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Effects of frequency and a radical scavenger on ultrasonic degradation of water-soluble polymers

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ABSTRACT

Ultrasonic degradation of methyl cellulose, pullulan, dextran and poly(ethylene oxide) in aqueous solutions was investigated at the frequencies of 20 and 500 kHz, where the ultrasonic power delivered into solutions was kept constant (22 W). The number average molecular mass and the polydispersity were obtained as a function of sonication time. The degradation under sonication at the 500 kHz frequency proceeded faster in comparison with the 20 kHz sonication for four polymers. The addition of a radical scavenger, *t*-BuOH, resulted in suppression of degradation of water-soluble polymers. The degradation rate constants were estimated from the plot of molecular weight against sonication time. The degradation rate of methyl cellulose was the largest one among the investigated polymers. The difference in the degradation rates was discussed in terms of the flexibility and the hydrodynamic radius of polymer chains in aqueous solutions.

1. Introduction

Ultrasonic degradation of polymers in solutions is one of interesting subjects to understand sonochemical phenomena. Microbubbles are produced in liquids and solutions by irradiation of high intensity ultrasound in the frequency range from 20 kHz to several MHz. Bubble collapse leads to high temperature and pressure localized field and consequently, many compounds in solutions are degradated by physical and chemical effects. Polymers in solution are also influenced by sonication. Ultrasonic degradation of polymers in solutions has been extensively investigated by many workers and reviewed [1,2]. Their results indicate that degradation or scission of polymers in organic solvents is mainly caused by shear force generated by the relative motion between solvent and polymer chains during bubble collapse, i.e. mechanical or physical effects [1]. The scission of polymer chains is conceivable to occur at the almost midpoint of a chain.

In aqueous solutions, there are many reports on ultrasonic degradation of polymers, such as poly(ethylene oxide) [3–9], poly(vinyl alcohol) [10–13], poly(vinyl pyrrolidone) [14,15], poly(acrylic acid) [5,16], poly(acrylamide) [3,17] and polysaccharides [18–33]. Most of these works indicate that ultrasonic degradation of water-soluble polymers in aqueous solutions follows the degradation mechanism for polymers in organic solvents, that is, the almost midpoint scission by mechanical effects induced by ultrasound. It is well known that ultrasonic irradiation in aqueous solution results in production of OH and H radicals. The yields of OH and H radicals depend on the sonicated frequency and intensity. The chemical effects due to the radicals are prominent in the frequency range from 200 to 600 kHz [34,35]. The chemical effects due to OH and H radicals influence the degradation of polymers in aqueous solutions at high frequency sonication more than at low frequency.

Grönroos et al. indicated that the most extensive degradation of poly(vinyl alcohol) in aqueous solution takes place at the lowest frequency, 23 kHz [10]. Czechowska-Biskup et al. suggested that at 350 kHz sonication, the rod-like chitosan is effectively degradated more than starch [28]. Portenlänger and Heusinger concluded that the efficiency of degradation of dextran with 35 kHz sonication is more effective with the other three frequencies (500, 800 kHz and 1.6 MHz) [24]. The influence of frequency on polymer degradation under sonication is not settled yet and it is desirable to clear the effect on water-soluble polymer degradation in aqueous solution. In addition, ultrasonic degradation is affected not only by the irradiated frequency but also by the molecular structure and the dissolved state. Thus, investigation along this line is also meaningful to interpret the polymer degradation mechanism in aqueous solution under sonication.

In this work, ultrasonic degradation of methyl cellulose together with dextran, pullulan and poly(ethylene oxide) in aqueous solutions was investigated to elucidate the degradation mechanism of water-soluble polymers. The three polysaccharides used here are composed of the monomer residues originated from glucopyranose ring, and their types of bonding are different, while

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poly(ethylene oxide) is a representative flexible polymer. This work is focused on elucidating the effects of the frequency and a radical scavenger on degradation of water-soluble polymers in aqueous solution. Ultrasonic irradiation was performed at 20 and 500 kHz frequency, because the sonochemical effects at the latter frequency are expected to be enhanced about 10 times larger than that at the former frequency [34,35]. In order to gain the deep insight into the degradation mechanism of water-soluble polymer, we discuss how the degradation rates are influenced by the different bonding manner of glucose unit and by the dissolved state.

2. Experimental

2.1. Samples

Methyl cellulose (M_w = 198,000, M_w/M_n = 2.8 where M_w and M_n mean the weight averaged molecular mass and the number averaged molecular mass, respectively) was kindly supplied from Sinetsu Chemicals Co., Ltd. Methyl cellulose was purified by dialysis for a week. After that, methyl cellulose was precipitated by addition of acetone and then was freeze-dried. Poly(ethylene oxide) (M_w = 158,000, M_w/M_n = 3.8), dextran (M_w = 151,000, M_w/M_n = 3.0) and pullulan (M_w = 228,000, M_w/M_n = 2.0) were purchased from Poly Science, Pharmacia and Sigma, respectively, and these samples were used without further purification. These polymers were dissolved in distillated water and the polymer solution was prepared at a concentration of 0.1 wt.%. A radical scavenger, 80 mM *t*-BuOH is added to polymer solution to suppress the effect of radicals on degradation of polymers. *t*-BuOH was special grade chemical purchased from Wako Pure Chemical Industries, Ltd. and was used without purification.

2.2. Ultrasonic irradiation

For sonication at 20 kHz frequency, a horn type homogenizer (Sonifier 450D, Branson) was used and at the 500 kHz frequency, a sonochemical reactor (HSR-01, Honda Electronic) was used. The prepared solution of 50 ml was poured into glass cell. The experimental details were given in a previous paper [36]. The temperature was regulated at 25 ± 1 °C.

The ultrasonic power delivered into solutions was measured by calorimetry. The ultrasonic power was estimated by the following equation,

$$\mathrm{Power(W)} = (dT/dt)C_pM \tag{1}$$

where C_p is the specific heat of water (4.2 J/g K), M the mass of water, and (dT/dt) the temperature increment per second, respectively. As we believe that the ultrasonic power consumed in solutions must be kept constant in order to compare the sonochemical effects at the different frequencies, all experiments were carried out at the ultrasonic power of 22 ± 2 W delivered into solutions.

2.3. GPC measurement

The molecular weights and distribution were estimated from the gel permeation chromatogram (GPC). A CCPD model was high pressure solvent delivery pump (Toshoh Co., Ltd.) was used. A differential refractometer was used as a detector, with TSK-GEL G300PW and G5000PW (Toshoh Co., Ltd.) as the columns. The calibration curve was obtained using standard samples of pullulan, which were purchased from Sigma.

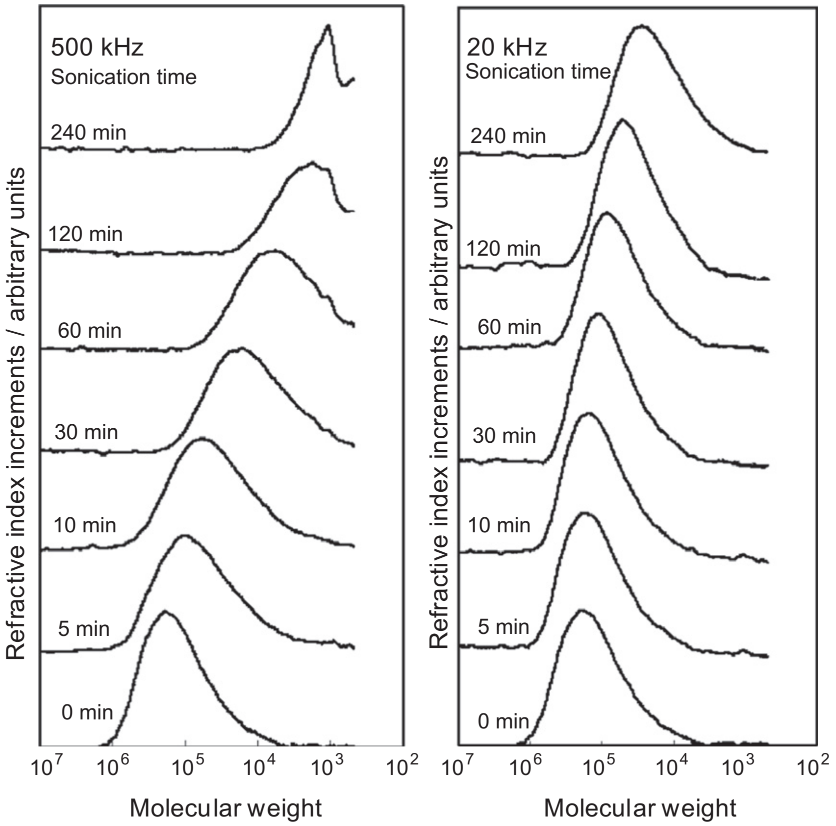

Fig. 1. GPC curves of methyl cellulose at different sonication times without *t*-BuOH (left: 500 kHz sonication and right: 20 kHz sonication).