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Effect of alcohols on the ultrasonic degradation of polyethylene glycol

ポリエチレングリコールの超音波分解におけるアルコール添加の影響

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1. Introduction

Ultrasonic degradation of polymers such as polyethylene glycol (PEG) has been reported by many researchers.[1-3] Some studies have concluded that the degradation mechanism for polymers is scission by mechanical effects via ultrasonication, whereas others have reported a chemical mechanism via species such as OH radicals.[4-5] In this work, ultrasonic degradation of PEG was investigated to elucidate the degradation mechanism of polymers. The effects of four alcohols (ethanol, 2-propanol, *n*-butanol and *tert*-butanol) on the degradation of PEG were investigated. Ultrasonic irradiation was performed at 400 kHz because this frequency produces the strongest chemical effect, particularly for OH radical.[6] In addition, sonoluminescence spectra from Ar-saturated water were measured in the range of 240–370 nm to observe the spectral peak from OH radical emission at 310 nm.[7-8]

2. Materials and methods

An aqueous solution (150 mL) of PEG 6000 (1.0 mg/mL) was placed in a stainless steel cylinder with a cooling jacket to keep the temperature in the range of 12–14 °C, and the solution was sonicated with a PZT ceramic disk transducer at 400 kHz and an acoustic power of 10 W. The precise acoustic power entering the system was determined by calorimetry prior to sonication. All experiments were performed in triplicate. Samples were taken after 0, 10, 20, 30 min of sonication. An alcohol (10 mM ethanol, 2-propanol, *n*-butanol, or *tert*-butanol) was added to the polymer solution to suppress the effect of radicals on the polymer degradation. MALDI mass spectra were acquired in positive reflection mode on an AXIMA-CFR time-of-flight mass spectrometer (Shimadzu) with a pulsed nitrogen laser (337 nm). PEG was dissolved in water, DCTB (10 mg/mL), and NaTFA (0.5 mg/mL) in THF. Sonoluminescence spectra were measured with an Acton Spectra Pro 2300i (Princeton Instruments) fitted with a Pixis 100 camera (Princeton Instruments) and a grating of 600 rulings mm^{-1}, which was blazed at 250 nm. Sonoluminescence spectra from Ar-saturated water were measured at 400 kHz, an acoustic power of 20 W, and an exposure time of 2 min.

3. Results and discussion

Figure 1 shows a representative example of the change in the mass spectra after sonication at 400 kHz for 30 min at an acoustic power of 10 W. A low molecular weight degradation product was observed after ultrasonic irradiation. Figure 2 shows the degradation of PEG 6000 as a function of irradiation time at 400 kHz with no alcohol, and with ethanol, 2-propanol, *n*-butanol, or *tert*-butanol. The addition of the alcohol to the solution suppressed the degradation of PEG 6000 in the order ethanol < 2-propanol < *n*-butanol < *tert*-butanol.

Figure 3 shows the sonoluminescence spectra at 400 kHz for Ar-saturated water. The sonoluminescence spectra consist of a superimposed continuum and the spectral peaks for OH radical emission at 290, 310, and 340 nm.[9] Furthermore, the sonoluminescence intensity in Ar-saturated water containing 2 mM alcohol was decreased. The quenching effect of sonoluminescence was in the order ethanol < 2-propanol < *n*-butanol < *tert*-butanol. Because the spectral peak from OH radical emission (310 nm) decreased simultaneously, the chemical effect was decreased by alcohol addition. In addition, the chemical effects from potassium iodide were

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decreased when the alcohols were added (Figure 4).[10] The decrease in the chemical effect was in the order ethanol < 2-propanol < *n*-butanol < *tert*-butanol.

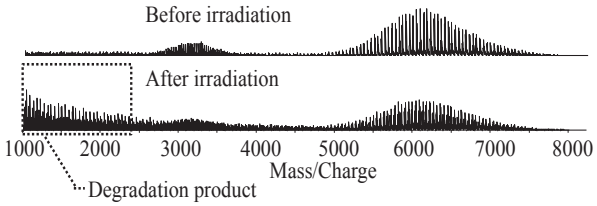

Fig. 1 Molecular weight distribution of PEG 6000 before and after ultrasonication.

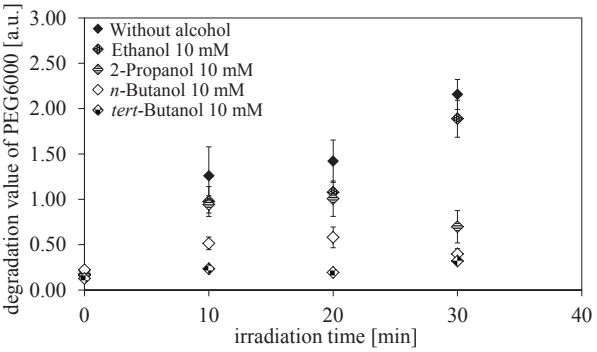

Fig. 2 Degradation value of PEG 6000 as a function of ultrasonic irradiation time (400 kHz, 10 W).

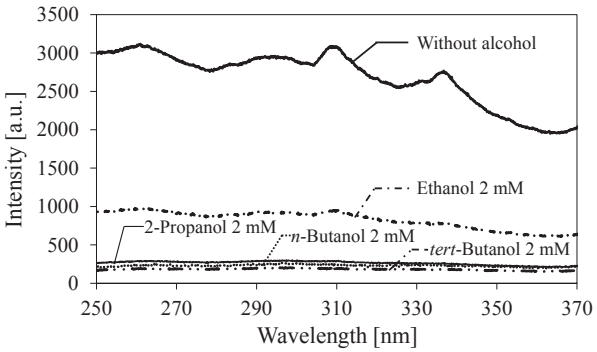

Fig. 3 Sonoluminescence spectra at 400 kHz of Ar-saturated water with or without 2 mM alcohol.

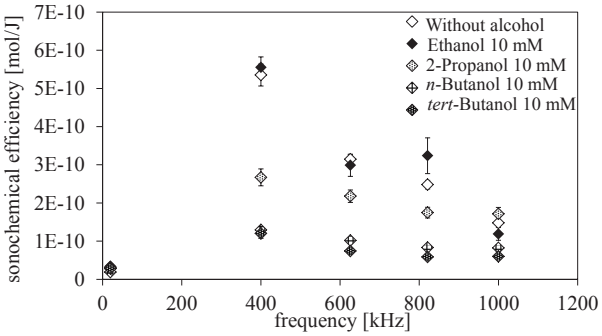

Fig. 4 Frequency dependence of sonochemical effect in 0.1 M KI solution with 10 mM alcohol.

Figure 2 shows that the addition of alcohol suppresses ultrasonic degradation of PEG 6000. Figure 3 shows that OH radical emission was decreased by the alcohol addition, and Figure 4 shows the decrease in the chemical effect. In addition, the effect of the type of alcohol in Figures 2–4 is consistent. These results indicate that ultrasonic degradation of PEG 6000 at 400 kHz is via a chemical mechanism, particularly by OH radicals. The alcohols act as radical scavenger, and the strength of the scavenging effect was in the order ethanol < 2-propanol < *n*-butanol < *tert*-butanol.

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