Atom Probe Analysis of One Dimensional Organic Chain: Polyethylene Glycol

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The synthetic polymer, poly(ethylene glycol) (PEG), was mass analyzed by using atom probe (AP). The AP mass spectrum of PEG showed no molecular ions but simple fragment ions of single charge. The sequential correlation between ions is also examined to make clear the requirement for future analyses.

Keywords Atom probe; Polyethylene glycol; Organic polymer; Mass spectrometry

I. INTRODUCTION

Atom probe (AP) is field ion microscope combined with time of flight (ToF) mass spectrometer [1, 2]. The sample material is ionized and emitted directly from surface (field evaporation) by strong field generated around the apex region of the sharp needle by applied voltage. The field evaporation can be pulsed by the application of the superposition of voltage pulse on the stationary voltage. It is fundamentally an adiabatic process preserving sample structure where the ionization proceeds without energy supply for vaporization of material in atomic scale. The ion-by-ion detection in AP gives the structural information of the sample material not only as integrated mass spectra but also as the detection sequence of the ions. The above advantage is clearly demonstrated by tomography analysis by three-dimensional-atom probe (3D-AP) of solid bulk materials such as metals and semiconductors [3].

The application of AP for non-metal, molecular materials in common chemistry such as carbon materials and small molecules has been examined by the authors [4–6]. In this study, the authors examined the field evaporation of one-dimensional (1D) chain structure material, polyethylene glycol [PEG, \((\text{C}_2\text{H}_4\text{O})_n\)] by using AP and the chain cleavage pattern was simulated to reproduce the mass spectrum. A sample fabrication method is also proposed here because no routine method like focused ion beam method has been established yet for AP analysis of non bulk materials.

II. EXPERIMENTAL

Commercially available polyethylene glycol (PEG1000, Wako165-09085, molecular weight: MW ∼1000, freezing point: 300–310 K) was used as a sample material. The larger molecular weight part of PEG 1000 was chosen by fusing-solidification cycles. The neat material was used without diluting by a solvent. An electropolished tungsten (W) tip was used as a support and a field emitter. As a melting PEG 1000 film moved from the tip apex to shank the region and to form a drop, PEG 4000, which has a larger MW (2700–3300) and a higher melting point (320–340 K), was attached on the W tip prior to the coating of PEG 1000 as shown in Figure 1. The sample fabrication and the transport to the vacuum chambers were all done in the atmosphere at ambient temperature.

The sample was AP analyzed applying voltage pulse for trigger at room temperature. A pulsed laser was not used because the heat dissipation of organic materials was slow compared to metals. Reflectron-AP was used for a high mass resolution analysis and 3D-AP was used for acquisition of spatial information of desorbed ions. Both instruments were equipped with extractor electrode positionable with a piezo-driven stage. The scheme of our home-built systems (reflectron-AP and 3D-AP) is described in Refs. 6, and 7.
III. RESULTS AND DISCUSSION

A. Mass spectrum of PEG 1000/W tip

Figures 2 and 3 show the mass spectra of PEG 1000 analyzed by reflectron-AP, where Figure 3 shows the smaller count region of the same data. The most commonly observed ion of tungsten used as substrate here is triply charged form of $m/z = 60.6−62.0$ amu but only a trace amount of ions were detected in the region. The mass peaks of H$^+$ and OH$^+$ were detected as minor components. No significant mass peak was observed in the mass region of $m/z > 100$ amu. The mass spectrum shows that PEG 1000 polymer (oligomer) chains desorbed not as in molecular ions but as small fragments generated by stepwise cleavage of covalent bond from terminal end of unfolded chain.

As most of the mass peaks were separated by 1 amu, the most mass peaks can be assigned to singly charged fragments. The mass deviation of fragments ($±1, ±2$ amu) from schematic chemical structure indicates that dynamic migration of hydrogen atoms cooperated during the field evaporation.

When small oligomer (dimer, trimer, tetramer, etc.) of ethylene glycol are ionized using conventional ion source (electron impact, EI method), mass peak of $m/z = 45$ amu is dominant in their mass spectra as shown in Figure 4 cited from public database [8]. Fragments of C$_2$H$_x$$^+$ and COH$_x$$^+$ are dominant only in mass spectrum (MS) of the ethylene glycol monomer which has no C–O–C bond.

B. Angular distribution of fragment ions from PEG 1000/W tip

The angular distribution of fragment ions from PEG 1000 obtained by 3D-AP analysis is shown in Figure 5. The detected ions are mapped in detector plane (x-y) and the progress of the analysis along z-direction in the bottom two figures in Figure 5. The image is projected along z-axis. It is noteworthy that the 3D-depicted images of Figure 5 on PEG 1000 should be discriminated from a reconstructed tomography of bulk solid structure of the material because the sample is measured at ambient temperature where the local

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**Figure 1:** The measurement of PEG 1000 and the sampling method. Photo: the sample facing to the miniature electrode of scanning atom probe. Inset: PEG 1000 coated on PEG 4000 drop supported on the W tip.

**Figure 2:** The mass spectrum of PEG 1000 analyzed by reflectron-AP. No significant mass peak is observed in the region $m/z > 100$ amu.

**Figure 3:** The small count region of the mass spectrum of PEG 1000. The count scale is magnified to show the region of less than 500 counts. The same data set is used as Figure 2. The mass peaks encircled are showing ion groups consisting of $n = 2, 3, 4$ C, O atoms.
Brownian motion of polymer chain should be active.

The distribution of each species shows no specific feature in the images in Figure 5. To find a specific correlation between ions in angular distribution, the same dataset was examined in the different mapping schema in Figure 6.

First, the angular distribution was checked by extraction of designated ions from the dataset. Fragments of two atoms (red), and three atoms (green) are mapped in images (a) and (b) in Figure 6. These two images show that two components show almost the same angular distribution. Second, the spatial correlation between the ions in the detection sequence during the analysis was checked by mapping the relative displacement. Figure 6(c) shows $x$-$y$ coordinates shift of all the ions against the precedent ion. Figure 6(d) shows $x$-$y$ coordinates shift of the heavy ions of more than two C, O atoms against the dominant ions of two C, O atoms.

The images shown in Figure 6 suggest that the angular or spatial correlation between fragments are not found in these analyses. The homogeneous distribution of fragment ions shown in Figures 5 and 6 indicates that the structural information of polymer chain does not emerge as in the case of bulk material analysis.

C. Ion-ion sequential correlation

To check the coincidence between the 1D-reflectron AP and 3D-AP analysis, the ion-ion sequential coherence was mapped in Figure 7 as follows; when a series of ions $m_1$, $m_2$, $m_3$, $m_4$, ⋯ ($m$: mass to charge ratio) are detected, the counts $n(m_1, m_2)$ projected on the two-dimensional space; $n(m_1, m_2)$, $n(m_2, m_3)$, $n(m_3, m_4)$, ⋯ were incremented. The ratio between $n(m_1, m_2)$ and $n(m_2, m_3)$ were taken and mapped with color bar in the left side of Figure 7. In this mapping, when the ratio $n(m_1, m_2)/n(m_2, m_3)$ is larger than 1 (painted with blue), it means that an ion of $m_2$ appears more frequently than in reverse order. When the ratio is smaller than 1, the dot is painted with yellow. The diagram is mirror symmetric against the $y = x$ line because the value $n(m_1, m_2)/n(m_2, m_3)$ of coordinates $(m_1, m_2)$ is the reciprocal of $n(m_3, m_4)/n(m_4, m_5)$ of coordinates $(m_3, m_5)$. It should be mentioned that this diagram does not

Figure 4: Mass spectra of ethylene glycol oligomers ionized in gas phase by electron impact method.

Figure 5: The angular distribution of PEG 1000 fragments analyzed by 3D-AP. Top: the colored mass spectrum of designated ions. Bottom left: the accumulated ions detected by two-dimensional $(x$-$y$) position and time sensitive detector in 3D-AP. The ions (dots) are painted using the same color as in the mass spectrum above. The $z$-axis coordinate of the image corresponds to the progress of analysis (from left to right). Bottom right: the distribution of detected ions projected along $z$-axis.

Figure 6: (a) The angular distribution of PEG 1000 fragments analyzed by 3D-AP. Top: the colored mass spectrum of designated ions. Bottom left: the accumulated ions detected by two-dimensional $(x$-$y$) position and time sensitive detector in 3D-AP. The ions (dots) are painted using the same color as in the mass spectrum above. The $z$-axis coordinate of the image corresponds to the progress of analysis (from left to right). Bottom right: the distribution of detected ions projected along $z$-axis.
reflect the magnitude of ion count of each mass peak but only the sequential order in data set.

The two data set obtained by reflectron-AP [Figure 7(a)] and 3D-AP [Figure 7(b)] shows the same trend that the smaller mass ion evaporated former than the larger mass ion. (The upper-left area is colored blue and the lower-right area is colored yellow.)

IV. DISCUSSION

Because it is not clear whether the dissociation/fragmentation occurs randomly or regularly inside polymer chain from angular distribution of fragment ions by 3D-AP measurements shown in Figures 5 and 6, the accumulated ions as mass spectra like Figures 2 and 3 can be the criterion for modeling this system. The mass peaks found in Figures 2 and 3 were assigned to fragments classified by number of C, O atoms. The dissociation preference (probability) was numerically simulated for major peaks which consists of 2–9 C, O atoms in fragment to reproduce the accumulated ion counts for each mass group as summarized in Table 1. Here, the final probability of each bond inside polymer chain is assumed to be determined by the product of two factors such as position (distance) from the terminal atom of chain and bonding atom pair.

The magnitude of local electric field should be determined by the protrusion of each bond from the substrate or PEG layer which forms the macroscopic field distribution around emitter. On the other hand, each covalent bond between C–O, C–C should have the specific probability of bond dissociation according to polarity of the bond.

The model based on above assumption was formulated as follows,

$$\text{bond cleavage probability of each bond } \propto p_{\text{bond}} \times \alpha^n$$

where $p_{\text{bond}}$ is the bond dissociation probability for bond between two atoms, $n$ is the position of bond counted from the outer end of the polymer chain and the probability decreases in proportional to $n$th power of decay parameter $\alpha$ For example, when the sequence of terminal chain is (O) C−C−O−C−O−C−O−(bulk), the dissociation probability is expressed as follows;

$$1 = \text{normalizing factor } \times (p_{C-C} + p_{C-O} \alpha + p_{O-C} \alpha^2 + p_{C-C} \alpha^3 + p_{C-O} \alpha^4 + p_{O-C} \alpha^5 + p_{C-C} \alpha^6 + p_{C-O} \alpha^7)$$

Figure 6: The distribution of the designated ions and the spatial correlation between ions. The same experimental dataset and the coloring as Figure 5 are used here. (a) and (b): the spatial distribution of COH$^+$, C$_2$H$_x^+$ ions (a) and C$_3$O$_x^+$, C$_6$H$_{2x}$ ions (b) extracted from z-axis projection of Figure 5. (c): relative displacement of hit position of detected ions against the precedent ions in the detection sequence. (d): relative displacement of hit position of heavy ions of more than three C, O atoms against the precedent COH$^+$, C$_2$H$_x^+$ ions.

Figure 7: Ion-ion sequential correlation of PEG 1000 data set analyzed by (a) reflectron-AP and (b) 3D-AP.
Table 1: Simulation of stepwise bond dissociation. The mass spectrum of PEG 1000 is numerically simulated using parameters listed in Table 2. Decay parameter α is 0.25 in this result. “Intensity” is the normalized count where each count is divided by the total count.

| No. of C, O atoms | m/z | assignment       | observed | Intensity calculated by |
|-------------------|-----|------------------|----------|-------------------------|
|                   |     |                  |          | set A                           | set B                           |
| 2                 | 28–31| COH\textsubscript{2}+, C\textsubscript{2}H\textsubscript{5}+  | 0.501    | 0.561 0.502               |
| 3, (6)            | 44  | C\textsubscript{2}OH\textsubscript{2}+, C\textsubscript{4}O\textsubscript{2}H\textsubscript{2}+ | 0.290    | 0.325 0.417               |
| (7)               | 51  | C\textsubscript{2}O\textsubscript{2}H\textsubscript{2}+ , C\textsubscript{4}O\textsubscript{2}H\textsubscript{2}+ | 0.031    | 0.02 0.01                  |
| 4, (8)            | 58–60| C\textsubscript{2}OH\textsubscript{2}+, C\textsubscript{4}O\textsubscript{2}H\textsubscript{2}+ | 0.069    | 0.104 0.071               |
| (9)               | 66  | C\textsubscript{4}O\textsubscript{2}H\textsubscript{2}+  | 0.009    | <0.001 <0.001             |
| 5                 | 72–74| C\textsubscript{2}OH\textsubscript{2}+, C\textsubscript{4}O\textsubscript{2}H\textsubscript{2}+ | 0.0082   | 0.009 0.008               |
| 6                 | 88  | C\textsubscript{4}O\textsubscript{2}H\textsubscript{2}+  | 0.018    | 0.005 0.006               |

As the mass peak of single atom ion of CH\textsubscript{4}+, OCH\textsubscript{3}+ were very small, the cleavage at first O–C (or C–C, C–O) bond is neglected. The fragments of m/z > 100 amu are excluded in this model. In a step during simulation, random value from 0 to 1 is generated to determine which bond is cleaved where the probability is proportional to the term \( p_{X-X} \alpha^n \) of the above equation. Let’s suppose that the terms in the above equation have the following values:

\[
1 = \chi \times \left( p_{\text{C-C}} + p_{\text{C-O}} \alpha + \sum_{n=3}^7 p_{X-X} \alpha^n \right)
\]

\( \chi \) is the normalizing factor here. When the randomly generated value is 0.75 which is larger than 0.7 and smaller than 0.8 (= 0.1 + 0.7), the second term \( \chi \times p_{\text{C-O}} \times \alpha \) is selected. In this case, the cleavage occurs at the bond between (O)–C–C– and –O–C–... Hence the bond dissociation probability is proportional to the value of each term \( p_{\text{bond}} \alpha^n \). After the dissociation of the terminal group determined by random value in one step, the probability factors \( p_{X-X} \) are shifted for the next step according to the new atom sequence of the terminal group.

Fragments of the same mass (composition) but have different structures such as C–O–C, C–C–C, and C–C–O which have the same composition C\textsubscript{2}H\textsubscript{4}O\textsubscript{2} are combined in one group in the accumulation. As for the formation of doubly charged ion, no peculiar parameter is used in this model. The ion is assumed to be doubly charged when the ion consists of more than 6 C, O atoms (m/z > 100 amu).

Table 2 shows an example of the numerical simulation when the decay parameter \( \alpha \) of 0.25 and the parameters listed in Table 2 are used. The relative intensities of fragments of 2, 3, and 4 C, O atoms (typed in bold font in Table 1) were used in the search of optimal parameter \( \alpha \) turned out to be the dominant parameter here by the comprehensive search over \( \alpha \) and \( p_{\text{bond}} \), where \( \alpha \) between 0.2 and 0.3 showed a good agreement.

Although the result reproduces the trend of MS of PEG 1000 on prominent mass peaks, it is not reasonable that the exchange of parameter \( p_{\text{C-O}} \) and \( p_{\text{O-C}} \) showed almost the same result. This suggests that this simple model is not simple enough or the difference between the C–O bond and the O–C bond in polymer might be negligible in the field evaporation in this case.

The AP analysis of organic polymer reported here was performed at the room temperature. In the common AP analysis dealing with solid bulk materials, the sample is cooled down to 100 K or lower temperature. The cooling down of the sample suppresses the vibration and the migration of atoms on surface. The former effect suppresses the unfavorable evaporation between the triggers out of ToF sampling window and improves the mass resolution. The latter effect assures the spatial resolution in 3D-AP.

Although the sample cooling is assumed to be essential to AP analysis, where mono atomic ions are the major component in AP mass analysis of bulk solid material such as metals and Si based semiconductors, it seems not suitable for the analysis of organic polymers where cluster ions are commonly detected. The mono atomic ion is minor component in AP analysis of low dimensional organic material in contrast to the bulk solid material. As shown in Figure 2, cluster ions are the major component in the mass analysis of PEG. The local Brownian motion of polymeric chain may cause the unfolding of polymer aggregate supported on metallic tip to promote the field evaporation from protruding terminal. On the other hand, the atomic vibration stimulates the field evaporation so that unfavored evaporation between the triggers out of ToF sampling window and improves the mass resolution. The latter effect assures the spatial resolution in 3D-AP.

Table 2: Bond cleavage parameter \( p \) used in Table 1.

| bond | C–C | C–O | O–C |
|------|-----|-----|-----|
| \( p \) | set A | 0.1 | 0.5 | 0.9 |
| set B | 0.9 | 0.5 | 0.1 |

* Left side atom is located outside of the sample.
atom induced an enhancement of evaporation of surrounding atoms in local scale [10]. In this case, the spatial correlation is extracted from data set of detected ions where the sequential correlation in data set is interpreted as the spatial correlation of depth direction of sample.

To avoid the local enhancement of evaporation during AP analysis, Gotoh et al. reported AP analysis method applying only DC field to sample [11]. Although the detection efficiency of DC method determined by the fraction of sampling window of ToF mass spectrometer is much lower than that of the conventional pulse-evaporation method, the DC method suppresses the preferential detection of ions and depresses the fluctuation of elemental composition.

Although the AP mass analysis of 1D chain polymer was demonstrated to be successful as shown in this report, there are several points which should be cleared for the successful observation of step-by-step bond cleavage to form fragment cluster ions under electric field. In contrast to solid bulk material, data set acquired by 3D-AP shown in Figure 5 should be interpreted not as cross section information (lateral coordinates) like in bulk material analysis but only as angular distribution from the 1D chain. The numerical model presented here based on stepwise bond cleavage reproduces the trend of observed mass spectrum. But the model examined here did not give an explicit set of parameters for the optimization.

For tracing the fragmentation of polymer in every step, the detection efficiency (smaller than 50% in our 3D-AP system) should be improved. Reflectron-AP has a better mass resolution than that of 3D-AP but the acceptance angle might be no significant anisotropy in angular distribution from the 1D chain. The numerical model presented here based on stepwise bond cleavage reproduces the trend of observed mass spectrum. But the model examined here did not give an explicit set of parameters for the optimization.

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V. CONCLUSIONS

The PEG supported on metal tip was successfully analyzed by AP. Although the information obtained by using projection type AP (3D-AP) shows should be evaluated not as structural information as solid state material, the result of PEG analysis by AP could be correlated to its sequential information of 1D polymer. To extend the AP mass analysis to other organic materials, the development of sample fabrication technique is also required.

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