Spectral Analysis of Eight Polymers in SIMS by MO Calculation. Prediction of Cleavage of Polymers and Structural Formula of the Positive-Ion Fragment

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ABSTRACT: Spectra of eight polymers $[(CH_2-CHR)_n]$ ($R=H, OH, F, Cl, OCH_3$, and $CONH_2$), $(CF_2-CF_2)_n$ and $(CH_2-CHCN)_n$ in time-of-flight (TOF)- and static(S)-secondary ion mass spectrometry (SIMS), respectively, were analyzed by semiempirical and *ab initio* molecular orbital (MO) calculations. We predicted where the cleavage of the polymers occurs on sputtering, due to two-center bond energies of the model pentamers by a semiempirical MO calculations using AM1 program; a) the cleavage can occur in any bonds (polyethylene, poly(vinyl methyl ether), polyacrylonitrile), b) the cleavage of the main chain occurs in any bonds, after side chain groups cleaved first (poly(vinyl chloride), poly(acrylamide)), c) the main chain carbons with the side chain group cleave at any bonds of the main chain (poly(vinyl fluoride), poly(tetrafluoroethylene), poly(vinyl alcohol)). We also determined the possible structural formulas of the secondary positive-ion fragments in the range of 0–100 amu by *ab initio* MO calculations using the HONDO7 program.

KEY WORDS Secondary Ion Mass Spectroscopy (SIMS) / *Ab Initio* and Semiempirical Molecular Orbitals
/ Positive Secondary Ions / Bond-Order / Polymer /

Time-of-flight secondary ion mass spectrometry (TOF SIMS) has become a powerful tool for studying polymer surfaces. TOF-SIMS provides a direct method of determining the mass resolved image on the order of micron along cross section of different polymers and other material/polymer blends. On the other hand, information^{1–5} of basic chemical analysis obtained from TOF SIMS includes monomer molecular weight, fragmentation patterns, molecular weight distribution of oligomers and spectra characteristic of a specific polymer family. However, there is no study about spectral analysis of polymers in SIMS by molecular orbital (MO) calculations, since the emission process of secondary ions, atoms or molecules on sputtering is very complicated. In a part of the previous work,⁶ we demonstrated that the cleavage of polymer-bond for polypropylene, polystyrene and poly(methyl methacrylate) could be predicted, as follows; bond-orders of the model 5- or 3-mers from semiempirical MO calculations.

This is a comprehensive study on prediction of the cleavage of bonds for polymers (polyethylene (PE), poly(vinyl alcohol) (PVA), polyacrylonitrile (PAN), poly(vinyl fluoride) (PVF), poly(vinyl chloride) (PVC), poly(vinyl methyl ether) (PVME), poly(acrylamide) (PAM), and poly(tetrafluoroethylene) (PTFE)) on sputtering in SIMS due to bond-orders (or two-center bond energies) of the model pentamers from semiempirical MO calculations using AM1 program.⁷ The cleavage sites of bonds were estimated from the size of two-center bond energies. We were thus able to classify the cleavage of the polymer

bonds into three cases. We also determined the possible structural formulas of the secondary positive-ions by *ab initio* MO calculations using HONDO7 program.⁸

MO CALCULATIONS

The electronic structures of model pentamers $[H-(CH_2-CHR)_5-H]$ ($R=H, OH, CN, F, Cl, OCH_3$, and $CONH_2$), $F-(CF_2-CF_2)_5-F$ were based on using a semiempirical AM1 program (version 6.0). Bond-orders and two-center bond energies⁹ of the model pentamers of (PE, PVA, PAN, PVF, PVC, PVME, PAM, PTFE) polymers were obtained from optimized results by the energy gradient method.

The electronic structures of the fragment positive-ions for eight polymers were obtained by *ab initio* calculations using the HONDO7 program. For the geometry of the fragment positive ions, we used optimized cartesian coordinates from the AM1 program. In the *ab initio* calculations, we used a restricted Hartree-Fock (RHF)/4-31G basis set for H, C, N, O, F, and Cl atoms.

EXPERIMENTAL

Materials

We used commercially-available polyethylene (PE) (Aldrich Chemical Co., Inc.; high density), poly(vinyl alcohol) (PVA) (Wako Pure Chemical Industries, Ltd.; M_w 22000), poly(vinyl fluoride) (PVF) (Scientific Polymer Products, Inc.), poly(vinyl chloride) (PVC) (Aldrich

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Chemical Co., Inc.; M_w 83500), poly(vinyl methyl ether) (PVME) (Scientific Polymer Products, Inc.), poly(acrylamide) (PAM) (Aldrich Chemical Co., Inc.), and poly(tetrafluoroethylene) (PTFE) (Scientific Polymer Products, Inc.).

Samples were prepared by cast-coating the polymer solution on an aluminium plate, while methyl ethyl ketone and water were used for PVC and (PVA, PVME, PAM) polymers, respectively. For PE, PVF, and PTFE, we used the film or the pressed disc. The film was found to be a few tens of micrometers thick. For PAN, we cite results using static SIMS measurements.¹⁰

TOF SIMS Measurements

We used a PHI TOF SIMS TFS-2000 spectrometer with a primary Ga^+ ion beam (12 keV Ga^+ , pulse with 13 ns, repetition rate 10 kHz, primary ion current of 700–800 pA measured as a continuous beam). The generated secondary ions were accelerated to 3 keV. The intensity changes of the given ion species during the irradiation of the primary ion beam (denoted as dose profiles) were evaluated through an ion dosage up to 2.5×10^{12} ions cm^{-2} . A new charge compensation system, based on a low-energy electron source (10 eV) and a pulsed extraction field of the mass analyzer, provides a self-adjusting surface potential for all kinds of insulators in positive and negative SIMS modes. In the present work, we used the positive and negative modes except for the PAN polymer.

RESULTS AND DISCUSSION

Cleavage and Secondary Ion Mass Spectra of Polymers

Let us consider a simplified process related to the emission of a fragment ion from solid polymer surface. When a polymer sample is bombarded by ions of a few ten keV kinetic energy, an impact cascade and excited

area are created around the point of primary particle impact through energy and momentum transfer from the bombarding particles to solid polymer. Fragment ions are then formed by dissociation of sputtered neutral molecular species. Surface fragment ions are thus emitted, if a sufficient amount of energy is transferred. The results of the dissociation of PP, PS, and PMMA polymers, as shown in previous work,⁶ seem to correspond to the thermal decomposition in Mass Spectrometry.

In the previous work, we obtained positive-ion fragment spectra of three polymers in the mass range of 0–100 amu. The fragment spectra seemed quite simple. We predicted where the cleavage of the polymers occurs on sputtering, although the emission process of secondary ions, atoms or molecules on sputtering is very complicated. We estimated the cleavage sites of polymer-bonds for eight polymers from the size of the bond-orders and two-center bond energies of the model pentamers by the semiempirical AM1 program (in Figure 1).

In Figure 1, the two-center bond energies of PE, PVME and PAN models in any atom-atom bonds without considering the C–H bonds are similar: 0.99–1.00 (14.0–14.2 eV), 0.96–0.99 (13.7–14.0 eV), and 0.96–0.98 (13.8–14.0 eV), respectively. We can, thus, see that the cleavage of the polymer-bonds occurs at any bonds.

For PVC and PAM, the two-center bond energies of C–Cl and C–CO(NH₂) showed 10.8 and 13.1 eV less than 14.3 and 14.0 eV for main chain C–C bonds, respectively. Thus, cleavage of the main chain of the polymers yield, after side chain groups (C–Cl and C–CO(NH₂)) cleaved first.

In Figure 1, the two-center bond energies of the main chain C–C bonds of PTFE were evaluated as 12.0 eV, thus being much less than 17.2 eV of C–F bonds. For PVA, the main chain bonds were estimated as 14.0 eV slightly less than 14.3 eV of C–OH bonds. In the case of PVF model, the two-center bond energies of the main

Figure 1. Bond-orders and two-center bond energies (in eV) of the pentamers of eight polymers by the semiempirical MO calculations using the AM1 program.

Figure 2. (a) Bond-orders and bond energies (in eV) of the pentamer of PE by semiempirical MO calculation using AM1 program (upper); positive and negative ions TOF-SIMS spectra of PE in the range of 0–100 amu. (b) Bond-orders and bond energies (in eV) of the pentamer of PVME by semiempirical MO calculation using AM1 program (upper); positive and negative ions TOF-SIMS spectra of PVME in the range of 0–100 amu.

Figure 3. Bond-orders and bond energies (in eV) of the pentamer of PAN by semiempirical MO calculation using AM1 program (upper); positive-ion S-SIMS spectra of PAN in the range of 0–100 amu.

chain C–C bonds are 14.0 eV much less than 16.4 eV of C–F bonds. We can assume that the cleavage of the PTFE, PVA, and PVF polymers occurs at any bonds of main chain with side chain groups.

Cleavage thus occurs as: (a) at any bonds, as shown in PE, PVME, and PAN; (b) cleavage of the main chain occurs at any bonds, after side chain groups cleaved first, as indicated in PVC and PAM; (c) the cleavage of main chain carbon with the side chain group occurs at any bonds of main chain, as shown for PVF, PTFE, and PVA. Therefore, we analyzed the positive- and negative-ion fragment spectra of the polymers in TOF-SIMS from the prediction of the cleavage for polymer-bond due to the two-center bond energy.

For PE (Figure 2a), there are many species of positive-ion fragment spectra in the mass range of 0–100 amu. This seems to correspond to cleavage at any atom-atom bonds in case a). We observed six high intense positive-ion fragments, C_2H_3^+ (27), C_2H_5^+ (29), C_3H_3^+ (39), C_3H_5^+ (41), C_3H_7^+ (43), and C_4H_7^+ . The negative-ion fragment consists of $\cdot\text{C}^-$ (12), the most high intense line CH^- (13), $\cdot\text{CH}_2^-$ (14), OH^- (17), and C_2H^- (25) which are considered stable.

In the case of PVME and PAN, many species of positive-ion fragment spectra were observed in the mass range of 0–100 amu (Figures 2(b) and 3), since the cleavage of the polymer-bonds between carbon, oxygen, cyanogen and carbons occurs at any atom-atom bonds. The former involves O-containing spectra of CHO^+ (29) (For mass 29 amu, we obtained two fragments for the intense ratio of 2.4/1.1 for $\text{CHO}^+/\text{C}_2\text{H}_5^+$), $\text{C}_2\text{H}_3\text{O}^+$

(43), $\text{C}_2\text{H}_5\text{O}^+$ (45), $\text{C}_3\text{H}_7\text{O}^+$ (59), $\text{C}_4\text{H}_7\text{O}^+$ (71), $\text{C}_3\text{H}_7\text{O}_2^+$ (75), and $\text{C}_3\text{H}_9\text{O}^+$ (85), while the latter does the N-containing fragments of $\cdot\text{N}^+$ (14), $\cdot\text{CN}^+$ (26), $\text{C}_3\text{H}_2\text{N}^+$ (52), and $\text{C}_3\text{H}_4\text{N}^+$ (54). For the negative-ion spectra of PVME, we obtained $\cdot\text{C}^-$ (12), CH^- (13), $\cdot\text{O}^-$ (16), OH^- (17), and C_2H^- (25) as stable fragments.

For PVC in Figure 4(a), the positive-ion fragment spectra are very similar to those of hydrocarbon polymer (PE) in Figure 2(a). This implies that remainder polymer chains consist of carbon and hydrogen atoms, since the Cl atom changes stable Cl^- s after the side chain atom Cl cleaved first. This is based on the finding that the two-center bond energies of 10.8 for C–Cl are much less than 14.3 for main chain C–C bonds of PVC. Thus, the negative-ion fragment spectra have intense isotope Cl^- s (35 and 37) in Figure 4(a). In the case of PAM in Figure 4(b), we see a little different mass spectra from hydrocarbon polymers. The cleavage of the polymer-bonds may yield in a little complicated process, because the two-center bond energy of C–CO(NH₂), 13.1 eV, is slightly less than that of main chain C–C bonds, 14.0 eV. Thus, the positive-ion fragments involving N and O atoms are CH_2N^+ (28), $\text{C}_2\text{H}_3\text{O}^+$ (43), $\text{C}_4\text{H}_5\text{O}^+$ (69), and $\text{C}_3\text{H}_7\text{NO}^+$ (73). In Figure 4(b), the stable negative-ion spectra give $\cdot\text{C}^-$ (12), CH^- (13), $\cdot\text{O}^-$ (16), OH^- (17), C_2H^- (25), and $\cdot\text{CN}^-$ (26).

For PVA in Figure 5a in case c, the positive-ion fragment spectra are simple, since cleavage of the bonds between main chain carbons occurs first though the two-center bond energies of the main chain C–C bonds were slightly less than the energies of C–O bonds. We

Figure 4. (a) Bond-orders and bond energies (in eV) of the pentamer of PVC by semiempirical MO calculation using AM1 program (upper); positive and negative ions TOF-SIMS spectra of PVC in the range of 0–100 amu. (b) Bond-orders and bond energies (in eV) of the pentamer of PAM by semiempirical MO calculation using AM1 program (upper); positive and negative ions TOF-SIMS spectra of PAM in the range of 0–100 amu.

Figure 5. (a) Bond-orders and bond energies (in eV) of the pentamer of PVA by semiempirical MO calculation using AM1 program (upper); positive and negative ions TOF-SIMS spectra of PVA in the range of 0–100 amu. (b) Bond-orders and bond energies (in eV) of the pentamer of PTFE by semiempirical MO calculation using AM1 program (upper); positive and negative ions TOF-SIMS spectra of PTFE in the range of 0–100 amu.

Figure 6. Bond-orders and bond energies (in eV) of the pentamer of PVF by semiempirical MO calculation using AM1 program (upper); positive and negative ions TOF-SIMS spectra of PVF in the range of 0–100 amu.

thus obtain the intensive spectrum $\text{C}_2\text{H}_3\text{O}^+$ (43) as O-containing positive-ion fragment. In the case of the negative-ion fragments, there exist $\cdot\text{C}^-$ (12), CH^- (13), the intense spectrum $\cdot\text{O}^-$ (16), OH^- (17), C_2H^- (25), and $\text{C}_2\text{H}_3\text{O}_2^-$ (59) as CH_3COO^- .

For PTFE, we observed F-containing positive-ion fragments except for $\cdot\text{C}^+$ (12), because the two-center bond energies of the main chain bonds of PTFE are much less than those of C–F bonds, as indicated at the top of Figure 5(b). In the negative-ion mass spectra of Figure 5(b), we see the most stable characteristic mass spectrum and intense F^- fragment.

In PVF in Figure 6, there are many positive-ion fragment lines, although two-center bond energies of the main chain C–C bonds are much less than the values of C–F bonds. The cleavage of PVF may occur in very complicated process with cleavage and recombination between positive-ion and neutral species. The F-containing positive-ion fragments are CH_2F^+ (33), $\text{C}_2\text{H}_2\text{F}^+$ (45), $\text{C}_3\text{H}_4\text{F}^+$ (59), $\text{C}_4\text{H}_4\text{F}^+$ (71), $\text{C}_4\text{H}_6\text{F}^+$ (73), and $\text{C}_3\text{H}_3\text{F}_2^+$ (77) in the middle site of Figure 6. The negative-ion fragment spectra at the lower site were obtained as $\cdot\text{C}^-$ (12), CH^- (13), the contaminants $\cdot\text{O}^-$ (16) and OH^- (17), the intensive line F^- (19) and C_2H^- (25).

Polypropylene (PP) and polystyrene (PS) except phenyl rings in our previous work⁶ belong to case a, while poly(methyl methacrylate) is considered cases b and a;

the pendant group ($-\text{COOCH}_3$) cleaved first, and then the remaining main-chains with side chain methyl groups cleave at any bonds as well as PP polymers.

Structural Formulas of the Secondary Positive-Ion Fragments

Chemical formulas of positive-ion fragments for eight polymers (in the left column of Tables I–III) were obtained from spectral mass analysis of TOF- and S-SIMS measurements. We here give reasonable structural formulas of positive-ion fragments of the polymers in SIMS by *ab initio* calculations using the HONDO7 program, although the formulas of positive-ion fragments were empirically written by organic chemists. The tables show the possible structural formulas, dipole moments, heat of formation and total energies of the fragments for the eight polymers.

For example, in Table II, the most possible structural formula of C_4H_7^+ fragment is determined as $\text{CH}_3-\text{CH}^{(1/2)+} \cdots \text{CH}=\text{CH}_2^{(1/2)+}$ of the four formulas, since the heat of formation (or the total energy) is the least value from the *ab initio* MO calculations. For another example in Table II, the most reasonable structural formula of $\text{C}_4\text{H}_7\text{O}^+$ fragment is $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}^+=\text{O}$ of the six formula.

Table I. Structure, diople moment, heat of formation, and total energy of ion fragments in positive SIMS spectra of eight polymers (PE, PVA, PVF, PVC, PAN, PVME, PAM, PTFE)

Composition (mass)	Structure	Structure		
		μ (dipole moment)	Heat of formation	E (total energy)
		D (debye)	eV	eV
$\cdot\text{C}^+$ (12)	$\cdot\text{C}^+$	[0.0000 D ;	17.30 eV,	−1017.661 eV]
CH^+ (13)	CH^+	[2.113 D ;	15.96 eV,	−1029.684 eV]
$\cdot\text{CH}_2^+$ (14)	$\cdot\text{CH}_2^+$	[0.130 D ;	13.35 eV,	−1054.143 eV]
$\cdot\text{N}^+$ (14)	$\cdot\text{N}^+$	[0.00000 D ;	20.18 eV,	−1460.967 eV]
CH_3^+ (15)	CH_3^+	[0.0004233 D ;	10.94 eV,	−1066.015 eV]
Na^+ (23)	Na^+	[0.000 D ;	5.48 eV,	−4347.915 eV]
$\cdot\text{C}_2\text{H}_2^+$ (26)	$\cdot\text{CH}^{(1/2)+} = \text{CH}^{(1/2)+}$	[0.000474 D ;	13.46 eV,	−2092.895 eV]
$\cdot\text{CN}^+$ (26)	$\cdot\text{C}^+ = \text{N}$	[1.941 D ;	18.21 eV,	−2406.406 eV]
C_2H_3^+ (27)	$\text{CH}_2 = \text{CH}^+$	[0.682 D ;	11.34 eV,	−2094.741 eV]
CH_2N^+ (28)	$\text{CH}^+ \equiv \text{NH}$	[0.686 D ;	9.32 eV,	−2531.231 eV]
C_2H_5^+ (29)	$\text{CH}_3 - \text{CH}_2^+$	[1.800 D ;	9.40 eV,	−2127.904 eV]
CHO^+ (29)	$\text{CH}^+ \equiv \text{O}$	[4.645 D ;	8.13 eV,	−3068.906 eV]
CF^+ (31)	$\text{C}^+ \text{F}$	[2.070 D ;	10.72 eV,	−3717.941 eV]
CH_2F^+ (33)	$\text{C}^+ \text{H}_2\text{F}$	[4.734 D ;	7.82 eV,	−3752.358 eV]
C_3H_3^+ (39)	$\text{CH}_2 \equiv \text{C} \equiv \text{CH}^+$	[1.938 D ;	11.85 eV,	−3123.057 eV]
C_3H_5^+ (41)	$\text{CH}_3 - \text{CH} = \text{CH}^+$	[2.382 D ;	10.90 eV,	−3155.916 eV]
	$\text{CH}_2^{(1/2)+} \equiv \text{CH} \equiv \text{CH}_2^{(1/2)+}$	[1.028 D ;	9.81 eV,	−3157.295 eV]
	$\text{CH}_2^+ - \text{CH} = \text{CH}_2$	[2.944 D ;	10.13 eV,	−3155.451 eV]
C_3H_7^+ (43)	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2^+$	[3.995 D ;	9.18 eV,	−3188.693 eV]
$\text{C}_2\text{H}_3\text{O}^+$ (43)	$\text{CH}_3 - \text{C}^+ \equiv \text{O}$	[3.619 D ;	7.14 eV,	−4131.210 eV]
	$\text{CH}_2 = \text{C}^+ \equiv \text{OH}$	[2.406 D ;	8.54 eV,	−4129.639 eV]
	$\text{CH}_2^+ - \text{CHO}$	[7.456 D ;	9.60 eV,	−4128.083 eV]
	$\text{CH}^{(1/2)+} = \text{CH}^{(1/2)+} - \text{OH}$	[3.641 D ;	9.90 eV,	−4128.208 eV]
$\text{C}_2\text{H}_5\text{O}^+$ (45)	$\text{CH}_3 - \text{CH}^+ \equiv \text{OH}$	[2.868 D ;	6.16 eV,	−4163.249 eV]
	$\text{CH}_2^+ - \text{CH}_2 - \text{OH}$	[4.694 D ;	7.62 eV,	−4155.104 eV]
	$\text{CH}_3 - \text{O} \equiv \text{CH}_2^+$	[2.842 D ;	6.86 eV,	−4162.574 eV]
$\text{C}_2\text{H}_2\text{F}^+$ (45)	$\text{CF}^+ = \text{CH}_2$	[4.098 D ;	9.27 eV,	−4780.288 eV]
$\cdot\text{CF}_2^+$ (50)	$\cdot\text{CF}_2^+$	[0.682 D ;	7.77 eV,	−6457.844 eV]

Table II. Structure, diople moment, heat of formation, and total energy of ion fragments in positive SIMS spectra of eight polymers (PE, PVA, PVF, PVC, PAN, PVME, PAM, PTFE)

Composition (mass)	Structure	Structure		
		μ (dipole moment)	Heat of formation	E (total energy)
		D (debye)	eV	eV
CHF_2^+ (51)	$\text{C}^+ \text{HF}_2$	[3.733 D ;	5.28 eV,	−6438.682 eV]
$\text{C}_3\text{H}_2\text{N}^+$ (52)	$\text{CH}_2 = \text{C}^+ - \text{C} \equiv \text{N}$	[6.182 D ;	12.76 eV,	−4586.492 eV]
C_4H_5^+ (53)	$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2^+$	[3.600 D ;	11.88 eV,	−4199.651 eV]

Table II. (Continued)

Composition (mass)	Structure	μ (dipole moment)	Heat of formation	E (total energy)
		D (debye)	eV	eV
$C_3H_4N^+$ (54)	$CH_3-CH^+-C\equiv N$	[5.384 D ;	11.00 eV,	-4619.612 eV]
$C_4H_7^+$ (55)	$CH_3-CH_2-CH=CH^+$	[4.213 D ;	10.56 eV,	-4216.662 eV]
	$CH_3-CH^{(1/2)+}\cdots CH\cdots CH_2^{(1/2)+}$	[1.639 D ;	8.93 eV,	-4218.628 eV]
	$CH_2=CH-CH_2-CH_2^+$	[5.845 D ;	10.03 eV,	-4216.944 eV]
	$CH_2^{(1/2)+}\cdots C(CH_3)\cdots CH_2^{(1/2)+}$	[2.714 D ;	9.42 eV,	-4218.119 eV]
$C_4H_9^+$ (57)	$CH_3-CH_2-CH_2-CH_2^+$	[4.547 D ;	8.81 eV,	-4149.566 eV]
	$CH_3-CH^+-CH_2-CH_3$	[2.555 D ;	8.01 eV,	-4250.256 eV]
$C_3H_2F^+$ (57)	$CH_2=C=C^+F$	[6.264 D ;	10.09 eV,	-5809.131 eV]
$C_3H_7O^+$ (59)	$CH_3-CH_2-C^+H\cdots OH$	[3.563 D ;	5.80 eV,	-5223.906 eV]
	$CH_3-CH_2-O\cdots C^+H_2$	[4.485 D ;	6.45 eV,	-5223.479 eV]
	$CH_3-CH^+\cdots O-CH_3$	[2.617 D ;	6.08 eV,	-5223.996 eV]
	$CH_3-C^+(CH_3)-OH$	[2.033 D ;	5.47 eV,	-5224.583 eV]
	$CH_3-CH(CH_2^+)-OH$	[4.097 D ;	7.37 eV,	-5222.310 eV]
$C_3H_4F^+$ (59)	$C^+HF\cdots CH\cdots CH_2$	[5.276 D ;	7.44 eV,	-5843.614 eV]
$C_5H_7^+$ (67)	$CH_3-CH=CH-CH=CH^+$	[5.419 D ;	8.97 eV,	-5245.315 eV]
	$CH_2=CH-CH_2-CH=CH^+$	[6.427 D ;	11.58 eV,	-5244.908 eV]
	$CH_2^{(1/2)+}\cdots CH\cdots CH\cdots CH\cdots CH_2^{(1/2)+}$	[1.316 D ;	9.65 eV,	-5247.502 eV]
$C_5H_9^+$ (69)	$CH_3-C^{(1/2)+}(CH_3)\cdots CH\cdots CH_2^{(1/2)+}$	[1.094 D ;	8.33 eV,	-5279.698 eV]
	$CH_3-CH_2-CH^{(1/2)+}\cdots CH\cdots CH_2^{(1/2)+}$	[2.571 D ;	8.69 eV,	-5279.217 eV]
	$CH_2=CH-CH_2-CH_2-CH_2^+$	[7.082 D ;	9.73 eV,	-5277.673 eV]
$C_4H_5O^+$ (69)	$CH_3-C(CH_2)-C^+\equiv O$	[2.877 D ;	7.70 eV,	-6220.682 eV]
	$CH_3-CH=CH-C^+\equiv O$	[2.282 D ;	7.36 eV,	-6220.985 eV]
CF_3^+ (69)	C^+F_3	[0.00315 D ;	3.56 eV,	-9125.565 eV]

Table III. Structure, diopole moment, heat of formation, and total energy of ion fragments in positive SIMS spectra of eight polymers (PE, PVA, PVF, PVC, PAN, PVME, PAM, PTFE)

Composition (mass)	Structure	μ (dipole moment)	Heat of formation	E (total energy)
		D (debye)	eV	eV
$C_5H_{11}^+$ (71)	$CH_3-C^+(CH_3)-CH_2=CH_3$	[1.827 D ;	7.22 eV,	-5311.651 eV]
	$CH_3-CH_2-CH_2-CH_2-CH_2^+$	[9.147 D ;	8.36 eV,	-5310.074 eV]
	$CH_3-CH(CH_2^+)-CH_2-CH_3$	[4.388 D ;	8.45 eV,	-5310.185 eV]
$C_4H_7O^+$ (71)	$(CH_3)_2-CH-C^+=O$	[1.445 D ;	6.49 eV,	-6252.824 eV]
	$CH_3-CH_2-CH_2-C^+=O$	[1.656 D ;	6.43 eV,	-6252.736 eV]
	$CH_3-C^+(CH)-O-CH_3$	[4.077 D ;	9.55 eV,	-6249.993 eV]
	$CH_3-CH-C^+\cdots O-CH_3$	[2.223 D ;	7.95 eV,	-6251.516 eV]
	$CH_2-CH-CH_2-CH^+-OH$	[6.591 D ;	6.90 eV,	-6252.090 eV]
		[2.160 D ;	8.29 eV,	-6252.672 eV]
$C_4H_4F^+$ (71)	$CHF=CH-CH=CH^+$	[6.920 D ;	9.74 eV,	-6870.674 eV]
$C_4H_6F^+$ (73)	$CH_2F-CH^{(1/2)+}\cdots CH\cdots CH_2^{(1/2)+}$	[7.193 D ;	7.23 eV,	-7448.795 eV]
$C_3H_7NO^+$ (73)	$CH_3-CH_2-(C=O)-NH_2^+$	[3.946 D ;	7.26 eV,	-6586.265 eV]
$C_3H_7O_2^+$ (75)	$CH_3-O-CH^+-O-CH_3$	[2.417 D ;	3.87 eV,	-7258.189 eV]
	$HO-CH^+-CH_2-CH_2-OH$	[7.484 D ;	3.95 eV,	-7257.595 eV]
	$HO-CH_2-CH^+-CH_2-OH$	[3.046 D ;	4.68 eV,	-7256.742 eV]

Table III. (Continued)

Composition (mass)	Structure	μ (dipole moment)		Heat of formation		E (total energy)	
		μ (debye)		eV		eV	
$C_3H_3F_2^+$ (77)	$CH_2 \equiv CF \equiv C^+HF$	[7.423 D	;	6.02 eV,		–8529.315 eV]	
	$C^{(1/2)+}HF \equiv CH \equiv C^{(1/2)+}HF$	[3.654 D	;	5.21 eV,		–8529.821 eV]	
$C_5H_9O^+$ (85)	$CH_3-C^+(OCH_3)-CH=CH_2$	[2.257 D	;	6.41 eV,		–7313.822 eV]	
	$CH_3-O-CH_2-CH_2-CH=CH^+$	[9.910 D	;	8.83 eV,		–7311.348 eV]	
	$CH_2=CH-CH^+(CH_2)-O-CH_3$	[4.653 D	;	8.58 eV,		–7311.416 eV]	
	$CH_2=CH-CH_2-CH_2-O \equiv CH_2^+$	[8.699 D	;	7.24 eV,		–7312.267 eV]	
	$CH_3-CH_2-CH_2-CH_2-C^+ \equiv O$	[3.727 D	;	6.12 eV,		–7313.402 eV]	
$C_5H_6F^+$ (85)	$CH_3-CH=CH-CH=C^+F$	[1.907 D	;	9.14 eV,		–7930.751 eV]	
$C_3F_3^+$ (93)	$C^+F_2-C=CF$	[0.940 D	;	9.81 eV,		–11181.387 eV]	
$\cdot C_2F_4^+$ (100)	$\cdot C^{(1/2)+}F_2-C^{(1/2)+}F_2$	[0.00623 D	;	2.18 eV,		–12931.402 eV]	

CONCLUSIONS

We analyzed the spectra of eight polymers in SIMS by MO calculation using model pentamers.

(1) The prediction for cleavage of polymer-bonds on sputtering can be determined by the bond-orders (two-center bond energies) of the pentamers by a semi-empirical MO calculation; a) cleavage occurs at any bonds (PE, PVME, PAN), b) cleavage of the main chain occurs at any bonds, after side chain groups cleaved first (PVC, PAM), c) the main chain carbons with the side chain group cleave at any bonds of the main chain (PVF, PTFE, PVA).

(2) We gave reasonable structural formulas, dipole moments, heat of formation and total energies of each positive-ion fragment of the polymers in SIMS by *ab initio* calculations using the HONDO7 program.

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