氏名	茅根　木田　ﾏﾙｼｱ
学位（専攻分野）	博士（学術）
学位記番号	総研大甲第９８号
学位授与の日付	平成　６　年　９　月２０日
学位授与の要件	数物科学研究科　放射光科学専攻 学位規則第４条第１項該当
学位論文題目	Soft x-ray induced fragmentation of polymethylmethacrylate thin films
論文審査委員	主　査　教　授　宮　原　恒　昱
	教　授　那　須　奎一郎
	教　授　小　林　正　典
	助教授　田　中　健一郎
	助教授　小　林　克　己
	助教授　柳　下　　明

博士論文内容の要旨

Purpose

The motivation of this thesis is to determine the mechanisms of surface photochemical reactions of large organic molecules induced by soft x-ray radiation.

Three key points were developed in this work:

(1) Development of an apparatus for the study of surface photochemical reactions.
(2) Study of the decomposition of poly(methyl methacrylate) (PMMA) using monochromatic soft x-ray radiation.
(3) Verification of the possibility of site specific reactions in large organic molecules.

The starting step of this research was the construction of an apparatus for the study of surface photochemical reactions in general. It was decided that the investigation of the surface photochemical reactions would be done by the analysis of the reaction products released during irradiation. For this purpose, an ultrahigh vacuum chamber was designed and constructed considering the utilization of mass spectrometric techniques for the detection of the released products.

The utilization of this newly constructed apparatus is very versatile allowing the analysis of different chemical systems. It would be desirable to make the initial test of the apparatus using a very simple chemical system. Thus, the study of the soft x-ray induced decomposition of PMMA was chosen due to the ease of its experimental feasibility. The studies using PMMA thin films are experimentally easy to be put in practice because of several points, namely:

(1) The ease of decomposition of PMMA during irradiation;
(2) The reaction does not involve reacting gases, and
(3) The experiments can be easily performed at room temperature.

Although this system can be considered as very simple from the point of view of its experimental execution, PMMA is a relatively complex molecule since it is constituted of carbon and oxygen atoms with different chemical characteristics.

The motivation of this study is the localized character of core electron excitations. When solids are excited by soft x-rays, a deeper-lying hole localized at a definite atom can be created. It is believed that this hole plays a crucial role in the following chemical reactions. Soft x-ray excitations in the 250-600 eV photon energy range on PMMA result in fragmentation of the original polymer with desorption of electrons, ions and neutral particles. In order to investigate the

primary steps in photochemical decomposition mechanism of this polymer, measurements of electron, ion and neutral particles yields were performed following carbon and oxygen 1s electron excitations.

The main contribution of this work is the first observation of site specific reactions in solid polymer films. To our knowledge, no examples of site specific reactions on solid samples of large molecules have been reported before. The present achievement became possible by a systematic measurement of the fine structure of ion yield spectra of the main ionic fragments from PMMA and other similar polymers.

Obtained new information

In the present work, useful information about the photon stimulated ion fragmentation of thin films of poly(methylmethacrylate) (PMMA) has been obtained in the 250-700 eV photon energy range that covers the carbon and oxygen K-edge regions.

In order to analyze the neutrals produced in etching or desorption processes it was necessary to design and construct a new vacuum system and use an efficient mass spectrometer. Using this new equipment, PMMA films of 0.4 to 1.0 μm thicknesses have been irradiated to various doses of monochromatic 300, 400, and 600 eV soft x-rays. It was observed that the main neutral species observed in the mass spectra come from the ester group scission. The decomposition rates of these species are dependent on the radiation dosage, and solid film thickness. The fragments of mass 15, 28, 29, 31, 44 and 60 amu, corresponding to CH_3^+, CO^+, CHO^+, CH_3O^+, CO_2^+ and $HCOOCH_3^+$, were chosen for monitoring this irradiation dose dependence. It was shown that the products decrease in intensity with dose with different decay curves. The etching rates represented by the yield of the released fragments are dependent on the original thickness of the sample and gradually decrease with dose. The absorption spectrum after irradiation suggests the abstraction of the ester group and formation of double bondings. All this observations suggest a degradation mechanism involving the ester group abstraction followed by main chain scission and, at large doses, crosslinking and the formation of a protecting overlayer of chemical nature similar to polybutadiene.

For the first time, site specific reactions were observed in solid polymer films. These site specific reactions were detected by the characteristic differences in the partial ion yield spectra of the main positive ions from PMMA thin films. The most intense positive ions produced from PMMA correspond to CH_3^+ and H^+. The CH^+, CH_2^+, CHO^+ and $COOCH_3^+$ ions are also observed in considerable

intensities. Using soft x-rays, the ion desorption mechanism of PMMA was shown to be directly related to the excitation from 1s core electrons at specific atomic sites to unoccupied orbitals at neighboring bondings. The efficient production of CH_3^+, CH_2^+ and CH^+ ions at 288 eV, was taken as evidence of the localized contribution of the σ^* state at the main chain carbons or methoxy group carbon. In order to determine the origin of CH_3^+, CH_2^+, and CH^+ ions a comparative investigation was done using poly(methyl methacrylate), poly(methyl acrylate) and poly(methacrylic acid). It was clearly observed that most of the CH_3^+ ions are originated from the side chain methoxy group.

Near the oxygen K-edge, two characteristic features were distinguished for the site selective production of CH_3^+ and CHO^+ ions. The strong and sharp peak observed at 537.7 eV for CH_3^+ and CH_2^+ ions was assigned as a O 1s eletrons to σ^* state transition localized at the methoxy group. The prominent broader feature at 539.3 eV observed in the CHO^+ spectra was assigned to transitions from the methoxy O 1s to the σ^* state of the carbonyl-methoxy C-O bonding. The good efficiency of production of CH_3^+ and CHO^+ ions observed at these characteristic features can be explained by the excitation of the methoxy oxygen core electrons to unnocupied orbitals that favors the breaking of the methoxy group O-CH_3 bonding and the carbonyl-methoxy C-OCH_3 bonding respectively.

The results of the neutral and ionic products detection should be considered together as two kinds of products involved in the same irradiation degradation mechanism. One of the most important differences resides in the characteristics of the used detection techniques and in the differences in sensitivity for surface and bulk reactions.

論文の審査結果の要旨

茅根マルシア君の学位論文（Soft x-ray induced fragmentation of polymethylmethacrylate thin films）は、軟Ｘ線領域の放射光を利用した高分子（ポリメチルメタクリレート、PMMA）薄膜の光化学反応の研究に関するものである。

本研究は、内殻励起によりPMMA薄膜の表面および内部で起こる光化学反応の機構を、イオンおよび中性の反応生成物を直接検出し、その挙動を調べることにより考察したものである。近年、電子線エネルギー損失分光法やＸ線吸収分光法などによる、電子状態や分子構造に関する研究が、気体から固体まで多種多様な分子について行われているが、内殻励起後に起こる化学反応についての研究は、一部の気体分子の場合を除いてほとんど例がなく、本研究の最も評価される点である。

本論文では、イオンと中性の反応生成物の観測による研究を２つの章で個別に議論している。その理由は、検出感度が両者で数桁異なるため、実験条件がかなり異なること、また、物質中からの脱出深さの差から、イオン種では、固体最表面での反応を、中性種では、固体内部での反応を主に観測するとする正しい判断に基づいている。

まず、中性種の観測による研究では、各種膜厚のPMMA薄膜に300、400、600eVの単色軟Ｘ線を照射し、真空中に飛び出した生成物の種類と強度の照射時間依存性を電子衝撃による高感度質量分析計で測定した。その結果、大部分の生成物は、PMMAの側鎖からのものであることが確認でき、代表的な６種類のフラグメントについての実験から、その強度は、膜厚および励起光エネルギーの増加とともに増加し、吸光係数と膜厚から算出した全吸収量と良い相関をもつことを見出した。以上の結果および別途行った光照射前後の試料についての内殻吸収端近傍の微細構造スペクトル（NEXAFS）の変化から、光照射により、まず側鎖が切れ、主鎖に２重結合を生じ、さらに照射量が増加するとポリブタジエンに類似した物質に変化することを明らかにした。

イオン種の観測による研究では、中性種と同様に、PMMAの側鎖からと思われるイオンが放射光の単バンチパルスを利用した高感度飛行時間型質量分析計で観測され、主たる６種のイオンについて、精密なNEXAFSスペクトルを測定した。PMMA単体には、５個の炭素と２個の酸素原子があり、いずれの原子も分子内の化学的性質の異なったサイトに位置している。イオンの種類により、特定のサイトの原子からの共鳴吸収構造が強く現れるものが見つかり、内殻電子励起による分子内サイトを指定した化学反応が起こっていると結論した。気相分子について、このような観点からの研究はあるが、固体表面からのイオン脱離を系統的に調べ、分子内サイトを指定した化学反応が起こることを見いだした研究としては、本研究が世界最初である。

以上、茅根マルシア君の研究は、軟Ｘ線領域の放射光による固体表面並びに固体内での光化学反応に関する新しい重要な知見をもたらすものであり、数物科学研究科放射光科学専攻の博士学位論文として相応しい内容を有していると判断し、合格とした。