

## Ultrasonic Polymerization of N-isopropylacrylamide at Soluble and Insoluble Temperatures

### N-イソプロピルアクリルアミドの相溶および非相溶温度下における超音波重合

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#### 1. Introduction

Ostroski and Stambauch [1] reported ultrasonic polymerization of styrene. After their study, various reactions were reported by, for example, Lindstrom [2], Henglin [3], and Allen [4]. We succeeded in realizing ultrasonic polymerization of N-isopropylacrylamide monomer aqueous solution as an example of a novel reaction for polymerizing a polymer from monomers. The N-isopropylacrylamide polymer has a characteristic called low critical solution temperature (LCST) [5-8]. The LCST polymer is soluble below a certain temperature (soluble point), but insoluble above the soluble point. The ultrasonic polymerization of an LCST polymer was carried out below and above the soluble point. The molecular weight and the yield of the polymer under each condition were measured.

#### 2. Experiment

A schematic of the sonoreactor was shown in Fig. 1. The N-21 ultrasound transducer (NEC TOKIN Corp.) was used. The diameter and resonance frequency of transducer were 20 mm and 1 MHz. This transducer was driven by the sinusoidal wave of 60 volts amplitude. The driving signal was generated from a pulse/function generator (P8116A, Hewlett-Packard Co.) with a power amplifier (NF4020, NF Electronics Instruments). The sound pressure was approximately  $1.8 \times 10^2$  kPa [9]. Pure water (Wako Chemical Co., Ltd.) and N-isopropylacrylamide (Acros Organics) were used as samples. The soluble temperature of poly-N-isopropylacrylamide in water is less than 32°C. The concentrations of samples were adjusted to varied from 0.1 to 1.6 mol/L. The temperature of samples was controlled using a compact handy cooler (Iuchi 200TN, As One Corp.) and a heater pump (Yamato Thermo-Mate BF400, Yamato Co., Ltd.). The amount of the sample was adjusted 5ml.

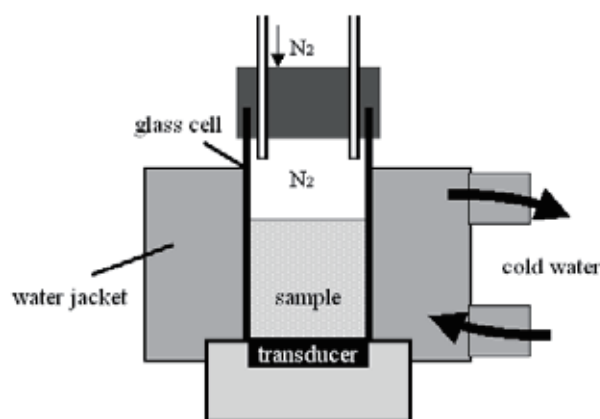


Fig. 1 Schematic of sonoreactor.

The samples were bubbled for 30 min with nitrogen, and then the ultrasound was irradiated to the samples also under nitrogen atmosphere. The molecular weight of the polymer precipitated was measured using GPC molecular weight measuring equipment (Shodex GPC System-21H, SHOWA DENKO K. K.). The molecular weight was estimated as polystyrene equivalents (Shodex GPC System-21H, SHOWA DENKO K. K.).

#### 3. Results and Discussion

##### 3.1. Polymerization at soluble temperature (22°C)

Ultrasound was irradiated to samples with concentrations of 0.1 to 1.6 mol/L to measure the yield of each sample (Fig. 2). The sonication duration was 6 hours. The yields of 0.1 and 0.2 mol/L samples were the highest, and 25% of the prepared monomer was polymerized. In long time sonication, the occurrence of cavitation was difficult because the viscosity of solution became higher. In the case of the 1.6 mol/L monomer sample, no polymer was observed at all. It is considered that the occurrence of cavitation is obstructed by decrease of the vapor pressure of the

aqueous solution.

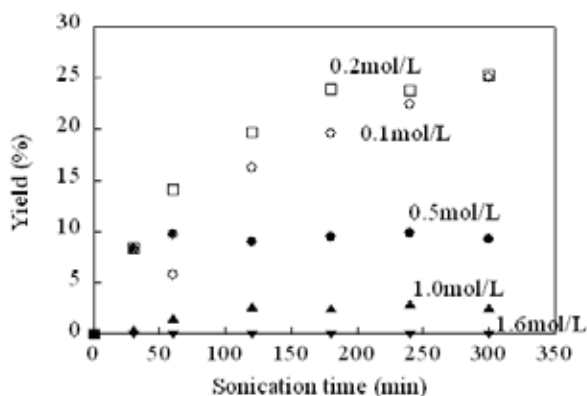


Fig. 2 Dependence of polymer yield on sonication time for monomers prepared at concentrations of 0.1 to 1.6 mol/L.

### 3.2 Comparison between soluble temperature (15°C) and insoluble temperature (33°C)

The experiment was carried out at 33°C (insoluble temperature) using a 0.5 mol/L sample. The polymerization of this sample stopped in the previous experiment at a soluble temperature, as shown in Fig. 2. Fig. 3 shows the results of ultrasonic polymerization at 15 and 33°C. The increase in the initial yield in the case of 15°C was approximately double that in the case of 33°C. This may be because a low temperature is advantageous for cavitation. When the sonication duration exceeds one hour, the yield of the sample at 15°C does not exceed 10%, whereas that of the sample at 33°C (insoluble temperature) gradually increases up to 6 hours, reaching approximately 25%.

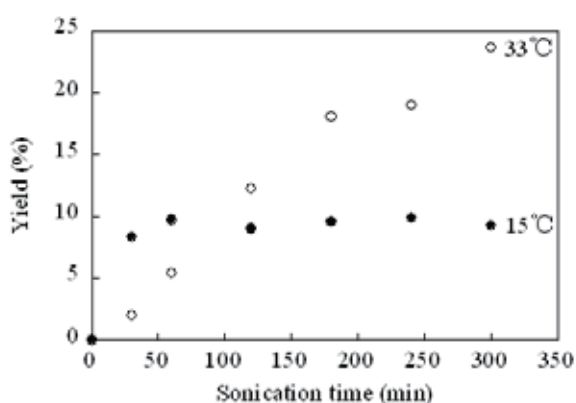


Fig. 3 Dependence of polymer yield on sonication time at compatible (15°C) and incompatible (33°C) temperatures.

### 4. Conclusion

We succeeded in realizing ultrasonic polymerization in N-isopropylacrylamide aqueous solution. Through the experiment at the compatible temperature (22°C), it was clarified that the occurrence of cavitation is inhibited with an increasing concentration of monomers, which decreases the production efficiency of polymer. It was demonstrated that monomers with a concentration of 1.6 M or greater are not polymerized by sonication at 1MHz and 180 kPa. In a similar experiment at the insoluble temperature, the produced polymer precipitated and the aqueous solution became cloudy. It was confirmed that polymerization proceeded even when the sonication duration exceeded 1 hour under this condition. The yield gradually increased up to a period of 6 hours, and the final polymer yield was 25%. This yield was approximately double that at the compatible temperature. The obtained polymer was not cut because it was precipitated and aggregated, and therefore, we successfully obtained polymer with a molecular weight higher than that of the polymer obtained at the soluble temperature.

### References

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