

수정진동자를 이용한 광중합의 측정

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Measurement of Photopolymerization Using a Quartz Crystal Oscillator

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1. Introduction

Though polymerization degree is an important factor determining the quality of polymerization products, it is estimated from other easily measurable polymerization conditions because a direct measurement of the degree is very difficult. For the purpose, a simple viscometrical method has been utilized in solution polymerization [1], but its application is limited.

A quartz crystal oscillator is a useful detector to monitor a mass change in nano-gram scale and microrheological variation, and its many applications were reviewed in Marx [2]. A stereocomplex assembly of poly(methyl methacrylate) was made on the oscillator surface to investigate the assembling mechanism [3]. A thickness shear mode oscillator has also been utilized in the characterization of an epoxy resin film. In an enzymatic polymerization, the quartz crystal oscillator was employed to monitor the variation of elastic mass for the interpretation of polymerization mechanism.

The oscillator has been widely used in the study of electrochemical polymerization because the oscillator surface can be utilized as an electrode. Efimov, et al. examined the polymerization mechanism and redox cycling, whereas the interfacial behavior of thin organic films was monitored using the oscillator in other study. A widely known conducting polymer, polypyrrole has been investigated by the electrochemical studies. While a phase changes on the oscillator surface, the resonant frequency and resistance of the oscillator vary to indicate mass and rheological variation in microscale. The technique was applied to monitor crystallization and condensation processes.

In this study, the quartz crystal oscillator was implemented in the monitoring of UV photopolymerization. A monomer of 2-hydroxyethyl methacrylate and a photoinitiator of 1-chloroanthraquinone were used for the polymerization. The effects of irradiation time and initiator amount were examined with the resonant resistance variation of the oscillator. The experimental results were compared with the measurements of FTIR for functional group change and GPC for molecular weight distribution.

2. Experimental

2.1 Chemicals

A monomer of 2-hydroxyethyl methacrylate (Sigma-Aldrich Co., U. S. A., Code No. 525464) and a photoinitiator of 1-chloroanthraquinone (Sigma-Aldrich Co., U. S. A., Code No. C23209) were used as received.

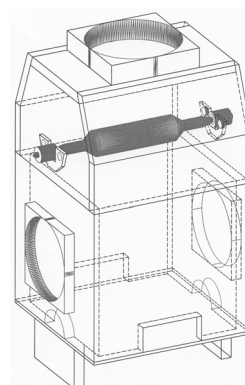
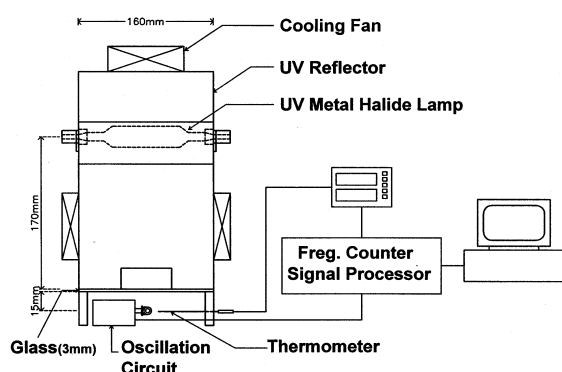


Fig. 1. Schematic diagram of experimental setup for UV irradiation. Fig. 2. A detailed view of irradiation room.

2.2 Analytical instruments

Spectroscopic analysis was conducted with an FT-IR spectrophotometer (Bruker Optics Inc., Germany, Model IFS 88), and molecular weight distribution was measured with a gel permeation chromatograph (Agilent Technologies, U. S. A., Model 1100 GPC-SEC Analysis System).

2.3 UV irradiation equipment and oscillator

The experimental setup of this study is shown in Figure 1. The light source was a metal halide UV lamp (Woong Jin Ultraviolet Co., Korea, Model WM600/CO) of 600 watt capacity with a UV wavelength between 320 nm and 450 nm. Three ventilation fans, one on top and two at both sides, were installed to evacuate hot air as illustrated in Figure 2. The lamp was positioned near the ceiling, which is an aluminum reflector. The oscillator was placed beneath a glass plate to prevent direct heating from the lamp. A thermometer and an oscillation circuit for the oscillator were also put at the same location. The resonant frequency and resistance and the temperature were measured using a home-made device, and an A/D converter was employed for signal processing. The digital signals of resonant frequency and resistance were provided to a PC for data analysis. An AT-cut quartz crystal oscillator having a base frequency of 8 MHz (Sunny Electronics Co., Korea) was utilized in this experiment. The electrodes of the oscillator were silver finished.

2.4 Photopolymerization

The monomer of 2-hydroxyethyl methacrylate was mixed with the initiator of 1-chloroanthraquinone in a known concentration of 0.5 %, 1 % or 2 %. In the beginning the known amount of the initiator was taken in a 20 mL vial, and the rest of 5 g was added with the monomer. A 1 μ L of the mixture was taken and spread on the oscillator surface. The prepared oscillator was placed beneath the glass plate in the irradiation chamber. After the arrangement, the cooling fans were on and the data gathering of the PC was started. The UV lamp was turned on after 30 seconds of the settlement. The irradiation time was 60 s, 90 s and 120 s for each reactants of 0.5 %, 1 % and 2 % concentration of the initiator. Figure 3 shows typical measurements of resonant frequency and resistance.

3. Results and Discussion

The initiator amount and irradiation time determine the polymerization degree in UV photopolymerization. The polymerization experiment was conducted with three different concentrations of initiator and three different irradiations, and the resonant resistance was measured for the cases. Because the resonant frequency is directly related with the viscosity of polymerization product, the resistance can be used as a measure of polymerization degree.

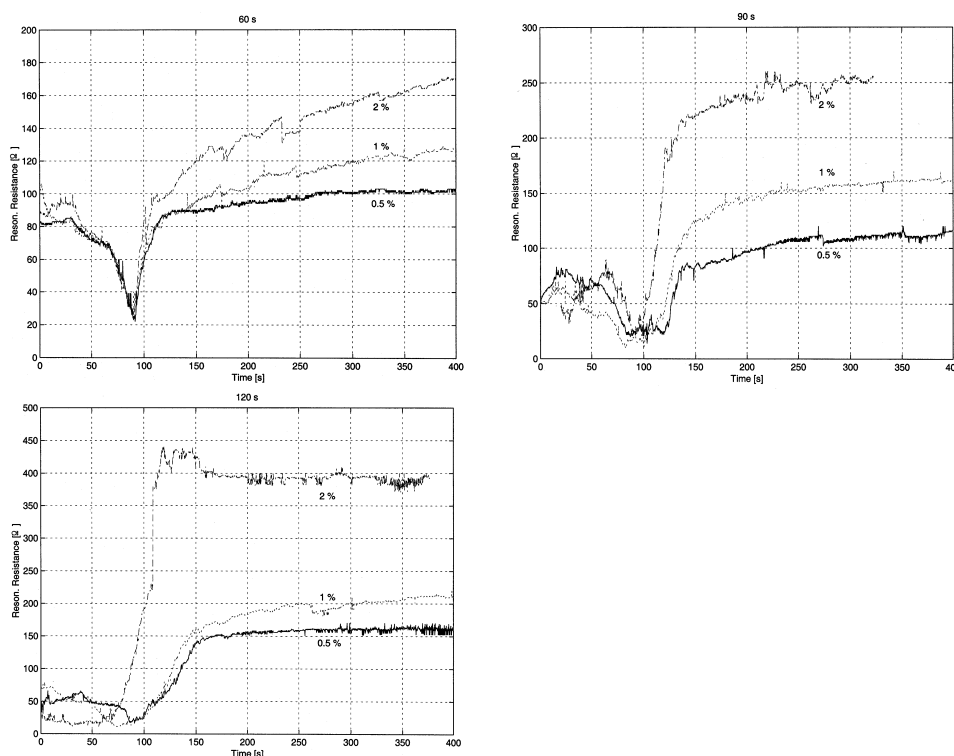


Fig. 3. The variation of resonant resistance for different concentrations of initiator with 60 second, 90 second and 120 second irradiation.

As a typical case the initiator concentration of 1 % and 90 second irradiation were applied. The temperature variation shows the beginning settling of 30 seconds, the increase of 90 seconds and steady reduction after the lamp is turned off. The pattern of frequency change is similar to the temperature variation. However, the resistance demonstrates quite different variation. The initial drop of the resistance is from the viscosity reduction caused by temperature increase. When the polymerization initiated, the resistance was elevated to a certain degree. The experiment without polymerization initiator does show the initial drop but does not the resistance increase. The increase of the polymerization degree with higher initiator concentration and longer irradiation time was observed with an FT-IR and a GPC.

With the UV irradiation of 60 seconds, the resistance variations of 0.5 %, 1 % and 2 % concentration of initiator are illustrated in Figure 3. The patterns of the initial decrease and rise of the resonant resistance are similar for all except the increased amounts are different. The highest concentration gives the largest. The same is shown in Figure 3. However, the time of polymerization initiation becomes apparently shorter with higher concentration at longer irradiation time. More irradiation also results in larger resistance increase meaning higher polymerization degree. In order to examine the polymerization degree FT-IR spectra are utilized.

4. Conclusion

A monitoring technique of UV polymerization using a quartz crystal oscillator was explained and applied to the polymerization of 2-hydroxyethyl methacrylate with a photoinitiator of 1-chloroanthraquinone. The resonant frequency of the oscillator indicates the polymerization degree. With the different initiator concentrations and UV irradiations, the resistance increase was measured and compared with the measured outcome from FT-IR and GPC.

The experimental results indicate that higher concentration of the initiator gives larger increase of the resistance and longer irradiation leaves higher ultimate resistance. The higher resistance means higher degree of polymerization as observed with FT-IR and GPC. This demonstrates the effectiveness of the quartz crystal oscillator for the in-line measurement of polymerization degree.

Acknowledgment

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References

- [1] Vega, M. P.; Lima, E. L.; Pinto, J. C. Polym 2001, 42, 3909.
- [2] Marx, K. A. Biomacromol 2003, 4, 1099.
- [3] Serizawa, T.; Hamada, K.; Kitayama, T.; Fujimoto, N.; Hatada, K.; Akashi, M. J. Amer. Chem. Soc. 2000, 122, 1891.