

Control of Responsiveness of Temperature-responsive Copolymer Using Ultrasonic Irradiation

超音波を用いた温度応答性コポリマーの応答特性の制御

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1. Introduction

Poly(*N*-Isopropylacrylamide) (PNIPAM) is a temperature-responsive polymer with a lower critical solution temperature (LCST). Poly (2-hydroxyethyl methacrylate) (PHEMA) has a high mechanical strength so that a copolymer of Poly(NIPAM-*co*-HEMA) is expected to be applied as advanced polymer materials in various fields, such as sensors, actuators, drug delivery system, and so on. Since the properties of copolymer are dependent on the molecular weight, polydispersity, copolymer composition and copolymer sequence distribution, it is necessary to control them.

Ultrasonic irradiation to liquid results in the formation and collapse of micro scale bubbles. A collapsing bubble generates local high temperature and high pressure fields, and extremely high shear flow. When ultrasound is irradiated to a solution containing polymer, the polymer is decomposed by shear stress.

In this study, copolymer Poly(NIPAM-*co*-HEMA) was decomposed by ultrasonic irradiation, and the effect of the condition of ultrasonic irradiation on the number average molecular weight, the polydispersity, and thermo-responsiveness was investigated.

2. Experimental method

Poly(NIPAM-*co*-HEMA) was prepared by radical polymerization in the mixture of water and ethanol at 15 °C. The volume fraction of ethanol in the solvent was 10 vol%. Ammonium persulfate was used as a radical initiator and *N,N,N',N'*-tetramethylethylenediamine was used as an accelerator. The molar fraction of NIPAM of copolymer was 0.7.

Fig. 1 shows the experimental apparatus for ultrasonic degradation. The synthesized copolymer was decomposed using a horn type ultrasonic generator. The solvent was the mixture of ethanol and water, and the volume fraction of ethanol was 70 vol%. The concentration of copolymer was 0.1 mol/dm³ and the volume of solution was 100 cm³. Ultrasound of frequency 20 kHz was irradiated to the solution for 8 hours at various ultrasonic power. The reaction temperature was 30 °C.

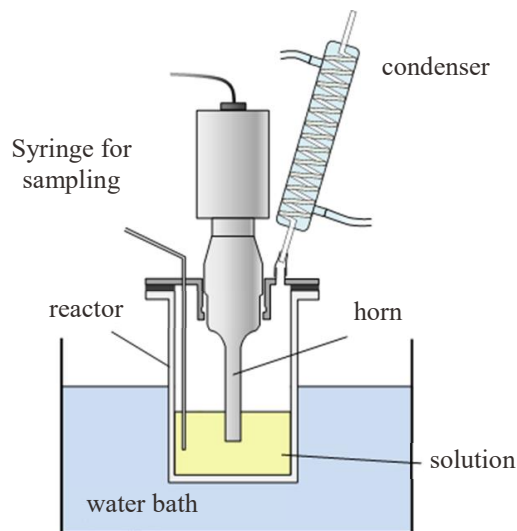


Fig. 1 Experimental apparatus for ultrasonic degradation.

During the reaction, 1 cm³ of the reaction solution was collected at specific time intervals. The number average molecular weight and polydispersity were analyzed by gel permeation chromatography (GPC). In order to evaluate the temperature responsivity of the copolymer, the decomposed copolymer was dried and dissolved in pure water with a concentration of 1 wt% and then the transmittance of the aqueous solution containing the copolymer was measured by ultraviolet-visible spectrophotometer. The temperature at the transmittance of 0.5 was defined as LCST.

3. Results and discussion

Fig. 2 shows the time courses of (a) the number average molecular weight (M_n), and (b) the polydispersity at various ultrasonic power. In each case, the molecular weight and polydispersity decreased sharply in the initial stage, and asymptotically converged to a constant value in the later stage. When the polymer is decomposed under ultrasonic irradiation, shear force corresponding to the length of the main chain is applied to the center

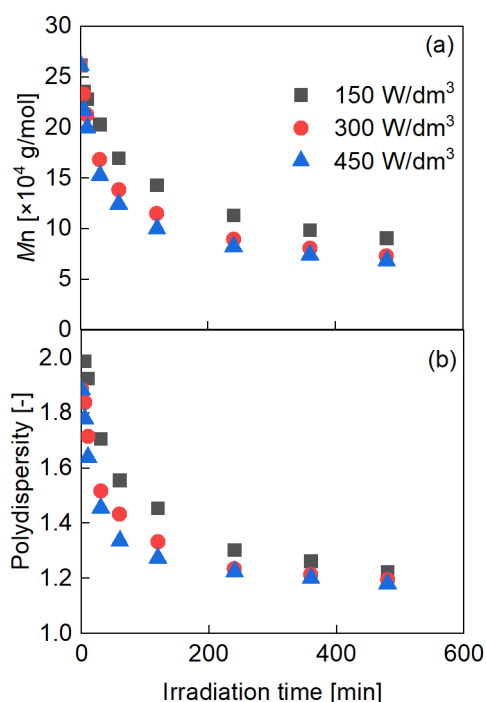


Fig. 2 Time courses of (a) number average molecular weight (M_n), and (b) polydispersity at various ultrasonic power.

of the main chain, and when the force exceeds the bonding strength, the polymer chain is broken. However, when the degree of polymerization is below a certain value, shear force is not enough to break the polymer chain, so that the molecular weight converged to a constant value asymptotically.

The higher ultrasonic power resulted in the faster polymer degradation rate. The larger number of bubbles was generated at the higher ultrasonic power. As a result, the copolymer was exposed to higher shear stress due to the collapse of cavitation bubbles.

After the ultrasonic irradiation for 8 hours, the polydispersity of copolymer was below 1.5 which is the theoretical minimum of the polydispersity for radical polymerization. Since the higher molecular weight takes the stronger shear force, high molecular weight polymer is decomposed preferentially. Thus, the polymer with low polydispersity can be obtained by the ultrasonic degradation method.

Fig. 3 shows the temperature dependence of transmittance of copolymer aqueous solution at various irradiation time. The ultrasonic power is 150 W/dm³. The LCST, the temperature at the transmittance of 0.5, increased with time. This might be because the phase transition temperature of copolymer depends on copolymer composition. The copolymer synthesized by radical polymerization might have a wide distribution of the copolymer composition. When the copolymer is decomposed by ultrasonic irradiation, the sequence of copolymer

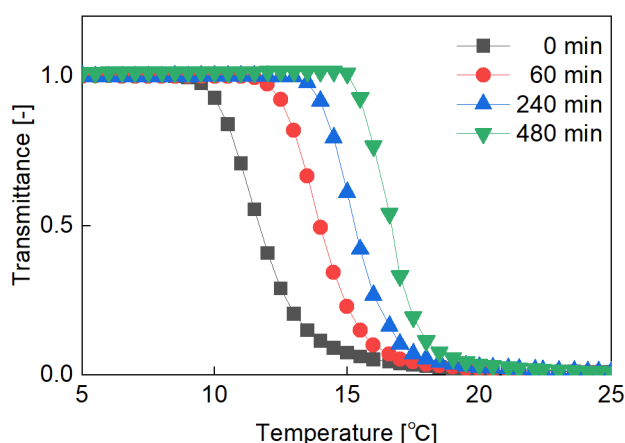


Fig. 3 Temperature dependence of transmittance of polymer aqueous solution at various irradiation time (ultrasonic power : 150 W/dm³).

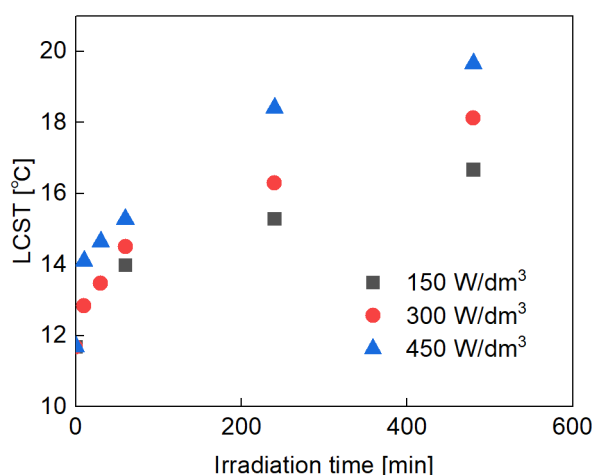


Fig. 4 Time courses of LCST of copolymer at various ultrasonic power.

might change and the distribution of copolymer composition might become narrow, and then the LCST increases.

Fig. 4 shows the time courses of the LCST of copolymer at various ultrasonic power. The higher the ultrasonic power, the higher the LCST of copolymer at same irradiation time. This was because the higher ultrasonic power resulted in the faster polymer degradation rate. Thus, the sequence of copolymer might change more frequently.

4. Conclusion

In this study, the effect of conditions of ultrasonic irradiation on the number average molecular weight, the polydispersity, and the thermo-responsiveness of Poly(NIPAM-co-HEMA) was investigated. By the ultrasonic polymer degradation, the polymer with low polydispersity can be obtained. The LCST of the copolymer can be controlled by the conditions of ultrasonic irradiation.