

Paper

Fragment Distribution of Polystyrene by QMD Method Using the Model Hexamer

Koichiro Hayashi,^a Kousuke Moritani,^b Kozo Mochiji,^b Norio Inui,^b and Kazunaka Endo^{c,*}

^a Department of Chemistry (Faculty of Science), Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan

^b Department of Mechanical and System Engineering, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2201, Japan

^c Center of Colloid and Interface Science, Research Institute for Science and Technology, Tokyo University of Science (Private address: Kamitakatsu-shinmachi 2-25, Tsuchiura-city 300-0819, Japan)

*endo-kz@nifty.com

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A quantum molecular dynamics (QMD) due to the force function of MO with the velocity Verlet algorithm using the polystyrene (PS) hexamer was performed to simulate secondary ion mass spectra (SIMS) of the polymer. We assumed that the QMD calculation corresponds to the thermal sputtering process in Sigmund proposal, and tried to analyze experimental mass spectra of PS with size-selected Ar gas cluster ion beam (GCIB) bombardments from the calculated mass spectra, because the Ar GCIB bombardments are considered as the sputtering by elastic collisions proposed by Sigmund. The calculated positive ion mass spectra for PS 6mer from the atomic charge analysis of the fragments at the 5000 MD (2.5 ps) step for total 60 trajectories of 0.77, 0.86 and 0.95 eV energy controls seem to be roughly in accordance with the experimental secondary positive ion results with the Ar⁺ primary ion bombardments. From analysis of energy-dependency (0.43 ~ 1.03 eV) for the PS model in QMD, the calculated relative intensities of fragments (C₂H₂⁺, C₃H₄⁺, C₄H₂⁺, C₆H₄⁺, C₈H₇⁺, C₉H₉⁺) may almost correspond to the experimental E_{atom} dependence of relative yields of fragments (C₂H₃⁺, C₃H₃⁺, C₄H₃⁺, C₆H₅⁺, C₈H₇⁺, C₉H₇⁺).

1. Introduction

Already for organic substances, lots of fundamental experiments [1-3] were performed by secondary ion mass spectrometry (SIMS) using various ion beam bombardment techniques. For these five years, primary cluster and polyatomic ion beam bombarded technologies [4-11] in SIMS have been used to increase secondary ion intensity, and suppress damages to sample molecules. Among cluster ion beam technologies, gas cluster ion beam (GCIB) bombardment techniques [12] have been demonstrated to be very effective for low damage SIMS. Moritani and coworkers have developed SIMS instrumentation in which the cluster size of Ar cluster ions was selected to adjust the kinetic energy per atom of the cluster ion [13]. They investigated secondary ion mass spectra of polystyrene (PS) thin film using a

size-selected Ar GCIB [14], and showed that the PS surface was bombarded with cluster ions involving 480 ~ 4600 Ar atoms, and thus had a low kinetic energy per atom (E_{atom}) between 1.0 and 22 eV. The E_{atom} dependency of secondary ion yield for fragment species of PS could be classified into three types based on the relationship between E_{atom} and dissociation energy of a specific bonding site in PS molecules.

Theoretically, the advanced molecular dynamics (MD) methods with empirical force fields have been quite successful in providing quantitative agreement with high-energy particle bombardment SIMS of organic film adsorbed on a metal substrate [15-18], and the bombardment of a polyethylene crystal [19]. For cluster ion beam bombardment efficiency, Winograd and

coworkers reviewed that SIMS after cluster projectile impact due to Au_3^+ , Bi_3^+ , SF_5^+ , and C_{60}^+ ion sources available commercially results in a radically different sputtering mechanism as the new physics than the linear collision cascades with traditional atomic ion bombarded SIMS technique [20, 21]. Very recent study [22] predicted that the sputtering yield, sputtered species, and damage to the substrate by sputtering from a thin organic PS layer can be controlled using large Ar cluster ions, which suggests that a GCIB could significantly improve the efficiency and performance of SIMS.

On the other hand, from quantum molecular dynamics (QMD) calculations due to the thermal decomposition, our previous works [23–26] compared the calculated fragments to the atomic mass unit of lignin monomers, dimers, and (PE, PS, PET) polymer models with the experimental results of SIMS. The QMD calculations at the ground state were performed by assuming the thermal decomposition process for the cleavage of chemical bonds of organic substances. The calculated fragments to the atomic mass unit of the organic substances were shown to almost correspond to the experimental results of SIMS.

In the present study, we calculated the positive ion mass spectra of PS model by the QMD, and tried to analyze experimental mass spectra of PS due to size-selected Ar GCIB bombardments with the calculated ones, because the Ar GCIB bombardments are considered as the sputtering by elastic collisions proposed by Sigmund [27]. The GCIB bombardments due to majority of neutral charged Ar atoms induce the direct atomic sputtering and excitations of the molecular motion (rotational motion, and vibration) of polymer chains on outer most surface polymers. After that, the scission of polymer bonds and the desorption of a variety of the fragments may occur through the thermal energy transfer sputtering process (as a process of sputtering) in Sigmund proposal. We assumed that the scission and desorption are involved into the thermal decomposition due to our QMD calculation of PS model.

2. Computational Method

In our QMD calculation, we used the velocity Verlet algorithm [28] for the integration of equation of motion with time step of 0.5 fs. The potential energy is given from the interatomic force function as the differential

calculus of the potential energy by quantum chemical calculation. The force function is obtained automatically from the Hartree-Fock SCF MO calculations of model molecules. The thermal decomposition of model oligomer was simulated by using the velocity scaling method [29, 30] with temperature control method [31].

The thermal decomposition of PS polymer has been simulated using the model hexamer molecule $\{\text{H}-(\text{CH}_2\text{CH}(\text{C}_6\text{H}_5))_6-\text{H}\}$ by QMD with semiempirical MO AM1 method [32] at the ground state. The sampling position data were carried out up to 2.5 ps (5000 step) with a time step of 0.5 fs. The theoretical positive, negative, and neutral charged fragments to the atomic mass unit for the polymer model were estimated from the net atomic charge analysis of fragments at the geometry-optimization of n times SCF MO calculations at the 5000 MD step for total 40, or 60 trajectories. The calculated fragment products to the atomic mass unit may be compared with the experimental results in SIMS.

3. Results and Discussion

Let's consider the polymer sputtering process after bombardments of primary inert Ar gas cluster positive ion with a few keV kinetic energy in TOF-SIMS. The bombardments on the outer most surface of the PS polymer sample must be elastic collisions and induce the atomic translational motion and excitations of translational, rotational motion, and vibration as the energy transfer for outer most surface polymers. The scission of bonds and the desorption of a variety of fragments of the polymers through the thermal transfer sputtering process after the bombardment is assumed to correspond to the thermal decomposition process. Thus we are able to compare the calculated positive- or negative-ion fragment spectra of the polymer model in our QMD calculation with the experimental mass spectra in the TOF-SIMS.

3.1 Fragmentation of PS simulated by QMD calculations

By considering the thermal decomposition, we simulated the decomposition of PS 6-mer model by QMD method in order to compare with the experimental result due to bombardments of primary inert gas cluster positive ion with a few keV kinetic energy. As an example of data, Fig. 1 shows the snap shots of the

thermal decomposition of PS model at 0, 0.5, 1.5 and 2.5 ps at 0.77 eV (9,000 K) energy control. The initial molecule $\text{H}-(\text{CH}_2\text{CH}(\text{C}_6\text{H}_5))_6-\text{H}$ cleaves five fragments (C_6H_6 , C_7H_9 , C_9H_9 , $\text{C}_6\text{H}_5\text{CHCCH}_2$, $\text{C}_6\text{H}_5\text{CCH-CH}_2\text{C}_6\text{H}_5\text{CHCH}$) at 0.5 ps, and decomposes 8 components (C_2H_2 , C_3H_3 , C_5H_5 , C_6H_4 , $2\text{C}_6\text{H}_6$, C_8H_8 , C_{12}H_7) at 1.5 ps through deprotonation and reiterative recombination with a H atom, respectively. Fragments at 2.5 ps become 9 components $\{\text{C}_2, \text{C}_2\text{H}_3, \text{C}_3\text{H}_3, \text{C}_6\text{H}_4, \text{C}_6\text{H}_5, \text{C}_6\text{H}_6, \text{C}_7\text{H}_7, \text{C}_8\text{H}_4, \text{C}_8\text{H}_7\}$ at 2.5 ps through deprotonation, and reiterative H recombination, respectively. The deprotonation and H recombination may cause the difference of atomic mass unit of ± 1 for fragmentations.

Table 1 shows the positive, negative, and neutral charged fragments from the net atomic charge analysis at geometry-optimization of n times SCF MO calculations

at the 5000 MD (2.5 ps) step for total 60 trajectories of 0.77, 0.86 and 0.95 eV energy controls (20 trajectories every three different energies). We gave the calculated positive ion spectra from Table 1 into Fig. 2 with experimental positive secondary ion spectra of PS bombarded with Ar^+ ions in Fig 3 a) [14]. The calculated fragments at (39, 40, 41), (50, 51, 52), (75, 76, 77, 78), (89, 90, 91), and (114, 115) amu in Fig. 2 roughly correspond to the experimental results at 39, 51, 77, 91, and 115 amu in Fig. 3 a). In Table 1, we also calculated the neutral, positive, negative charged fragments of PS model as 93.0, 2.6, 4.4 %, respectively. The ratio seems to approximate to the values considered experimentally in SIMS (In general, the vast majority of the sputtered particle flux is neutral, with secondary ions comprising of the order of 1%).

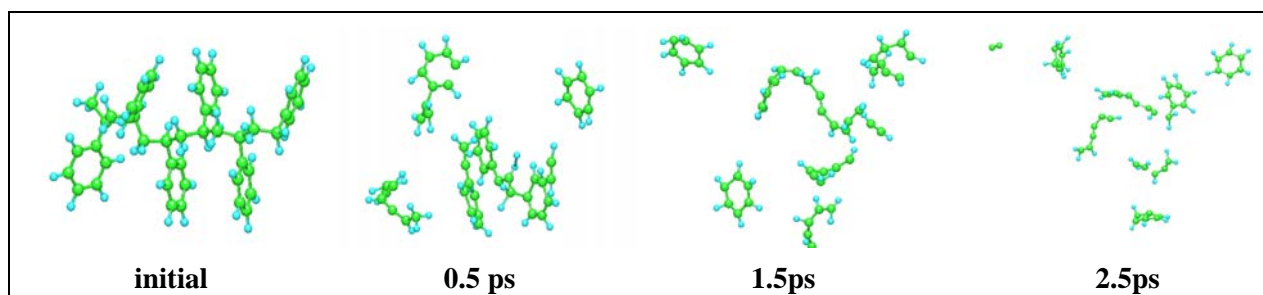


Fig. 1. MD snap shots of PS 6-mer at 0.77 eV.

Table 1. All fragments with the intensity to the atomic mass unit for PS by a QMD calculation using the Hexamer model *
(neutral fragments 93.0 %, positive 2.6 %, negative 4.4 %)

Polystyrene(PS) fragment distributions(total 6235)(ground-state)							
neutral charge fragments			Positive fragments*		negative fragments*		
mass	formula		mass	formula	mass	formula	
	(×25)	127	2C ₁₀ H ₇	14	3CH ₂ ⁺	24	8C ₂ ⁻
14	10CH ₂	128	2C ₁₀ H ₈	15	6CH ₃ ⁺	25	10C ₂ H ⁻
16	2CH ₄	130	C ₁₀ H ₁₀	25	3C ₂ H ⁺	27	2C ₂ H ₃ ⁻
26	27C ₂ H ₂	138	C ₁₁ H ₆	26	3C ₂ H ₂ ⁺	36	7C ₃ ⁻
28	2C ₂ H ₄	140	C ₁₁ H ₈	27	10C ₂ H ₃ ⁺	38	11C ₃ H ₂ ⁻
30	C ₂ H ₆	142	C ₁₁ H ₁₀	29	2C ₂ H ₅ ⁺	39	9C ₃ H ₃ ⁻
36	C ₃	154	C ₁₂ H ₁₀	39	C ₃ H ₂ ⁺	40	6C ₃ H ₄ ⁻
38	17C ₃ H ₂	166	4C ₁₃ H ₁₀	40	9C ₃ H ₄ ⁺	48	19C ₄ ⁻
39	3C ₃ H ₃	181	C ₁₄ H ₁₃	41	6C ₃ H ₅ ⁺	49	20C ₄ H ⁻
40	12C ₃ H ₄	194	2C ₁₅ H ₁₄	49	C ₄ H ⁺	50	C ₄ H ₂ ⁻
50	19C ₄ H ₂	202	C ₁₆ H ₁₀	50	5C ₄ H ₂ ⁺	51	3C ₄ H ₃ ⁻
51	C ₄ H ₃	204	C ₁₆ H ₁₂	51	3C ₄ H ₃ ⁺	60	12C ₅ ⁻
52	11C ₄ H ₄	206	2C ₁₆ H ₁₄	52	C ₄ H ₄ ⁺	62	2C ₅ H ₂ ⁻
54	3C ₄ H ₆	210	C ₁₆ H ₁₈	63	2C ₅ H ₃ ⁺	63	14C ₅ H ₃ ⁻
62	5C ₅ H ₂	216	C ₁₇ H ₁₂	75	8C ₆ H ₃ ⁺	64	6C ₅ H ₄ ⁻
64	6C ₅ H ₄	218	C ₁₇ H ₁₄	76	24C ₆ H ₄ ⁺	66	3C ₅ H ₆ ⁻
66	3C ₅ H ₆	330	C ₂₆ H ₁₈	77	5C ₆ H ₅ ⁺	75	7C ₆ H ₃ ⁻
74	2C ₆ H ₂			78	11C ₆ H ₆ ⁺	77	4C ₆ H ₅ ⁻
75	C ₆ H ₃			89	11C ₇ H ₅ ⁺	87	15C ₇ H ₃ ⁻
76	11C ₆ H ₄			90	C ₇ H ₆ ⁺	88	10C ₇ H ₄ ⁻
77	2C ₆ H ₅			91	C ₇ H ₇ ⁺	89	20C ₇ H ₅ ⁻
78	21C ₆ H ₆			105	C ₈ H ₆ ⁺	91	4C ₇ H ₇ ⁻
86	2C ₇ H ₂			108	4C ₈ H ₉ ⁺	94	4C ₇ H ₁₀ ⁻
88	2C ₇ H ₄			114	3C ₉ H ₆ ⁺	103	12C ₈ H ₇ ⁻
89	C ₇ H ₅			115	6C ₉ H ₇ ⁺	104	C ₈ H ₈ ⁻
90	4C ₇ H ₆			120	C ₉ H ₁₂ ⁺	113	10C ₉ H ₅ ⁻
92	5C ₇ H ₈			202	10C ₁₆ H ₁₀ ⁺	116	4C ₉ H ₈ ⁻
94	2C ₇ H ₁₀			219	C ₁₇ H ₁₅ ⁺	129	2C ₁₀ H ₉ ⁻
98	C ₈ H ₂					138	7C ₁₁ H ₆ ⁻
102	15C ₈ H ₆					158	9C ₁₃ H ₂ ⁻
103	3C ₈ H ₇					162	10C ₁₃ H ₆ ⁻
104	8C ₈ H ₈					164	C ₁₃ H ₈ ⁻
105	C ₈ H ₉					166	C ₁₃ H ₁₀ ⁻
106	2C ₈ H ₁₀					175	5C ₁₄ H ₇ ⁻
117	C ₉ H ₉					192	6C ₁₅ H ₁₂ ⁻
118	C ₉ H ₁₀					203	10C ₁₆ H ₁₁ ⁻

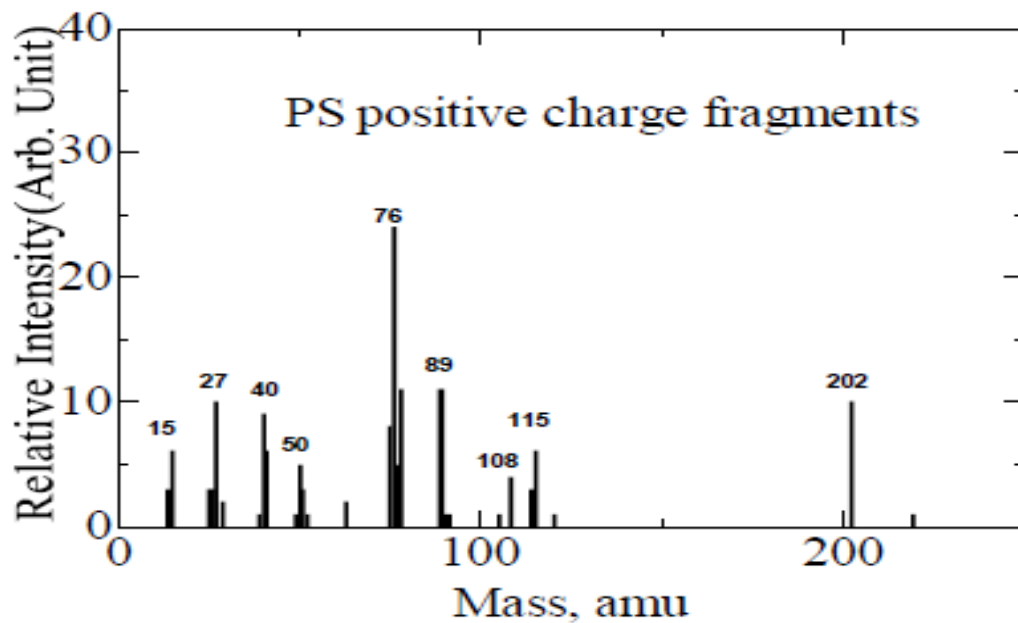


Fig. 2. Calculated positive ion spectra of PS 6mer by QMD calculation

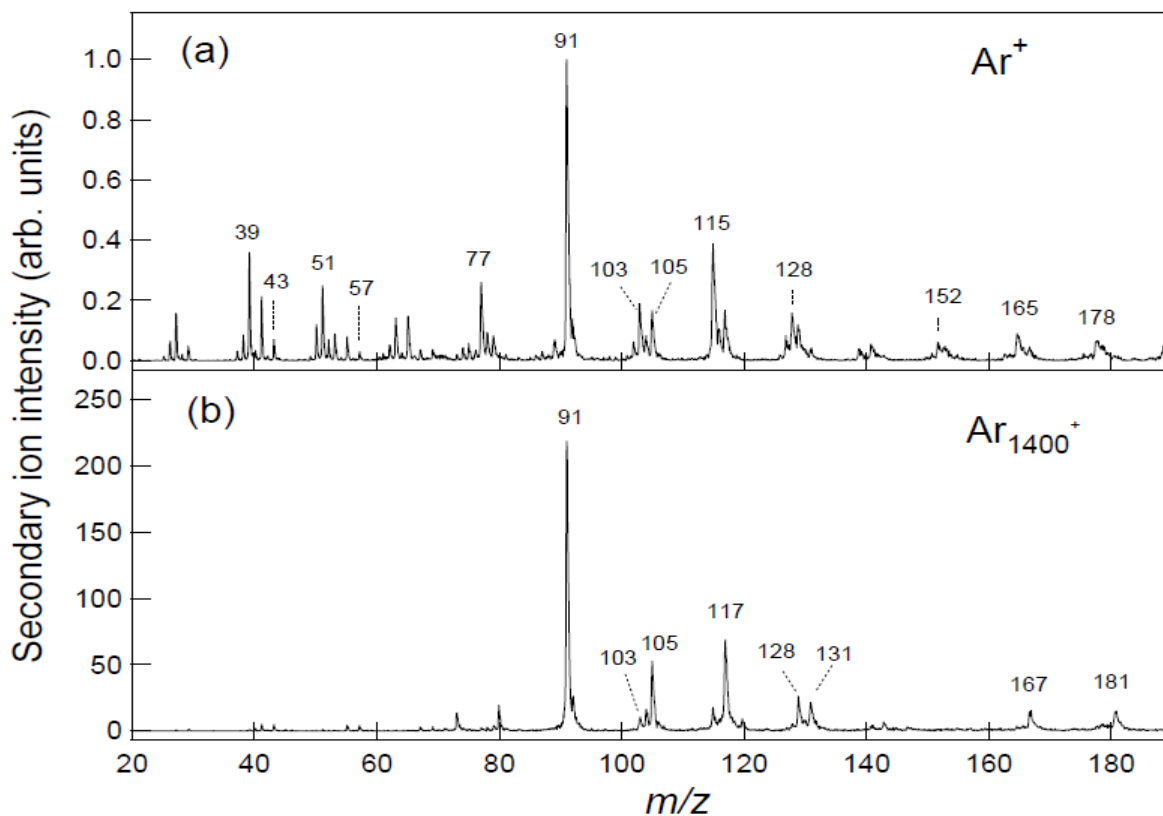


Fig.3. Positive secondary ion spectra of PS bombarded with Ar^+ (a), and Ar_{1400}^+ (b) at an acceleration of 5 keV.

3.2 Energy-dependency for the PS model

The most interesting point is to discuss experimental secondary positive ion fragmentations of PS due to adjusting E_{atom} of 1~ 22 eV (the energy value denotes for the bombardment of an Ar atom in Ar gas clusters ion) using size-selected Ar GCIB in comparison with theoretical results of energy-dependency for the PS model in QMD calculation especially to obtain microscopic pictures in the process.

In order to compare the calculated energy-dependence with the experimental E_{atom} energy, Fig. 4 showed the MD snap shots of PS 6-mer model at 2.5 ps in the energy control range of 0.43 ~ 1.03 eV (5000 ~ 12000 K). It can be shown from the results that decomposed smaller fragments increase with sampling MD data of larger temperature control. In Fig. 5, we plotted theoretical positive ion fragment spectra of the PS model from the

total net atomic charge analysis of all fragments at 5000 MD step for 40 trajectories at three different energy controls of 0.69, 0.86, 1.08 eV (8000, 10000, 12000K), respectively. The net atomic charges of the fragments at each 5000 MD step were obtained with the geometry-optimization from n times SCF MO calculations in AM 1 method. We adopted the positive and negative ions of more than ± 0.05 as the threshold of both charge values. In the comparison of the theoretical positive ion spectra (in Fig. 5) with experimental SIMS results (in Fig. 3), the simulated result at 0.69 eV energy control seems to correspond to the positive secondary ion spectra in the amu range of 91~ 181 in Fig. 3b (with Ar_{1400}^+ primary ion bombardments), while the result at 1.08 eV energy control almost approximates to the experimental one in the amu range of 0 ~ 128 in Fig. 3a (with Ar^+ primary ion bombardments).

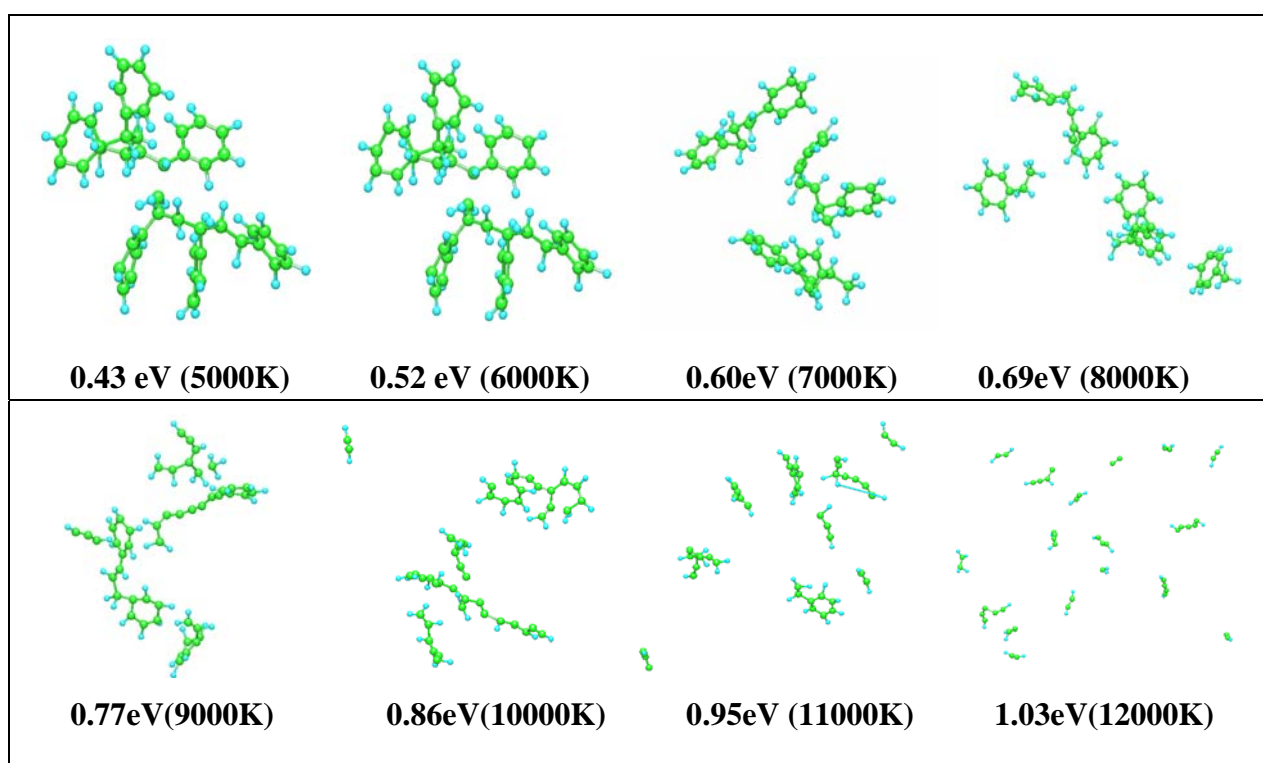


Fig. 4. MD snap shots of PS 6-mer model at 2.5 ps in the energy range of 0.43 ~ 1.03 eV (5000 ~ 12000K).

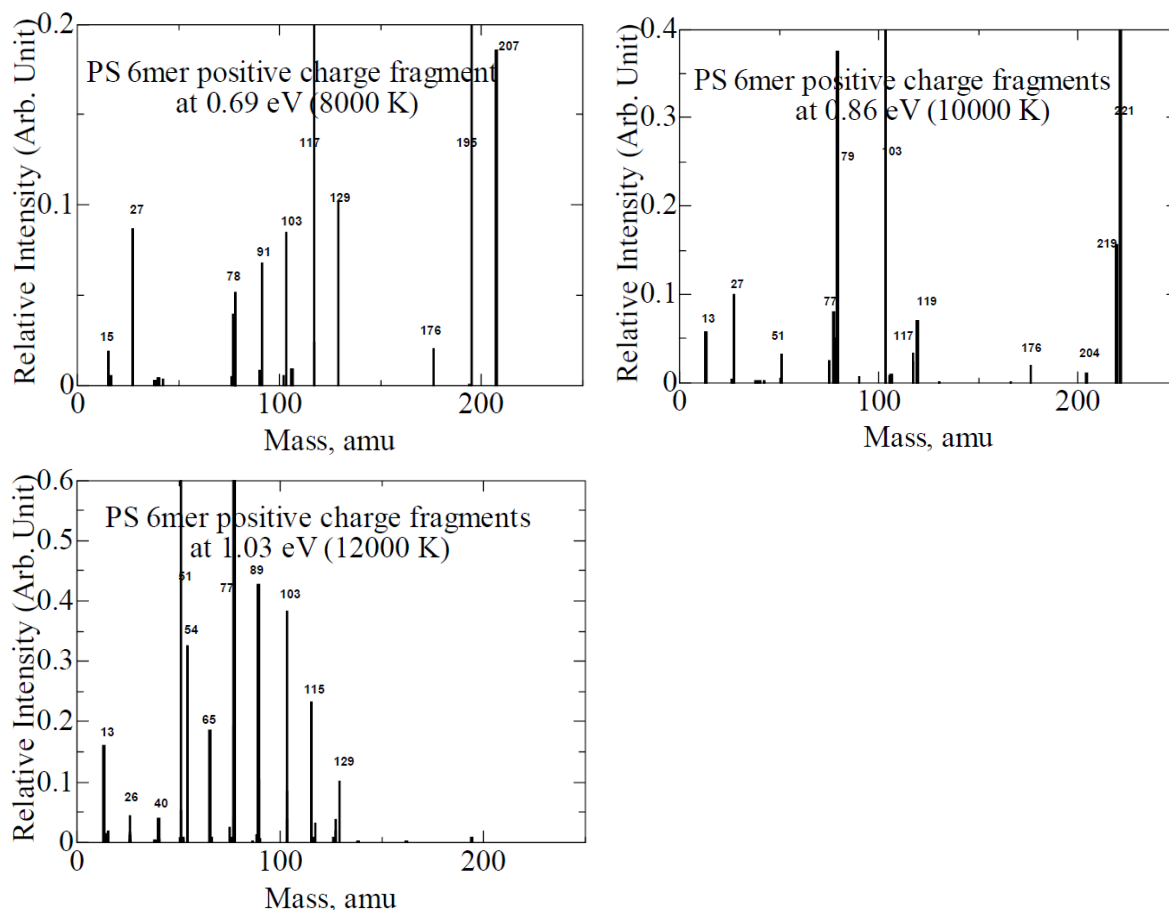


Fig. 5. Theoretical positive ion spectra of PS 6mer model from the total net atomic charge analysis of all fragments for 40 trajectories at three different energy (0.69, 0.86, 1.08 eV) controls.

Furthermore, in the QMD calculation, we examined the energy dependency (0.69 ~ 1.12 eV (8000 ~ 13000 K)) of the relative intensity for six species of fragments $\{C_2H_2^+(26), C_3H_4^+(40), C_4H_2^+(50), C_6H_4^+(76), C_8H_7^+(103), C_9H_9^+(117)\}$ in Fig. 6, in order to compare the experimental E_{atom} dependence of relative yields of several fragments $\{C_2H_3^+(27), C_3H_3^+(39), C_4H_3^+(51), C_6H_5^+(77), C_8H_7^+(103), C_9H_7^+(115)\}$ with 1~22 eV Ar energy/atom bombardments in Fig. 7. The relative intensity of $C_2H_2^+$, and $C_4H_2^+$ fragments in Fig. 6 occurred from scission of C-C bonds in phenyl groups are seen to decrease with total energy (temperature) of the thermal bath, and the tendency seems to match

similar experimental fragments $C_3H_3^+$, and $C_4H_3^+$ in Fig. 7. The calculated result of fragments for $C_3H_4^+$, $C_8H_7^+$, and $C_9H_9^+$ due to cleavages of main chain C-C bonds in PS model may be almost flat to the temperature, as seen in experimental results of fragments ($C_2H_3^+$, $C_6H_5^+$, $C_8H_7^+$). For the $C_6H_4^+$ fragment, the energy dependence with the temperature seems to be an intermediate case between both dependencies in the fragment $C_9H_7^+$ of Fig. 7. The calculated results roughly approximate to the experimental E_{atom} dependence of relative yields of several fragments with 1~22 eV Ar energy/atom bombardments in Fig. 7.

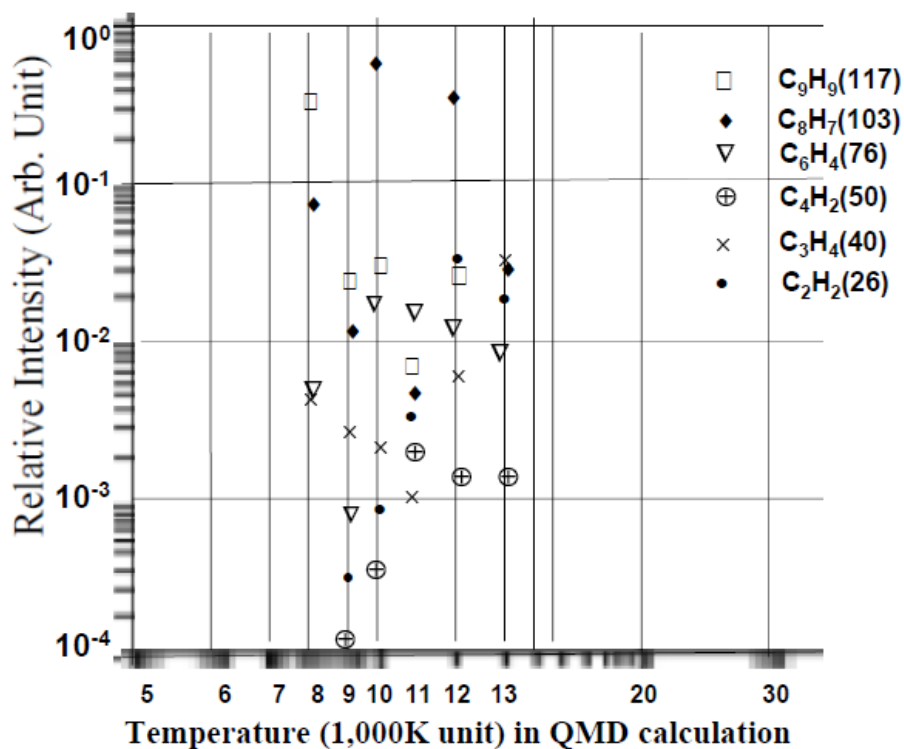


Fig. 6. Calculated energy dependency of the relative intensity for six species of fragments in QMD calculation.

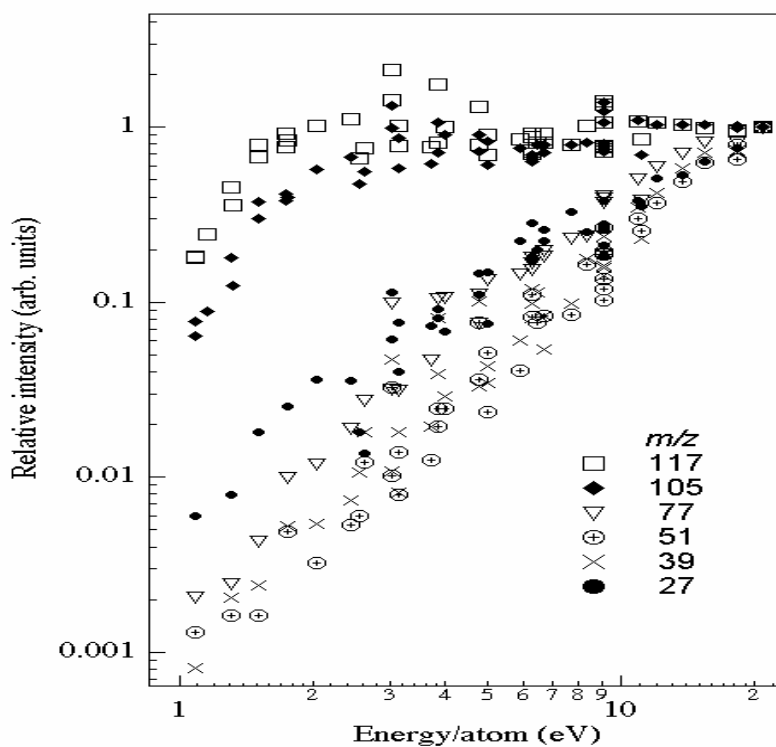


Fig.7. Experimental E_{atom} dependence of relative yields of several fragments with 1- 22 eV Ar energy/atom bombardments

4. Conclusion

Theoretical positive ion spectra of PS polymer model in a QMD under the thermal decomposition were compared with positive secondary ion ones using size-selected Ar GCIB bombardments with a low kinetic energy per atom (E_{atom}) between 1 ~ 22 eV. Assuming that the QMD calculation corresponds to the thermal sputtering process in Sigmund proposal, we used the QMD due to the force function of MO with the velocity Verlet algorithm. The theoretical positive, negative, and neutral charged fragments to the atomic mass unit for the polymer model were estimated from the net atomic charge analysis of the fragments at the final MD steps of total 40 or 60 trajectories. Thus, we obtained the following things:

(1) The calculated positive, negative, and neutral charged fragment mass spectra for PS 6mer are obtained as 93.0, 2.6, 4.4 %, respectively.

(2) The positive ion mass spectra at the 5000 MD (2.5 ps) step for total 60 trajectories of 0.77, 0.86 and 0.95 eV energy controls roughly approximate to the experimental secondary positive ion fragments of Ar^+ primary ion bombardment.

(3) From energy-dependency (0.43 ~ 1.12 eV) of the PS model in QMD calculation, the calculated relative intensities of several fragments (C_2H_2^+ , C_3H_4^+ , C_4H_2^+ , C_6H_4^+ , C_8H_7^+ , C_9H_9^+) almost correspond to the experimental relative yields of similar fragments (C_2H_3^+ , C_3H_3^+ , C_4H_3^+ , C_6H_5^+ , C_8H_7^+ , C_9H_7^+) due to E_{atom} dependence using size-selected Ar GCIB bombardments with a low kinetic energy per atom (E_{atom}) between 1 ~ 22 eV.

Finally, we describe that we need to perform the QMD calculations more than 60 trajectories with energy control of 0.68, 0.77, 0.86, 0.95, and 1.03 eV, respectively, in order to reproduce fragment spectra by the size-selected Ar GCIB bombardments with a low kinetic energy per atom.

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査読コメント

査読者 1. 青木学聡(京都大学)

SIMS の新しい応用分野である有機材料を取り上げ、そのイオン照射による分解機構を調べるという意欲的な研究であると拝見いたしました。ただし、定性的、定量的に実験結果を説明できる部分、更なる仮定や条件付けが求められる部分、の切り分けが多少不明瞭に感じられます。その部分を補強するようお願いいたします。

[査読者 1-1]

PS 6mer の熱分解温度、フラグメントパターンは実験的に調べられているのでしょうか。refs 23-26 は SIMS データとの比較とみうけますが、イオン衝突以外の励起過程に先行事例があるならば触れていただきたいと思えます。

[著者]

PS-6mer の熱分解温度は 700K ぐらいと考えられますが、そのフラグメントパターンは、実験的にはまだ未報告です。refs23-26 では、やはりモデル分子の MO 計算は基底状態が中心ですので、Introduction に基底状態の QMD 計算と加えました。

The QMD calculations at the ground state were

performed by assuming the thermal decomposition process for the cleavage of chemical bonds of organic substances.

[査読者 1-2]

Table1 は 0.78eV, 0.86eV, 0.95eV の結果すべてをまとめたものでしょうか。

[査読者 1-3]

3.1 節の”The calculated positive ion spectra for PS 6er in fig.2 approximate to the experimental spectra of Fig. 3a”は Fig3 の実験結果の表記に倣って Table1 を整理したという意味でしょうか。

[著者]

非常に貴重なご指摘のコメントを纏めて答えさせていただきます。確かに不明瞭でしたので、この部分を書き直しました。3.1 節の以下の文をご参考下さい。また改訂版では Table1 の後に Figs.2,3 を表示しました。

Table 1 shows the positive, negative, and neutral charged fragments from the atomic charge analysis at geometry-optimization of n times SCF MO calculations at the 5000 MD (2.5 ps) step for total 60 trajectories of 0.77, 0.86 and 0.95 eV energy controls (20 trajectories every three different energies). We gave the calculated positive ion spectra from Table 1 into Fig. 2 with experimental positive secondary ion spectra of PS bombarded with Ar⁺ ions in Fig 3 a) [14]. The calculated fragments at (39, 40, 41), (50, 51, 52), (75, 76, 77, 78), (89, 90, 91), and (114, 115) amu in Fig. 2 roughly correspond to the experimental results at 39, 51, 77, 91, and 115 amu in Fig. 3 a). In table 1, we also calculated the neutral, positive, negative charged fragments of PS model as 93.0, 2.6, 4.4 %, respectively. The ratio seems to approximate to the values considered experimentally in SIMS (In general, the vast majority of the sputtered particle flux is neutral, with secondary ions comprising of the order of 1%.

[査読者 1-4]

3.2 節の Energy-dependency for PS model の部分で E_{atom} が 1~22eV とありますが、これは衝突する Ar クラスターの 1 原子あたりのエネルギーをさすものでしょうか。

[著者]

ご指摘のとおりで、3.2 節に以下の文章を書き加えました。

“due to adjusting E_{atom} of 1~ 22 eV (the energy value

denotes for the bombardment of an Ar atom in Ar gas clusters ion)"

[査読者 1-5]

つづいてエネルギーが 0.43 ~ 1.03eV (5000 ~ 12000K)の間での分解過程を調べていますが、これと、上記の E_{atom} との関連はあるのでしょうか。

[著者]

モデル分子の熱分解エネルギー依存性のフラグメントが、実験の E_{atom} エネルギー依存によって検出されるフラグメントと対応させるために行いました。3.2 節 2 つ目の段落の書出しに以下の文を加えました。

In order to compare the calculated energy-dependence with the experimental E_{atom} energy, Fig. 4 showed the MD snapshots of PS 6-mer model at 2.5 ps in the energy control range of 0.43 ~ 1.03 eV (5000 ~ 12000 K).

[査読者 1-6]

Fig.5 の 'the net atomic charge analysis' とはどのような操作をさすのでしょうか。

[著者]

分子軌道計算プログラムでは、SCF 計算が収束すると結果の中に各フラグメントの net atomic charge が算出されますので、これを拾い出して 40 又は 60trajectories 分を合計して中性電荷、正電荷、負電荷フラグメントを出しています。説明としては、3.2 節に以下の文章を書き加えました。

The net atomic charges of the fragments at each 5000 MD step were obtained with the geometry-optimization from n times SCF MO calculations in AM 1 method. We adopted the positive and negative ions of more than ± 0.05 as the threshold of both charge values.

[査読者 1-7]

Fig.5 の一部の強度がグラフ枠の上限を超えているのですが、問題ないのでしょうか

[著者]

本稿では、フラグメント強度の小さいものを引立たせるために作成しましたので、問題ないと思います。

[査読者 1-8]

Fig.5 (0.86eV) のグラフが Fig.2 (0.78, 0.86, 0.95 の総計?) と大きく異なるように見えます。Fig.5 でのメジャーコンポーネントが 103, 221, 79 あたりに見られるが、Fig.2 では 76, 89, 202 となっている、Relative intensity の意味づけが違う、等

[著者]

ご指摘の強度分布の違いは、Fig.5(0.86eV)はこのエネルギーで 40trajectories を合計し、Fig.2 は 0.77, 0.86 と 0.95 eV のエネルギー計算のそれぞれ 20trajectories を合計して 60trajectories から得たフラグメントの強度分布ですので違いは出て来ます。

[査読者 1-9]

Fig.5(シミュレーション)と Fig.3(実験)との比較、考察として

- ・クラスター衝突では、0.69eV, $m=91\sim 181$ の範囲に一致が見られる
- ・単原子衝突では、1.03eV, $m=0\sim 128$ の範囲に一致が見られる

としていますが、本来ならばすべての質量レンジにわたってそのスペクトル形状の一致、不一致を検討すべきではないでしょうか。

[査読者 1-10]

0.69~1.03eV のデータをみますと、0.69eV より低エネルギーである 0.43eV の方が、Ar クラスターの衝突を再現するように予測されますが、そのような結論は得られなかったのでしょうか。

[著者]

ご指摘の 2 つのコメントに対して纏めて答えさせていただきます。確かにすべての質量レンジにわたってスペクトル形状を計算すべきですが、著者らが使用しているデスクトップの容量依存 (1trajectory5000MDstep の QMD 計算は約 7 時間) を考えて simulation しています。PS は、主鎖とペンダントフェニル基では結合エネルギーが 1.5 倍ほど違いますし、結合エネルギー計算から熱分解で切断されて出て来るフラグメントも定性的には簡単に予想できます。このような予想のもとに分解のエネルギー依存性を調べて実験と比較致しました。

それから、Ar クラスターの衝突を再現するには、Fig.4 を見て頂ければ、0.69eV 以下のエネルギーでは、質量が 200 以上のフラグメントばかり算出されますので、この QMD 計算では 0.69eV が低エネルギーと対応させることが出来ました。

[査読者 1-11]

Fig.6 Fig.7 の比較について、Relative Intensity 規格化方法が異なるように見えますが、問題ないでしょうか。

実験結果では、 $m\leq 77$ と $m\geq 105$ でエネルギー依存性に大きな違いが見られます。このような傾向を今回のシミュレーション結果から説明することは可能でしょうか。

[著者]

QMD 計算での算出した正・負電荷のフラグメントの閾値を本文にも(We adopted the positive and negative ions of more than ± 0.05 as the threshold of both charge values.)と書き加えましたように、 ± 0.05 としましたので、実験の相対強度と規格化は異なりますが、比較議論は出来ます。図6と図7の比較では、 $m \leq 77$ と $m \geq 105$ は $m=77$ を境として定性的説明が出来ていると考えられます。もう少し計算データを加えれば、このようなシミュレーション結果から説明可能と考えています。

[査読者 1-12]

結論部分(2)について、フラグメントスペクトルは Ar^+ に近いとしておりますが、 Ar クラスターによるフラグメントスペクトルを再現するために必要な条件とはどのようになるかと予想されるでしょうか。(コメント1-10とも重複しますが)

[著者]

結論部分(2)が曖昧でしたので以下のように書き加えました。

The positive ion mass spectra at the 5000 MD (2.5 ps) step for total 60 trajectories of 0.77, 0.86 and 0.95 eV energy controls roughly approximate to the experimental secondary positive ion fragments of Ar^+ primary ion bombardment.

それから Ar クラスターによるフラグメントスペクトルを再現する為には、この QMD 法では 0.69, 0.77, 0.86, 0.95, 1.03 の各エネルギーでそれぞれ 60 Trajectories 以上の計算を行えば再現可能と思われる。

そこで本文結論の最後に、以下を書き加えました。

Finally, we describe that we need to perform the QMD calculations more than 60 trajectories with energy control of 0.68, 0.77, 0.86, 0.95, and 1.03 eV, respectively, in order to reproduce fragment spectra by the size-selected Ar GCIB bombardments with a low kinetic energy per atom.

査読者 2. 眞田則明(アルバック・ファイ)

著者らは、工業的に重要なポリマーの一つであるポリスチレンの TOF-SIMS スペクトルを、量子化学的手法によってシミュレートした熱分解イオン化のエネルギー(温度)依存性と、 Ar GCIB による TOF-SIMS とを比較して議論している。

クラスターイオンを用いたソフトなイオン化は、

TOF-SIMS ポリマー分析における議論の焦点の一つとって過言ではない。エネルギーの低い一次イオンによる有機物のスパッタリングと二次イオン生成を分子動力学などで計算するのは困難であり、本論分は TOF-SIMS の可能性に有益な議論を提供しており、掲載の価値が十分にある。

なお、以下の点について詳しい議論を提供いただければ、読者の理解がさらに進むと考えます。

[査読者 2-1]

第一節末尾、We think the scission and desorption seem to correspond to our QMD calculation of PS model. の一文は、一般の読者に対して十分に説明されていないと感じます。scission について、Sigmund のスパッタリング過程の予言と Ar GCIB 一次イオンによる TOF-SIMS スペクトルとの関連を著者がどのように考えているのか、わかりやすく記していただけませんか？ また、desorption については、この論文の中であまり議論されていないと思いますが、ここではどのような主張をなされているのでしょうか？

[著者]

著者らは、Sigmund のスパッタリング過程及び Ar GCIB 一次イオンによる TOF-SIMS スペクトルは弾性衝突によって熱伝達エネルギーで PS ポリマーの結合解離によるフラグメントの生成やそれを含むものとその他オリゴマーが脱着すると考えています。この QMD 計算の熱分解では、 Ar GCIB 一次イオンの PS ポリマーへの衝突後の結合解離によるフラグメントの生成やそれを含むものとその他オリゴマーが脱着したフラグメントすべてが、PS-6mer の熱分解過程にすべて含まれるという仮定から出発しています。充分明解ではないですが、1 章の最後を以下のように書換えました。

After that, the scission of polymer bonds and the desorption of a variety of the fragments may occur through the thermal energy transfer sputtering process (as a process of sputtering) in Sigmund proposal. We assumed that the scission and desorption are involved into the thermal decomposition due to our QMD calculation of PS model.

[査読者 2-2]

実験結果(Fig.7)から議論される質量数{117, 105, 77, 51, 39, 27}と著者の計算結果(Fig.6)で議論される質量数{117, 103, 76, 50, 40, 26}には、それぞれ-1~+2の違いがあります。何故この質量数の正イオンを選ばれたのか、詳しく議論していただけませんか？

[著者]

有機化合物分子の水素原子と炭素との結合エネルギーは、炭素間結合のエネルギーより低いのでその脱離と再結合は頻繁に起こります。QMD 計算では少し強調されるかもしれませんが、実験結果との差が-1 から +2 の違いがでるわけです。3.1 節に追加した以下の文で理解して頂けると幸いです。

The initial molecule $\text{H}-(\text{CH}_2\text{CH}-(\text{C}_6\text{H}_5))_6-\text{H}$ cleaves five fragments (C_6H_6 , C_7H_9 , C_9H_9 , $\text{C}_6\text{H}_5\text{CHCCH}_2$, $\text{C}_6\text{H}_5\text{CCH-CH}_2\text{C}_6\text{H}_5\text{CH-CH}$) at 0.5 ps, and decomposes 8 components (C_2H_2 , C_3H_3 , C_5H_5 , C_6H_4 , $2\text{C}_6\text{H}_6$, C_8H_8 , C_{12}H_7) at 1.5 ps through deprotonation and reiterative recombination with a H atom, respectively. Fragments at 2.5 ps become 9 components $\{\text{C}_2$, C_2H_3 , C_3H_3 , C_6H_4 , C_6H_5 , C_6H_6 , C_7H_7 , C_8H_4 , $\text{C}_8\text{H}_7\}$ at 2.5 ps through

deprotonation, and reiterative H recombination, respectively. The deprotonation and H recombination may cause the difference of atomic mass unit of ± 1 for fragmentations.

[査読者 2-3]

I.S. Gilmore, M.P. Seah, Appl. Surf. Sci., 161 (2000) 465-480 は、ポリスチレンの TOF-SIMS スペクトルの解釈の点で Delcorte[18]と並ぶ重要な指摘を含んでいると考えます。読者の便宜のために引用されることを願います。

[著者]

Gilmore さんと Seah さんの素晴らしい研究と思いますが、今回の Intro の流れの中で引用箇所がありませんでした。