

## SHORT COMMUNICATION

## MALDI-MS Analysis of Ultrasonic Degradations of Uniform PMMA

By Yoshiki TAKEDA,<sup>1</sup> Hideya KAWASAKI,<sup>1</sup> Takehiro WATANABE,<sup>1</sup> Koichi UTE,<sup>2</sup> and Ryuichi ARAKAWA<sup>1,\*</sup>

KEY WORDS: MALDI / Uniform PMMA / Ultrasonication / Polymer Degradation /

The application of ultrasonication on the degradation of synthetic- and bio-polymers has attracted considerable amounts of attention.<sup>1–7</sup> The molecular weights of the polymers are reported to drastically decrease in the initial stage, and then gradually approach a molecular weight limit.<sup>2</sup> It has been proposed that polymers in a solution can undergo chemical transformations under the influence of ultrasound through at least the following three mechanisms: 1) reactions with  $\bullet\text{OH}$  and  $\text{H}\bullet$  radicals because of the implausible collapse of a bubble by high-frequency ultrasound, 2) mechanochemical effect from the forces generated around collapsing cavitation bubbles, and 3) pyrolysis in the hot inter-facial region between the bubble and surrounding liquid.<sup>7</sup> Thus, the ultrasonic degradation of polymers has been extensively studied to date. However, the structural details of polymers induced by ultrasonic degradation remain uncertain, because the ultrasonic degradation of polymers has generally been examined using gel permeation chromatography (GPC) and viscometry to record changes in the molecular weight of the polymer.

The recent development of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) for the analysis of polymers has dramatically increased the mass range; depending on the kinds of polymers,<sup>8–11</sup> this modality can detect intact polymer molecules of high molecular mass. Ions in the mass spectra originated from the ions of intact polymer chains. More recently, we investigated ultrasonic degradations of poly(ethylene oxide) (PEG) and poly(methyl methacrylate) (PMMA) in aqueous media by MALDI-TOFMS.<sup>12</sup> Our MALDI-TOFMS study revealed structural details of ultrasonically degraded polymers, such as their average molar masses, chemical formulas, and molecular structures of the chain end groups. Several degradation pathways with free radical reactions for the ultrasonic degradation of polymers have been suggested. However, in the previous study we chose polymers with relatively broad molecular weight distributions. Thus, we could not determine the time required for one molecular revolution and position of scission in the polymer for the ultrasonic degradation products. In this paper, we report the results of our investigation on ultrasonic degradations of poly(methyl methacrylate) (PMMA) in an acetonitrile/water (1:1) mixture by MALDI-TOFMS (AXIMA CFR, Shimadzu/Kratos) in a linear mode, using uniform PMMA (polymerization degree,  $n = 29$ ). The ultrasonic degradation of PMMA ( $n = 29$ ) was recorded as a function of ultrasonication times to examine the structural details resulting from the ultrasonic degradation of PMMA. The uniform oligomer with 29 units of methyl methacrylate (MMA) was obtained by fractionating syndiotactic PMMA ( $M_n = 3020$ ,  $M_w/M_n = 1.12$ ,  $rr$  triad content 98.1%), using supercritical fluid chromatography as previously reported.<sup>13</sup> The st-PMMA was prepared following the procedure reported in the literature.<sup>14</sup> The ultrasonic degradation was performed, using a horn type sonicator (UR-20P, TOMY SEIKO, 20 W) at 28 kHz in a similar way in our previous paper.<sup>12</sup>

Figure 1 shows MALDI mass spectra ( $m/z = 800\text{--}3500$ ) for different sonication times at 15 °C. Before sonication ( $t = 0$ ), the uniform PMMA ( $n = 29$ ) is detectable at  $m/z = 2981$  as a sodium adduct ion, indicating identification of the PMMA using the end groups of *tert*-butyl and hydrogen (Figure 1A). At the short sonication time of  $t = 20$  s, the mass

spectrum consists of mixtures of ions from the complete chain of PMMA ( $n = 29$ ) at  $m/z = 2981$  and degraded chains around  $m/z = 800\text{--}2000$  with a spacing of 100 Da, which have near normal distribution curves. The ion peaks of the degraded chains have their maxima around  $m/z = 1350$ , which is approximately half the mass of the undegraded chain. On further ultrasonication, the molecular weight of PMMA continues to gradually decrease and then approaches a molecular weight of approximately 500–1000 after a sonication time of 8 h, as shown in Figure 1B. Although we continued to sonicate the PMMA solution for more than 10 h, the molecular weight remained unchanged. Thus, there exists a molecular weight limit in the ultrasonic degradation of polymers,<sup>15</sup> but the cause for the limit is unclear. The MALDI mass spectra shown in Figure 1 indicate that the molecular weight of PMMA drastically decreases at the initial stage and then gradually approaches a molecular weight limit of 500–1000. This ultrasonic degradation process is qualitatively consistent with that described in previous reports using GPC and viscometry to monitor molecular weight changes in other polymers.<sup>1–7</sup>

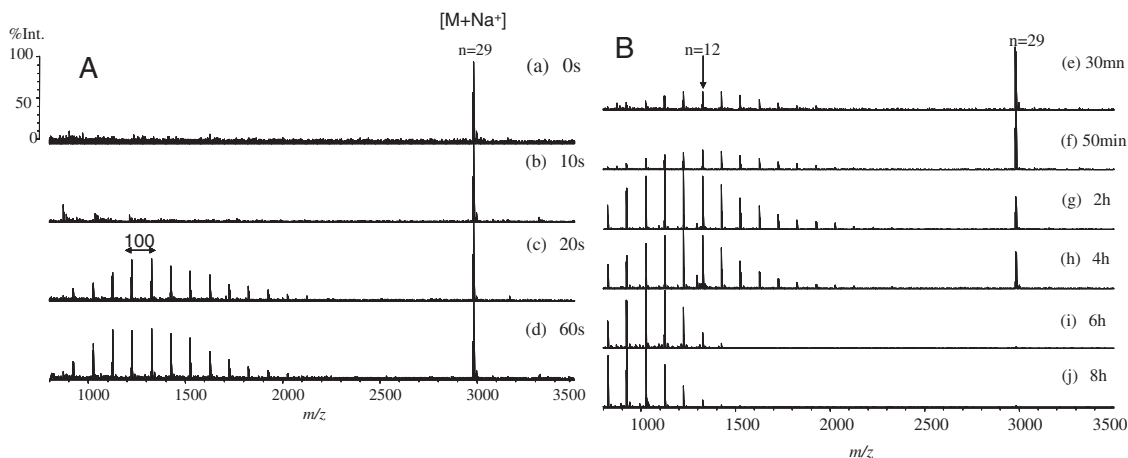
The end groups of the ultrasonic degradation products of PMMA are determined as follows: Considering the Na adduct ions observed at  $m/z$   $M_{\text{obs}}$  in the MALDI mass spectra, the sum of the end group masses can be obtained as,  $(E_1 + E_2) = M_{\text{obs}} - 100n - 23$ , where  $E_1$  and  $E_2$  are the masses of the end groups, and  $n$  is the number of repeating units. The PMMA molecular ion observed at  $m/z = 2981$  gives  $n = 29$  and  $E_1 + E_2 = 58$ , indicating that the end groups comprise of a hydrogen atom ( $m = 1$ ) and a *tert*-butyl group ( $m = 57$ ). Figure 2 shows the expanded spectrum ( $m/z = 850\text{--}1350$ ) of PMMA at a sonication time of 4 h. The spectrum of the degraded PMMA indicates a primary degradation product designated by A (A'), in addition to a minor degradation product designated by B. For the primary ion series of A with the Na adduct, both end groups of PMMA are single hydrogen atoms. The minor ion series, corresponding to A', are identified as the K adduct ions.

We emphasized that degraded PMMA with *tert*-butyl end-group are not observed in the spectrum at any sonication time. This indicates that the *tert*-butyl end-group of undegraded PMMA was converted into a hydrogen atom by ultrasonication. Note that the times required to attain ultrasonic degradation of PMMA depend on the kinds of end groups. For example, the ultrasonic degradation of PMMA occurred within 20 s for the PMMA with the *tert*-butyl end-group. The time required to achieve ultrasonic degradation was much shorter than that for systems with an end group of hydrogen atoms, and took approximately 2 h. This may be because of a quick release of the end group from the PMMA for the *tert*-butyl end group, which may initiate ultrasonic degradation reactions in them.

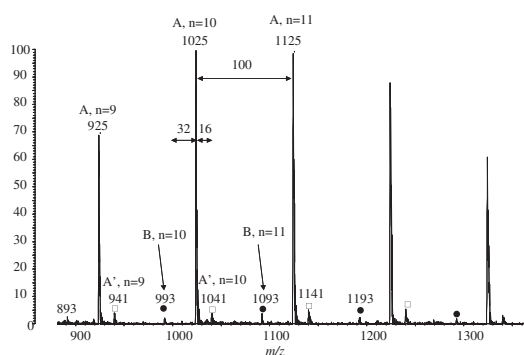
In pyrolysis/thermal degradation of PMMA, the polymer is known to be depolymerized to monomeric units above a given pyrolysis temperature.<sup>16,17</sup> In pyrolysis/thermal degradation of PMMA, the chain scission is known to be primary induced by the release of monomers from the end group (*i.e.*, unzipping). This unzipping degradation pathway could be checked by investigating the existence of MMA monomer, using GC-MS studies of the ultrasonic degradation of the PMMA. In fact, the GC-MS

<sup>1</sup>Department of Applied Chemistry, Kansai University, Suita 564-8680, Japan<sup>2</sup>Department of Chemical Science and Technology, The University of Tokushima, 2-1 Minamijosanjima-cho, Tokushima 770-8506, Japan

\*To whom correspondence should be addressed (E-mail: araki@ipcku.kansai-u.ac.jp).



**Figure 1.** MALDI-TOF mass spectra of PMMA ( $n = 29$ ) in acetonitrile/water (1:1) mixture. Ultrasonication times A: (a) 0s, (b) 10s, (c) 20s, and (d) 60s. B: (e) 30min., (f) 50min., (g) 2h, (h) 4h, (i) 6h, (j) 8h.



**Figure 2.** Expanded spectrum ( $m/z = 850\text{--}1350$ ) of PMMA at a sonication time of 4 hours.

spectrum indicated no existence of MMA monomer in the ultrasonic degradation products of PMMA, suggests that the unzipping degradation path ways are not likely for the ultrasonic degradation of the PMMA. Further study will be needed to clarify the detailed mechanism responsible for the ultrasonic degradation of the PMMA.

**Acknowledgments.** We are grateful to Y. Nishimoto for the helpful discussions.

Received: January 22, 2008

Accepted: April 25, 2008

Published: June 25, 2008

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