2E-11

Frequency Dependence of Acoustic Degradation of Polymer in Solution

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1. Introduction

Ultrasound has tremendous advantages: simple apparatus with no reaction initiator; creating tremendously high change in temperature and pressures during cavitation at room temperature. Therefore it has a broad application in industry: organic synthesis, nanoparticles preparation, extraction, cleaning, environment improvement, etc. For industrial application, in order to assure the precise reproducibility, it is necessary to study the influence of acoustic parameters such as frequency, intensity, acoustic impedance on a sonochemical reaction. Among these parameters, frequency is a very important part that strongly influences reactions and mass transfer. In fact, Koda et al[1] had shown that chemical effects are influenced by frequency. In this research, polymer degradation in solution is studied to clarify the influence of frequency on physical effects.
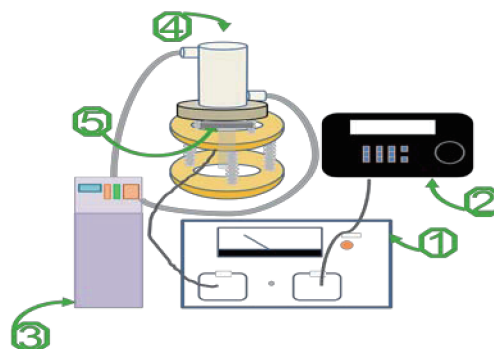
2. Experiment

For experiments with aqueous solution, 50 mL of 2 g/L aqueous solution of Polyethylene oxide (PEO) (SIGMA) with M_W=900,000 was used. Polymer degradation was carried out at different frequencies in the range of 19 kHz to 1 MHz. Apparatus in used have three types: horn, indirect and direct ones (**Figure 1**). The indirectly irradiation sonichemical reactors were operated at the frequencies of 200 kHz and 500 kHz. Horn was used for 20 kHz. For the other frequencies, direct ones were used. Although solutions were irradiated at different frequencies, the ultrasonic power was setting at the same power (5 W). The power delivered into solution was measured by calorimetry. In order to suppress the chemical effects, *t*-BuOH (guaranteed grade - Wako) was dissolved at 100 mM into the solution. The irradiation experiments were carried out at 20 ^{o}C. The degradation was evaluated with viscometry (at 25 ^{o}C) by Ubbelohde viscometer. Molecular weight was calculated from Mark-Howink-Sakurada equation of PEO at 25 ^{o}C[2].

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Fig. 1 Direct sonication apparatus
1. Power Amplifier
2. Function Generator
3. Temperature Controller
4. Irradiation Cell
5. Transducer

3. Results and discussion

Viscosity of PEO solution without *t*-BuOH dramatically decreases at the first minutes of irradiation and slowly decreases as the irradiation time increases. The decrease in viscosity indicates polymer degradation in solution by ultrasound.
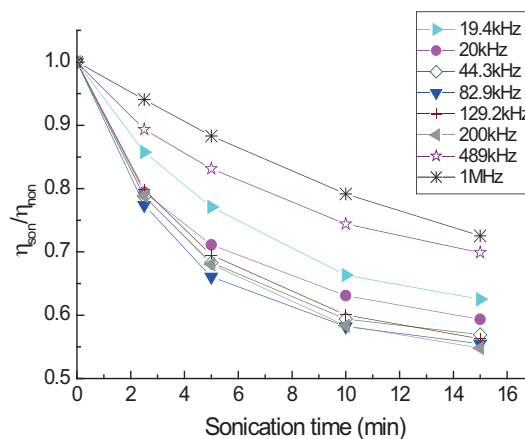

Fig. 2 Relationship between viscosity ratio and sonication time at different frequencies for PEO solution without presence of *t*-BuOH

Long time sonication seems to lead to a constant viscosity which means the limiting molecular weight depending on the irradiated frequency.

The viscosity ratio is calculated from the viscosity of samples before and after sonication. The viscosity ratio decreases with the sonication time. At the first period of irradiation, the viscosity ratios decrease rapidly with all samples (**Figures 2 and 3**). After that, degradation slows down. For water soluble polymers in aqueous solution, the physical and chemical effects contribute to acoustic polymer degradation. The addition of radical scavengers such as *t*-BuOH suppresses the chemical effects due to radical production. At 20 kHz and 1 MHz, there are almost no physical effects while physical effects of frequencies in the range of these two frequencies obviously influence degradation. **Figures 2 and 3** indicated that at 200 kHz and 489 kHz, the chemical effects strongly influence polymer degradation. Therefore, the degradation in the above frequencies slows down by addition of *t*-BuOH.

For the short time of sonication, degradation is assumed to be a first order degradation (**Figure 4**):

$$\ln \frac{M}{M_o} = -k_{app} \, t \quad (1)$$

where *M* is the molecular weight at time t of irradiation, M_o is the molecular weight of non sonicated samples, k_{app} is the apparent rate constant of degradation. As shown in **Figure 4**, k_{app} is calculated from the first 5 minutes of degradation by equation (1).

Relationship between the apparent rate constant and frequency is plotted in **Figure 5**. The trend how frequency influenced polymer degradation in case of physical effects is well understood from this plot. Except 19 kHz, other frequencies have a slower degradation when the frequency increases. The difference of 19 kHz samples with others is still under investigation.

References
1. S. Koda, T. Kimura, T. Kondo, H. Mitome, A standard method to calibrate sonochemical efficiency of an individual reaction system, Ultrasonics Sonochemistry, **10** (2003) 149-156.
2. Mehrdad, M.R. Rostami, Effects of temperature and solution concentration on the ultrasonic degradation of the aqueous solutions of polyethylene oxide, *Iranian Polymer Journal*, **16** (2007) 795-801.
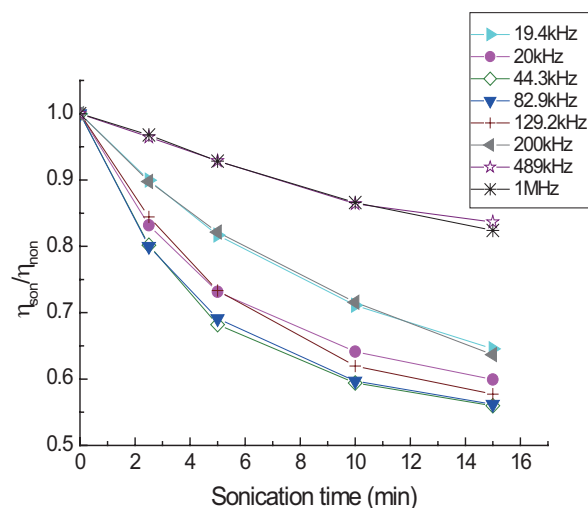
Fig. 3 Relationship between viscosity ratio and sonication time for PEO solution with the presence of *t*-BuOH
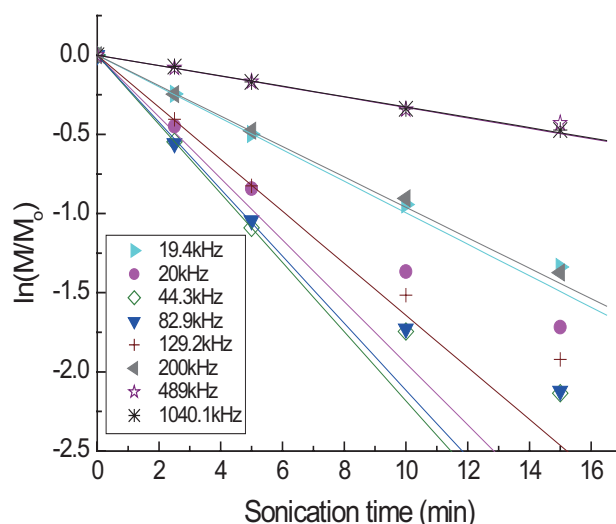

Fig. 4 Relationship between ln(*M/Mo*) and sonication time for PEO solution with presence of *t*-BuOH
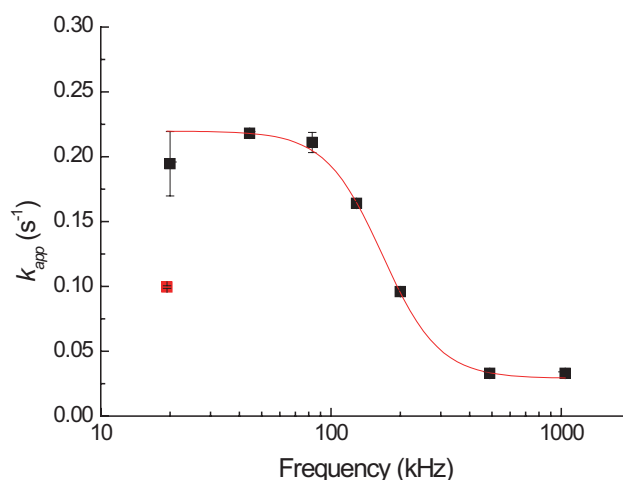

Fig. 5 Relationship between apparent degradation rate constant and frequency for PEO solution with the presence of *t*-BuOH