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**Radiation Chemistry of Molecular Compounds and Polymers by Soft X-ray
Spectroscopy and Microscopy**

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Abstract

Soft X-rays induced radiation chemistry in selected Fe molecular compounds and some aliphatic polymers was studied using soft X-ray absorption spectroscopy, and scanning transmission X-ray microscopy. X-ray absorption near-edge structure (XANES) spectroscopy was used to elucidate the radiation chemistry. The results show that damage to the Fe molecular complexes involves Fe-ligand bond breaking, ligand damage and subsequent photoreduction of Fe(III) if it is not tightly bonded to oxygen. Upon radiation damage, polymer PAN primarily undergoes chemical structure changes without mass loss, PECA experiences chemical structure changes as well as small mass loss, while PPC and PEC suffer large mass loss with chemical structure changes. These studies are not only important to X-ray analysis of radiation sensitive materials, but also are valuable to the applications of X-ray lithography and other types of nanofabrication involving photoresist.

Keywords: soft X-ray, radiation damage, STXM, iron compounds, polymers

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1. Introduction

Ionizing radiation damage of molecular compounds and polymer materials has been studied for about half a century and industrial scale radiation processing of polymers with electrons and γ -rays has been achieved for several decades.^{1,2} However, soft X-rays, as one of the important ionizing radiations, has received much less attention in regard to the radiation damage effects of materials. In the past two decades, with growing applications of soft X-rays from synchrotron radiation in materials analysis, particularly for organic and biological materials,³⁻⁸ the accompanied radiation damage effects and chemistry are of increasing importance, and in-depth studies on radiation damage to molecular compounds and polymers, including synthetic and natural polymers, have been conducted.⁹⁻¹³ In addition, quantitative characterization of soft X-ray damage to materials has been systematically developed through X-ray absorption near edge structure (XANES) spectroscopy¹⁴ and spectromicroscopy.¹⁵⁻²⁴ Radiation damage effects typically include chemical bond breaking and associated mass loss, redox processes, generation of free radicals as well as long-range crystalline rearrangements,²⁵ etc.

Radiation damage to molecular compounds, such as Cu complexes,¹³ has indicated that photoreduction and mass loss due to bond breaking are the primary radiation damage effects. However, relatively few studies have been systematically conducted to investigate the photoreduction mechanisms for other transition metal compounds. As the photoreduction effect is very critical in soft X-ray spectroscopy and microscopy where the X-ray attenuation coefficient is large, the accuracy of characterization of metal oxidation states in samples will be significantly affected. Molecular iron compounds are important in both living organisms and in the environment, therefore it is of high importance to characterize radiation damage associated XANES evolution for them. Radiation damage to polymer materials has shown that aromatic

polymers, such as PET and PS, are generally much more robust than aliphatic polymers^{17,20} upon irradiation, in terms of less spectroscopic changes and less mass loss. This is also consistent with other radiations, such as electron radiation damage in polymers.^{21,26,27} The damage mechanism is described as cross-linking between aromatic groups initiated by the radiation-induced scission of C-H bonds of aromatic rings, and delocalization of the primary excitation over the extended π system.²⁶ Contrary to aromatic polymers, the behavior of radiation damage to aliphatic polymers may be more diverse in terms of different degree of mass loss and spectroscopic changes.

In this work we are concerned with characterizing the chemical changes and mechanisms of radiation damage to selected molecular compounds and aliphatic polymers by soft X-rays. This work complements previous radiation damage studies and provides a more integrated view of the soft X-ray radiation damage to materials. Similarly, soft X-ray absorption spectroscopy, i.e. XANES, and Scanning Transmission X-ray Microscopy (STXM)^{28,29} were used as the platform of the soft X-ray radiation damage and as analytical tools in determination of XANES spectroscopic variations and chemical changes. The radiation damage studied in this work can be classified into the following categories, (i) photoreduction dominated chemistry change, (ii) other chemistry change without mass loss, (iii) other chemistry change with small mass loss, and (iv) other chemistry change with large mass loss. The damage chemistry was deduced by comparing XANES spectra at the Fe 2p, C 1s, N 1s and O 1s of the undamaged and damaged materials.

2. Experimental

2.1. Materials

Iron compounds, i.e. Fe(III) citrate, and Fe(II) oxalate, were purchased from Sigma Aldrich. The two-line ferrihydrite was synthesized according to the method described in our

previous study.³⁰ All compounds were used without further purification and were confirmed by XRD. The aliphatic polymers involved in this work include polyacrylonitrile (PAN), poly(ethyl cyanoacrylate) (PECA), poly(propylene carbonate) (PPC) and poly(ethylene carbonate) (PEC). PAN ($M_w = 150K$) was obtained from Aldrich; PECA was obtained commercially (Instant Krazy Glue®, PECA - Elmer's Products, Inc. & Toagosei Co. Ltd.) and polymerized when exposed in the air; PPC ($M_w = 250 K$) and PEC ($M_w = 150 K$) were both obtained from Empower Materials. All of them were used without further purification. Free standing single layer films of PAN, PPC and PEC for STXM radiation damage were made according to the same spin coating procedure as previous studies.¹⁸⁻²⁰ The spun cast single layer films had a thickness of 30 - 40 nm according to STXM measurements. The PECA single layer film was prepared by ultramicrotoming a solid block to form 60 nm thick uniform films.¹⁸

2.2. SGM Radiation Damage

Fe $L_{3,2}$ -edge XANES radiation damage measurements were performed at the 11ID-1 Spherical Grating Monochromator (SGM) Beamline of the Canadian Light Source (CLS).³¹ The powder samples were mounted on double-sided, conducting carbon tape. XANES was recorded in total electron yield (TEY) using quick-scan mode.³² The estimated radiation dose was several thousand MGy^{13,33} for each scan at the Fe $L_{3,2}$ -edge, with full beam intensity (beam spot size 1000 $\mu m \times 100 \mu m$) and beamline slits set at 50 $\mu m \times 50 \mu m$, and the total scan time is 20 seconds. XANES data were normalized to the incident photon flux I_0 measured with a refreshed gold mesh prior to the measurement, i.e. TEY (I_{yield}/I_0). Detailed information on the data collection and processing were described in previous publications.^{13,30}

2.3. STXM Radiation Damage

STXM radiation damage measurements were performed using the polymer STXM at Beamline 5.3.2.2 at the Advanced Light Source (ALS),²⁸ and on the STXM of the 10ID-1SM Beamline at CLS²⁹. STXM uses a Fresnel zone plate to focus monochromated soft X-rays to a fine spot of ~50 nm. The sample is raster scanned with synchronized detection of transmitted X-rays to measure the energy dependent absorption from a thin thickness of the sample material. To conduct radiation damage of the sample, adjacent small square regions (pads) of the sample (typically 0.6 μm x 0.6 μm , using 10 x 10 pixels) were exposed at 300 eV using systematically varied dwell times so as to span a range of doses that adequately sample the dose-damage curve.²⁰ After exposure, analysis images were recorded at selected photon energies for each polymer, which give the best contrast between damaged and undamaged regions as a result of chemistry change and mass loss. In addition, XANES spectra of the damaged and undamaged regions were acquired using an image sequence³⁴ (i.e. stack scan in STXM) with much lower photon flux and dwell time as low as 1 ms at the C 1s, N 1s and O 1s edges. The detailed settings of STXM and the beamline, and the methodology of radiation damage studies were described elsewhere.²⁰⁻²⁴ STXM radiation dose evaluation using the Beer-Lambert law to calculate the absorbed radiation dose, and damage kinetics and critical dose determination followed the same procedure used in previous studies.²⁰⁻²⁴ All STXM data were analyzed by aXis2000, <http://unicorn.mcmaster.ca/aXis2000.html>. XANES spectra from each damaged region (pad) and from the undamaged region were extracted from the image stacks using an image mask which allows only selecting the region(s) of interest. More details of the STXM experimental and data analysis procedures can be found elsewhere.³⁵⁻³⁸

3. Results

3.1. Radiation Chemistry and XANES of Fe Molecular Compounds

Radiation chemistry of selected Fe compounds was revealed in the Fe $L_{3,2}$ -edge at the CLS SGM beamline, as shown in **Fig. 1**. Fe $L_{3,2}$ -edge XANES spectra of five continuous scans were measured for all three samples, which probe the dipole allowed transitions of Fe 2p electrons to the unoccupied 3d orbitals that were partially mixed with the valence molecular orbitals of the ligands. Due to spin-orbital coupling, two main spectral regions were resolved at 706 - 713 eV (L_3 -edge) and 720 - 725 eV (L_2 -edge), respectively, and the splitting in each of the main spectral regions is caused by Fe-ligand electronic interactions.

In the XANES spectra of Fe(III) citrate of **Fig. 1a**, the spectrum of Scan 1 is characterized by two main features. The higher energy dominant feature, denoted as Peak 3, is attributed to $2p_{3/2} \rightarrow 3d^{5*}$ (low-spin e_g) transition, and the lower energy shoulder peak can be assigned to $2p_{3/2} \rightarrow 3d^{5*}$ (low-spin t_{2g}) transition. From continuously scanning the same sample region, we can see Peak 3 intensity is decreasing. Meanwhile, the lower energy shoulder peak showed increasing intensity in the XANES spectra, and eventually its intensity surpassed the intensity of Peak 3 after three scans. The evolved lower energy peak can be roughly aligned to the dominant XANES feature of Fe(II) oxalate, denoted as Peak 2 and assigned to $2p_{3/2} \rightarrow 3d^{6*}$ (low-spin e_g) transition, in **Fig. 1a**. Therefore, the spectroscopic evolution of Fe(III) citrate upon X-ray irradiation indicated Fe(III) was reduced to Fe(II) due to radiation damage. A close look at the spectra shows that there is a small blue shift, i.e. spectroscopy shifted to higher energy, of the Fe(II) feature generated from Fe(III) citrate damage relative to the main peak of Fe(II) oxalate. This is readily understandable that the chemical structure and environment of the damaged Fe(III) citrate is different from that of Fe(II) oxalate. A reasonable explanation is that radiation damage to Fe(III) citrate primarily generates FeO-like species with more oxygen in the second shell of Fe(II) center compared to

Fe(II) oxalate, therefore Fe(II) of damaged ferric citrate experiences higher inductive effect from oxygen, which results in small blue shift of the XANES feature. Furthermore, the weak pre-edge feature, denoted as Peak 1 in **Fig. 1a**, also shows some similarity and coincidence between Fe(II) of damaged ferric citrate and Fe(II) oxalate. These observations strongly indicate Fe $L_{3,2}$ -edge XANES is very sensitive to the Fe-ligand interactions,^{39,40} such as covalence, coordination, types of ligand, and it can be highly valuable in chemical speciation and fingerprinting identification of Fe species in materials analysis. X-ray induced metal photoreduction is a common phenomenon, and our previous systematic study of Cu(II) complexes had obtained similar results and deduced detailed radiation damage mechanisms.¹³ In addition, the photoreduction can be characterized by a first order kinetics, which is well established by our previous works.¹⁵⁻²⁴

Compared to Fe(III) citrate, radiation damage to ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O}$) is quite different, as shown in **Fig. 1b**. From continuous Scan 1 to 5, Fe(III) of ferrihydrite didn't undergo photoreduction and significant spectroscopic changes, instead only the overall intensity was slightly decreased. As the key chemical component of ferrihydrite is Fe_2O_3 , Fe(III) is tightly bonded and coordinated with oxygen, therefore upon radiation damage, only the hydrated water molecules could be removed by the energy of impinging X-rays. However, there is a possibility that the water molecules also removed some Fe_2O_3 species during they were leaving the sample matrix, and therefore small intensity decrease in the Fe $L_{3,2}$ -edge XANES was observed over the multiple scans. This is much different from Fe(III) citrate damage, in which damage of the citrate ligands not only resulted in mass loss in terms of ligands, ligand fragments, together with iron species, but also caused the Fe(III) metal center reduced to Fe(II) during the bond breaking between Fe(III) and the citrate ligand. It is worth pointing out that the mass loss observed in XANES spectroscopy could be much smaller than the reality. This is partly because the detection depth of TEY in

XANES spectroscopy is about 10 nm, and as long as the sample thickness is much larger than tens of nanometers like in the case of this work, there will always be a mixture of damaged and undamaged materials providing somehow equivalent TEY signals until the damaged materials dominated the top 10 nm of the sample. In this regard, XANES spectroscopy is much more sensitive to spectroscopic changes instead of mass loss. This is exactly the case as shown in our previous radiation damage study of Cu(II) complexes, in which Cu 2p and O 1s spectra show larger spectroscopic variations than intensity changes. In this work, we didn't further explore the O 1s spectroscopy as similar observations are expected.

Finally, radiation damage to Fe(II) oxalate through five repeating scans is shown in **Fig. 1c**. Based on previous discussions, the damage result is still conceivable. As Fe(II) oxidation state is a stable form under vacuum, unless the radiation dose is significantly higher that metallic Fe might be observable, no photoreduction was actually observed during the scans, even if the bond breaking between Fe(II) and the oxalate ligands, and damage to the oxalate ligands in terms of mass loss are inevitable. A very careful examination of the series of XANES spectra in **Fig. 1c** indicates a very small spectroscopic blue shift from Scan 1 to Scan 5. This is exactly the case like Fe(III) citrate damage that the damage products of Fe(II) oxalate are FeO-like species. To this end, we can conclude that damage to Fe molecular complexes involves Fe-ligand bond breaking, ligand damage and subsequent photoreduction if relevant, toward FeO-like product. If Fe(III) is tightly bonded to oxygen like in oxide, photoreduction will not be observed in normal XANES spectroscopy measurements, unless radiation dose is way beyond normal conditions.

3.2. Radiation Chemistry and XANES of PAN

The C 1s XANES spectra of undamaged and heavily radiation damaged PAN were

presented and discussed in previous studies.^{18,23} Here it is reproduced in **Fig. 2a** to compare with N 1s edge and other polymers. The major XANES features of undamaged PAN and new features created in damaged PAN in both C 1s and N 1s edges are listed in **Table 1**. The main spectroscopic changes in the C 1s edge due to radiation damage are a significant decrease of the strong C 1s $\rightarrow\pi^*_{\text{C}\equiv\text{N}}$ transition at 286.8 eV, an increase of the C 1s $\rightarrow\pi^*_{\text{C}=\text{C}}$ transition at 285.1 eV arising from C=C bonds formed in the damaged polymer backbone, and almost no decrease of the intensity in the C 1s continuum. These observations suggest PAN radiation damage primarily undergoes chemical structure changes without mass loss, as the intensity decrease in the continuum, i.e. the spectroscopic region above the inner shell ionization potential, usually reflects mass loss upon radiation damage.¹⁷

Fig. 2b compares the N 1s XANES spectra of undamaged and substantially damaged PAN. The spectroscopic variations of damaged PAN at the N 1s edge are the decrease of the N 1s $\rightarrow\pi^*_{\text{C}\equiv\text{N}}$ transition at 399.8 eV, and a rise of the pre-edge feature at 398.7 eV, which is attributed to the formation of C=N double bonds, similar to the N 1s $\rightarrow\pi^*_{\text{C}=\text{N}}$ transitions in polyaniline⁴¹ and in quinoide molecules.⁴² Similar N 1s spectroscopic changes were also observed in soft X-ray radiation damage to amide functional groups in amino acids⁴³ and proteins,²⁰ which attributed the created pre-edge features to the formation of C-N multiple bonds or C=N bonds with different local environments. Note that a resonant Auger spectroscopy study has assigned a close feature at 398.9 eV to N 1s $\rightarrow\pi^*_{\text{C}=\text{C}}$ transition in solid acrylonitrile.⁴⁴ However, this should be different from the pre-edge feature created in damaged PAN as will be discussed in detail in the next section. Just like the C 1s edge, the N 1s continuum of PAN doesn't change in intensity at all upon radiation damage, which confirms the damage is free of mass loss regarding nitrogen.

3.3. Radiation Chemistry and XANES of PECA

The C 1s XANES spectra of undamaged and a series of radiation damaged PECA are shown in **Fig. 3a**. The damage was made by exposure at 300 eV for a series of radiation dose in terms of exposure time. Some important XANES features of undamaged PECA and new features created in damaged PECA in C 1s, N 1s and O 1s edges are summarized in **Table 1**. As expected from our previous studies,¹⁸ both functional groups, i.e. C≡N and C=O, were non-selectively damaged in terms of similar intensity decrease of the C 1s →π*_{C≡N} transition at 286.7 eV and the C 1s →π*_{C=O} transition at 288.6 eV. Other spectroscopic changes caused by radiation damage are increase of the C 1s →π*_{C=C} transition at 285.1 eV due to the same reason as above, and small decrease of the intensity in the C 1s continuum. These changes reflect PECA radiation damage undergoes both chemical structure changes and small mass loss.

Fig. 3b presents the corresponding N 1s XANES spectra of undamaged and a series of radiation damaged PECA. The spectroscopic changes of damaged PECA at the N 1s edge are the decrease of the N 1s →π*_{C≡N} transition at 399.8 eV, the creation of two pre-edge features at 398.7 and 399.0 eV respectively, and small intensity decrease in both the pre-edge and the N 1s continuum. The pre-edge feature at 398.7 eV is attributed to the formation of C=N double bonds, same as that in damaged PAN. The other pre-edge feature at 399.0 eV is attributed to N 1s →π*_{C=C} transition, just like the same transition at 398.9 eV in solid acrylonitrile.⁴³ This suggests an additional depolymerization mechanism during radiation damage of PECA since a detectable amount of undamaged or damaged monomers with structure C=C-C≡N or C=C-C=N may be produced through the depolymerization process, and due to the spatial proximity of the C=C group and the N atom, N 1s →π*_{C=C} transition can occur. Actually industrial purification of alkyl cyanoacrylate monomers is achieved by depolymerization of the corresponding polymers at

elevated temperatures of 150 - 190 °C.⁴⁵ In this case, the depolymerization is believed introduced by radiation damage instead of thermal effect since the temperature-rise can be neglected during irradiation of soft X-rays in STXM.¹⁸ Although PAN damage also involves creation of C=C double bonds in the damaged polymer, it does not ensure the created C=C groups are in direct or close bonding with nitrogen atoms, so the N 1s $\rightarrow\pi^*_{\text{C}=\text{C}}$ transition is not observable. Also contrary to PAN, the N 1s continuum of PECA does decrease by a small amount, which confirms small mass loss during radiation damage, presumably by emission of small fragments or undamaged and damaged monomers. In conclusion, since mass loss and the created C=C intensity are both small, the depolymerization process should be a very small fraction within the total radiation damage.

The corresponding O 1s XANES spectra of undamaged and a series of radiation damaged PECA are presented in **Fig. 3c**. The spectroscopic variations of damaged PECA at the O 1s edge are dominated by the decrease of O 1s $\rightarrow\pi^*_{\text{C}=\text{O}}$ transition at 532.1 eV, the decrease of O 1s (OMe) $\rightarrow\pi^*_{\text{C}=\text{O}}$ transition at 534.8 eV, and relatively larger intensity decrease in both the pre-edge and the O 1s continuum compared to those of the C 1s and N 1s edges. More mass loss in the O 1s edge of PECA is due to readily emitted small fragments and molecules, such as OC₂H₅, CO₂, COOC₂H₅, during radiation damage, which is similar to soft X-ray radiation damage of polymethylmethacrylate (PMMA).^{9,10,20}

3.4. Radiation Chemistry and XANES of PPC and PEC

The C 1s XANES spectra of undamaged and a series of radiation damaged PPC are shown in **Fig. 4a**. The damage was also made by exposure at 300 eV for a series of radiation dose. The main XANES features of undamaged PPC (PEC) and new features created in damaged PPC (PEC) in C 1s and O 1s edges are listed in **Table 1**. The damaged PPC was characterized by a number of

spectroscopic changes: (1) large decrease of the C 1s $\rightarrow\pi^*_{\text{C=O}}$ transition intensity of the carbonate group at 290.4 eV; (2) decrease of the shoulder peak at 289.4 eV, which is due to the C 1s (CH₂-O) $\rightarrow\pi^*_{\text{C=O}}$ transition; (3) large decrease of the C 1s continuum and some associated σ^* features shown as broad peaks at 293.5, 297.4 and 304.5 eV; (4) relatively small decrease of the C 1s pre-edge; and (5) creation of some small peaks at 285.0 (C 1s $\rightarrow\pi^*_{\text{C=C}}$), 286.6 (C 1s $\rightarrow\pi^*_{\text{C=O}}$, isolated carbonyl groups generated by two C-O bonds scission from the initial carbonate group), and 288.5 eV (C 1s $\rightarrow\pi^*_{\text{C=O}}$, ester groups generated by one C-O bond scission from the carbonate group). These spectroscopic changes suggest PPC damage not only involves extensive chemical structure changes, but also includes significant mass loss, presumably due to lots of polymer backbone scissions which lead to emission of small molecules and fragments. The C 1s XANES spectra of undamaged and completely damaged PEC regarding the carbonate functional groups are shown in **Fig. 4b**. Due to same generic chemical structure and composition between PEC and PPC, exactly same XANES spectroscopic changes were observed in damaged PEC.

The O 1s XANES spectra of undamaged and a series of radiation damaged PPC are presented in **Fig. 4c**. The spectroscopic characterization of damaged PPC is shown as large decrease of the overall intensity, including both the resonant features, such as O 1s $\rightarrow\pi^*_{\text{C=O}}$ transition at 532.9 eV and O 1s (CH₂-O) $\rightarrow\pi^*_{\text{C=O}}$ transition at 536 eV, and the O 1s continuum. The O 1s XANES spectra of undamaged and completely damaged PEC are shown in **Fig. 4d**. The completely damaged PEC has almost no spectroscopic features and has much lower intensity. These spectroscopic observations at the O 1s edge of PPC and PEC confirm major structure collapse of the carbonate groups and simultaneous large mass loss upon radiation damage. Similar to PECA, more mass loss is observed in the O 1s edge than that of the C 1s edge under similar

exposure conditions as comparing **Fig. 4b** and **4d**, which implies that the lost fragments and molecules have more abundance of oxygen.

4. Discussion and Conclusion

Soft X-ray radiation damage to molecular compounds and polymers essentially includes two successive stages, i.e. the primary processes and the secondary processes.^{18,20} The primary processes include photoabsorption in terms of photo ionization and photo excitation, and immediate decay of the core ionized or core excited states by Auger process.^{46,47} Although these processes occur similarly in the Fe compounds and three categories of polymers in this work, the overall radiation damage behaviors are rather different, which are believed due to the secondary processes of radiation damage and their consequences in different chemical environments. The secondary processes involve the generation of secondary electrons, free radicals and ions directly from Auger process and from the transportation of photoelectrons in bulk materials. The chemical consequences of the secondary processes involve electron, radical or ion induced chemical reactions, such as photoreduction, fragmentation, polymer backbone scission and crosslinking, depolymerization, etc. Specifically, Fe molecular complex damage involves Fe-ligand bond breaking, ligand damage and subsequent photoreduction if Fe(III) is not tightly bonded to oxygen. The nitrile groups in PAN mainly undergo reduction instead of being eliminated. This is probably due to first the photo absorption is not capable of introducing many bond cleavages between nitrile groups and the polymer backbone, second the perturbation from secondary electrons, and some hydrogen atoms or ions, being a result of the C=C bond formation in the damaged polymer backbone, is also not strong enough. When an ester side chain is present in the repeating unit of PAN to form PECA, damage to nitrile groups changes substantially. Since ester group is sensitive

to soft X-rays, such as in PMMA,^{9,10,20} multiple bond cleavages within the ester group may occur to produce C₂H₅, OC₂H₅ and COOC₂H₅ fragments in PECA, as reflected by carbon and oxygen mass loss in **Fig. 3a** and **3c**, respectively. It is speculated that these energetic fragments make a strong impact on the nitrile groups in spatial proximity within PECA, i.e. causing bond cleavage between nitrile groups and polymer backbones, as reflected by nitrogen mass loss in **Fig. 3b**. So fragmentation of nitrile groups changes dramatically in different chemical environments. The oxygen containing functional groups in aliphatic polymers are generally all sensitive to soft X-ray radiation damage, such as carbonyl group in poly(vinyl methyl ketone) (PVMK),¹⁷ ester group in side chain in PMMA^{15-18,20} and in polymer backbone in poly(ethylene succinate) (PES)¹⁷, amide group in nylon 6¹⁷, and ether group in poly(propylene oxide) (PPO).¹⁷ In this work, we also demonstrate that aliphatic carbonate groups are very sensitive to soft X-ray damage. Furthermore, functional groups located in polymer backbones instead of in polymer side chains are even susceptible to mass loss, and radiation damage results in much more backbone scissions, such as PES¹⁷ compared to PMMA. Since aliphatic carbonate groups of PPC and PEC are also present in the polymer backbones, PPC and PEC suffer great mass loss as much as 65% during radiation damage, similar to 68% mass loss in PES.¹⁷

The soft X-ray radiation damage studies in this work complement some important previous works.^{13,17,20} All these studies are not only essential to X-ray spectromicroscopy analysis for radiation sensitive materials such as molecular compounds, polymers, biological and environmental samples, but also are fundamental studies for potential applications of soft X-ray radiation damage in X-ray lithography and other types of nanofabrication involving surface or bulk chemistry modification using soft X-rays, such as lithography or damage of self-assembled monolayers (SAMs).⁴⁸⁻⁵³ We have successfully demonstrated a novel approach, i.e. chemically

selective soft X-ray direct-write patterning of multilayer polymer films with STXM,^{18,19} based on similar systematic radiation damage studies. With further understanding of the radiation damage mechanisms and kinetics, more applications of soft X-ray radiation damage will be possibly designed and developed in the future. One predicable application is to design the photoresist polymers regarding oxygen containing functional groups and their locations in the polymer materials, so as to control mass loss during exposure, or to convert a positive photoresist to a negative one, and vice versa.

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459 **Table 1:** XANES features of undamaged polymers and new features created in damaged polymers

PAN		PECA		PPC (PEC)		Assignment
Undamaged	Damaged	Undamaged	Damaged	Undamaged	Damaged	
C 1s						
	285.1		285.1		285.0 (285.0)	$\pi^*_{\text{C}=\text{C}}$
					286.6 (286.6)	$\pi^*_{\text{C}=\text{O}}$
286.8		286.7				$\pi^*_{\text{C}\equiv\text{N}}$
		288.6			288.5 (288.5)	$\pi^*_{\text{C}=\text{O}}$
288.7						$2\pi^*_{\text{C}\equiv\text{N}}$
				289.4 (289.4)		$(\text{CH}_2\text{-O}) \rightarrow \pi^*_{\text{C}=\text{O}}$
				290.4 (290.4)		$\pi^*_{\text{C}=\text{O}}$
293.0		293.0		293.5 (293.4)		$\sigma^*_{\text{C-C}}$
				297.4 (297.5)		$\sigma^*_{\text{C-C}}$
	301.0					$\sigma^*_{\text{C}=\text{N}}$
				304.5 (304.4)		$\sigma^*_{\text{C}=\text{O}}$
306.0						$\sigma^*_{\text{C}\equiv\text{N}}$
N 1s						
	398.7		398.7			$\pi^*_{\text{C}=\text{N}}$
			399.0			$\pi^*_{\text{C}=\text{C}}$
399.8		399.8				$\pi^*_{\text{C}\equiv\text{N}}$
405.7		405.8				$\sigma^*_{\text{C}\equiv\text{N}}$
O 1s						
		532.1				$\pi^*_{\text{C}=\text{O}}$
				532.9 (532.8)		$\pi^*_{\text{C}=\text{O}}$
		534.8				$(\text{O-CH}_3) \rightarrow \pi^*_{\text{C}=\text{O}}$
				536.4 (535.9)		$(\text{O-CH}_2) \rightarrow \pi^*_{\text{C}=\text{O}}$
		541.3		540.3 (539.5)		$\sigma^*_{\text{C}=\text{O}}$

460

Fig. 1 Five continuous XANES spectroscopy scans to radiation damage of (a) Fe(III) citrate; (b) Ferrihydrite; and (c) Fe(II) oxalate.

Fig. 2 XANES spectra of undamaged and radiation damaged PAN by STXM, (a) C 1s edge,²³ reprint with permission; and (b) N 1s edge.

Fig. 3 XANES spectra of undamaged and a series of radiation damaged PECA, (a) C 1s edge, the inset shows the pattern created on an initially undamaged, free standing PECA thin film by exposure at 300 eV using a 10x10 pixel, 0.6x0.6 μm raster scan with the indicated per-pixel dwell times (25, 50, 75, 125, 250, 375, 500, 750, 1000 ms) for nine pads, and imaged at 288.6 eV. The numbers in the lower and upper right boxes are the optical density scale of the image; (b) N 1s edge; and (c) O 1s edge.

Fig. 4 XANES spectra of undamaged and radiation damaged PPC and PEC, (a) and (b) C 1s edge; (c) and (d) O 1s edge.