV light for the specified time.

RESULTS AND DISCUSSION

The measured resistances for known amounts of monomer are shown in circles in Fig. 2. A small amount of TMPTA dissolved in toluene was spread on the electrode surface as a thin film, and the solvent toluene was evaporated as soon as the sample was applied. The resonant frequency drop in the bottom figure of Fig. 3 indicates the sample application, and no frequency increase after the sample dropping means that the vaporization of the solution is momentary. Though there is some scattering of the data from the fitted curve in Fig. 2, it is evident that the measured resistance using the quartz crystal resonator can be used for the determination of mono-

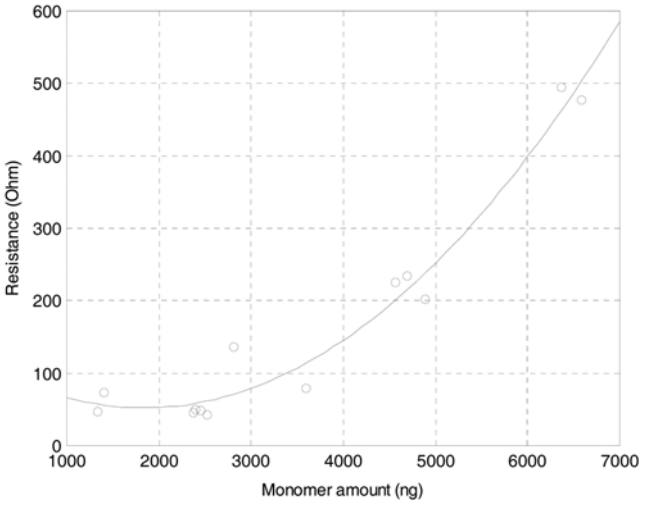

Fig. 2. Relationship between monomer amount and resonant resistance.

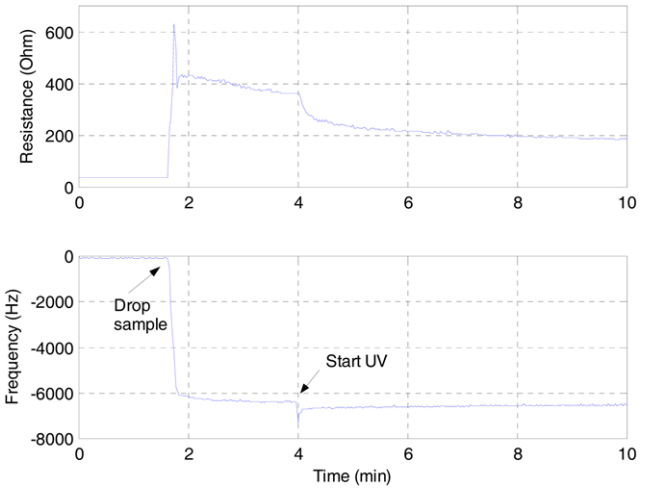

Fig. 3. Variations of resonant resistance and frequency in UV photopolymerization of trimethylolpropane triacrylate with a photoinitiator of 2-ethylanthraquinone applying UV irradiation for 1 second.

mer amount. As more monomer having high viscosity is placed on the electrode surface, the resonant frequency drops more, as predicted from Eq. (1), and the viscosity elevation due to the polymerization increases the resistance, as predicted from Eq. (2).

Fig. 3 shows the frequency drop due to the sample application and resistance decrease after the UV irradiation for one second. The moments of sample dropping and UV irradiation are indicated in the bottom figure. From the resistance measurement the calculated monomer amount is demonstrated in Fig. 4. The bottom figure of Fig. 3 demonstrates the variation of total amount of reactant on the resonator surface. No significant variation after a sudden drop for the sample dropping indicates that the total amount is not altered during the polymerization. Though the UV application was for one second only, the polymerization was continuous even after the UV was cut. The free radical generated by the UV irradiation was not entirely consumed during the irradiation, and the remaining radicals initiated the polymerization without the UV irradiation. Because

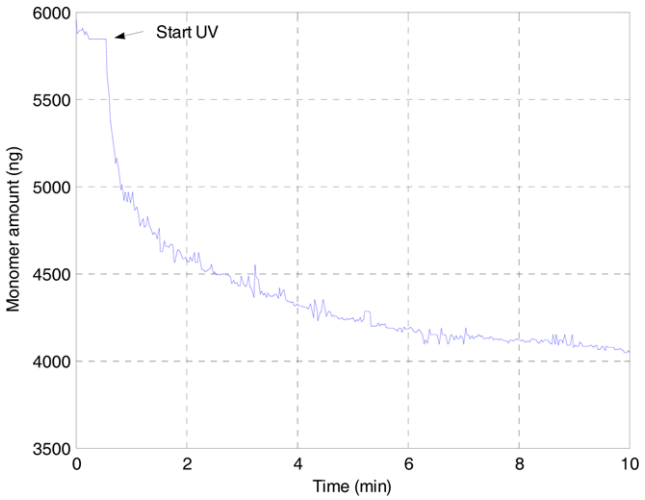

Fig. 4. Depletion of monomer after the UV irradiation for 1 second.

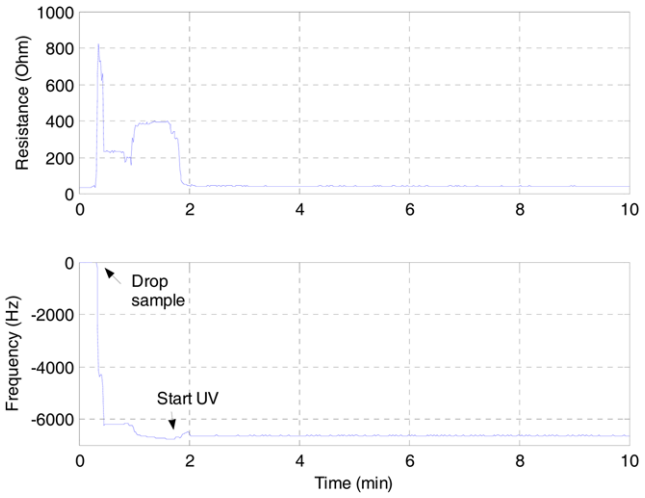

Fig. 5. Variations of resonant resistance and frequency in UV photopolymerization of trimethylolpropane triacrylate with a photoinitiator of 2-ethylanthraquinone applying UV irradiation for 10 seconds.

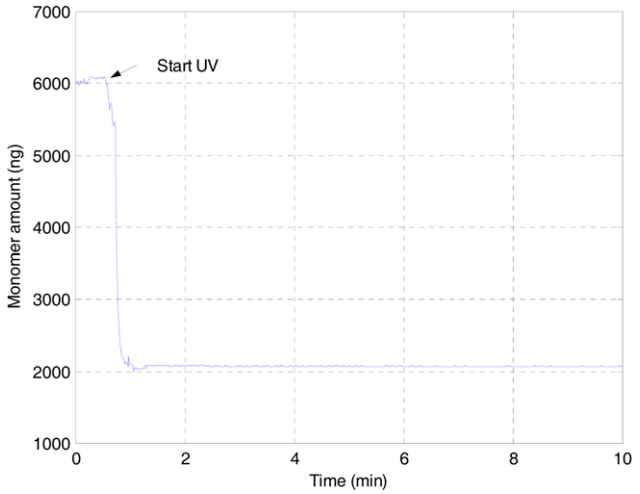

Fig. 6. Depletion of monomer after the UV irradiation for 10 seconds.

the unreacted monomer was available, the continuous consumption of the monomer is observed in Fig. 4.

When the UV light was applied for 10 seconds, the variations of the resonant frequency and resistance were demonstrated in Fig. 5. A large change of resistance in the first half of the period between the sample dropping and UV light application was due to the disturbance incurred from the sample spread on the resonator surface. The calculated amount of monomer from the resistance is shown in Fig. 6. The sharp decrease at the beginning and steady amount indicate that the polymerization is quickly completed because of the sufficient irradiation of the UV light. However, the remaining amount of monomer is not the actual value. As noticed from Fig. 2, the sensitivity of monomer amount determination is low with small resistance, and therefore the remaining amount is not an accurate value. The steady decrease shown in Fig. 4 is not found in Fig. 6, which represents a complete polymerization.

The on-line measurement of monomer amount in polymerization is difficult, though it is critically necessary for the process operation. The measurement in thin film processing, such as the UV photopolymerization, is even more difficult. The proposed measurement technique of this study is relatively simple and easy for polymerization monitoring. The quartz crystal resonator has been used for many different applications, but its utilization in monomer measurement has not been attempted before. The usefulness of the resonator in polymerization is experimentally demonstrated here.

CONCLUSION

It is difficult to measure the monomer concentration in thin film polymerization, such as the UV photopolymerization of acrylates, though measuring the concentration is important for the control of polymerization. A quartz crystal resonator widely used in the determination of tiny amount of mass load and rheological variation has been applied to the measurement of monomer amount in the UV photopolymerization of trimethylolpropane triacrylate with an initiator of 2-ethylanthraquinone. The relationship between the resonant resistance and monomer amount obtained from the experimental

results is used in the determination of monomer concentration in the UV photopolymerization. The measurement results of monomer concentration in the test applications indicate that the proposed measurement technique is effective for determining the concentration. The simplicity and usefulness of the proposed device have been demonstrated here.

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