# Supplemental Information to

# Effect of UV radiation damage in air on polymer film thickness, studied by soft X-ray spectromicroscopy

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# S1. Same areas studied by STXM and UV-SR

The polymer film was mounted on SiNx windows and covered the thin SiNx film in areas with and without the underlying Si frame as shown in Figure S1a. The part of the polymer film deposited on the window area (i.e. without underlying Si) was used for STXM and UV-SR correlation measurements. This area is highlighted in Fig. S1a and shown in Fig. S1b,c before STXM and UV-SR measurements, respectively. This allows measurements by both instruments on areas of the polymer films which are at the same position within a few tens of microns. Fig 1c highlights the area (blue square) used to acquire UV-SR measurements and Fig. S1d highlights the same area (blue square) that was used to acquire STXM measurements for the thickness determination.



**Figure S1** (a) is an optical microscope image of a PS samples in reflective mode using 5X magnification. The white square indicates the region of interest shown in higher magnification in (b) and (c). (b) STXM image at 285.2 eV of the region indicated in (a). (c) Image in reflection mode taken from the Filmetrics equipment. The blue square indicates the region of the UV-SR measurement. (d) Higher magnification of the STXM image at 285.2 eV. The blue square indicates the selected region from the stack for thickness determination (excluding dust particles).

# S2. Thickness determination using Scanning Transmission X-ray Microscopy (STXM)

The sample is raster scanned in X and Y at a Z-value corresponding to the focus of a stationary X-ray beam. I(E,x,y), the transmitted intensity at each (X,Y) pixel and photon energy, E is measured and converted to optical density, OD, using the Lambert-Beer law,

 $OD(E) = -\ln(I(E)/I_o(E))$ 

where I(E) is the intensity transmitted through the sample and  $I_0(E)$  is the intensity of the incident photon beam at photon energy *E*. For material in the probe area composed of multiple chemical species (components), the measured *OD* is a linear combination of the absorption of all components:

$$OD(E) = \sum_{i} OD1(E)_{i} h_{i}$$

where  $OD1(E)_i$  is the reference spectrum of component *i* obtained from experiment, and  $h_i$  is the effective thickness of component *i* (where the term "effective" is used to describe the situation where the component is distributed non-uniformly along the beam direction, Z coordinate). If the  $OD1(E)_i$  for each component are known, then  $h_i$  can be determined by least square fitting the measured *OD* spectrum with the relevant  $OD1_i$  spectra. A valid reference spectrum must be obtained for each pure component. The reference spectra on a relative intensity scale are converted to an absolute  $OD1(E)_i$  intensity scale (optical density per 1 nm thickness) by scaling the measured spectrum of the pure component outside of the near edge region to the spectrum of the component mass absorption coefficient  $\mu_i$ (E):<sup>S.1</sup>

$$OD1_i = \mu_i(E)\rho_i$$

where  $\rho_i$  is the gravimetric density of the pure component, *i*. Outside of the near edge spectral region, the component mass absorption coefficient  $\mu_i(E)$  is the sum of the atomic mass absorption coefficients  $\mu_a(E)$  of each element present in the component species<sup>8.2</sup>

$$\mu_i(E) = \left(N_A / M_r\right) \sum_q x_q \mu_{a,q}(E)$$

where  $M_r$  is the molecular mass,  $N_A$  is Avogadro's number, q is the index of the element, and  $x_q$  is the number of times element q is found in the molecular formula or repeat unit of the component (see Scheme 1 in the paper). The molecular mass and  $x_q$  are known and the elemental spectra  $\mu_{a,q}(E)$  are tabulated<sup>S.2</sup> so the component mass absorption coefficient  $\mu_i(E)$  can be calculated. The  $OD_i(E)$  spectrum of a single pure component is derived by a least square fit (LSF) of the measured relative spectrum to the product  $\mu_i(E)\rho_i$  in the pre and post edges of the appended multi edge spectra (the number of edges depends on the chemical formula; C 1s, O 1s and/or F 1s in this study). The resulting LSF coefficients  $a_i$  and  $b_i$  are then used to compute the reference spectrum  $OD1_i(E)$  of component i:

 $OD_i(E) = a_i + b_i OD1_i(E)$ 

using computer algebra software Mathematica 8.0 (Wolfram Research Inc., IL).

Image sequences or stacks were recorded at specific edges (C 1s, O 1s, F 1s) to increase the accuracy of the STXM thickness determination. The same area was measured for several edges i.e. C 1s for all 3 polymers, O 1s for PMMA and F 1s for PFSA. The measured stacks for each

polymer were appended.  $I_0$  was recorded for each Y pixel line of the (X,Y) image and used to convert the transmitted intensity to optical density per each Y line of pixels (this method allow to bypass the X-ray beam instabilities with characteristic time ~ of the Y-line scan time). The  $OD_{X,Y}(E)$  spectrum was then divided by the OD1(E) reference spectrum for that particular polymer to get a thickness map, h(x,y)=OD(E,x,y)/OD1(E), in which each pixel provides an independent thickness measurement.

# S3. Raw UV-SR data (Reflectance and refractive index)

The measured raw  $R(\lambda)$  spectra for PMMA and PS are presented in Figures S2 and S3. The raw spectra change significantly over the 30 min exposure time and were used to calculate the thickness and refractive index.



**Figure S2** Reflectance spectra for PMMA, recorded over time intervals between 1 and 45 min for (a) a 91nm thick PMMA film spun cast from a 3 wt% toluene solution and transferred on to a 75 nm  $SiN_x$  window. (b) Raw reflectance data from a 48 nm thin PMMA film based on a 2 wt% toluene solution. This is the raw data used for the results shown in Figure 3. To show the substrate effect, (c) is the raw data for the 80 nm PMMA film on the Si frame used in Figure 5.



**Figure S3** Reflectance spectra for PS, recorded over time intervals between 1 and 45 min for (a) 110 nm thick PS film spun cast from a 2 wt% toluene solution and transferred on to a 75 nm  $SiN_x$  window. (b) Raw reflectance data from a 49 nm thin PS film spun cast from a 1 wt% toluene solution and transferred on to a 75 nm  $SiN_x$  window. This is the raw data used for the results shown in Figure 4.

The refractive index values for each datapoint in Figure 5 is shown in Figure S4. As shown, the error increases for the film as the thickness decreases. There is also evidence of the PMMA refractive index changing due to exposure of UV.



**Figure S4** plots the refractive index values for each of the points of Figure 5, determined using method ii.  $\Box$  = PMMA on 75 nm SiNx on a Si frame,  $\bullet$  = PMMA on a Si wafer with native oxide.

#### S4. Additional STXM data analysis and peak assignments

Figure S5 presents the (a) optical image taken from the UV-SR instrument, (b) optical image taken from an optical microscope after the 5 mins exposure from UV-SR and (c) STXM image at 285.2 eV depicting the areas where there was UV exposure. Spectra shown in (d) and (e) are the C 1s and O 1s for the 5 min PS exposed sample to UV. The spectral assignment for the C 1s and O 1s NEXAFS spectra shown in Figure 6 and S5 is summarized in Table S1 for PS.



**Figure S5** Characterization of a PS thin film after 5 min exposure to UV-SR illumination. (a) visible light image (15x) recorded during the measurements. (b) visible light image (50x) of the same area after the UV-SR measurements. (c) STXM transmission image at 285.2 eV (C 1s  $\rightarrow \pi^*_{C=C}$  transition) of the same area. The intensity of the 285.2 eV peak is only slightly reduced. (d) STXM C 1s spectra of the damaged (blue) and undamaged (green) areas as indicated in (c). (e) STXM O 1s spectra of the damaged (blue) and undamaged (green) areas as indicated in (c).

	undamaged			UV/air damaged			
#	Energy (eV)	Assignment	#	Energy (eV)	Assignment		
C 1s							
1	285.2	1π*	1	285.2	$\pi^*_{C=C}$		
2	287.5	exciton	2	286.6	$\pi *_{C=O}$		
3	288.9	2π*					
4	290.4		3	288.5	σ* <sub>C-0</sub>		
5	293.4	$\sigma_{C=C}^{*}$	4	293.6	$\sigma^*_{C=C}$		
O 1s							
	-		1	531.6	$\pi *_{C=O}$		
	-		2	539.0	σ* <sub>C-0</sub>		

**Table S1** Energies and tentative assignments of features in the C 1s and O 1s spectra of unexposed and 30 min UV/air damaged polystyrene (PS).

Figure S6 compares the (a) undamaged OD1(E) spectrum for PS and the (b) new OD1(E) spectrum with the respective theoretical spectra. For (b), a new theoretical spectrum was generated by changing the net-chemical formula to incorporate oxygen for the PS that was damaged by UV-SR during the 30 min exposure. A relatively good match between the pre and post-edge indicates the new formula is adequate.



**Figure S6** X-ray absorption spectra of (a) undamaged and (b) 30 min UV/air damaged PS in the C 1s and O 1s regions fit to OD/h curves, where h = 35 nm for undamaged PS (C8H8, d=1.04 g/mL) and h = 23 nm for 30 min UV/air damaged PS (C8O4H8, d=1.04). The elemental composition for the damaged PS was derived as outlined in the main paper.

Figure S7 presents the PMMA exposed to 5 mins during the UV-SR measurements with images taken (a) from the objective lenses in the UV-SR instrument, (b) from an optical microscope after the 5 mins exposure from UV-SR and (c) with STXM at 288.4 eV depicting the areas where there was UV exposure. Spectra shown in (d) and (e) are the C 1s and O 1s for the 5 min PS exposed sample to UV. Table S2 shows the spectral assignment for damaged and non damaged PMMA. Figure S8 presents the quantification of the (a) undamaged and (b) 30 min damaged *OD1(E)* spectrum overlaid with the PMMA chemical formula in (a) and (b) new net-chemical formula for the 30 min UV/air radiation damaged area calculated as  $C_5O_4H_{8}$ , obtained by the same method used to analyze the composition of the damaged PS.



**Figure S7** Characterization of a PMMA thin film after 5 min exposure to UV-SR illumination. (a) visible light image (15x) recorded during the measurements. (b) visible light image (50x) of the same area after the UV-SR measurements. (c) STXM transmission image at 288.4 eV (C  $1s(C=O) \rightarrow \pi^*_{C=O}$  transition) of the same area. (d) STXM C 1s spectra of the damaged (blue) and undamaged (green) areas indicated in (c). (e) STXM O 1s spectra of the damaged (blue) and undamaged (green) areas indicated in (c).

_	undamaged			UV/air damaged			
#	Energy (eV)	Assignment <sup>47</sup>	#	Energy (eV)	Assignment		
C 1s							
1	287.6	σ* <sub>C-H</sub>	1	286.7	$\pi^*_{C=O}$		
2	288.45	$\pi^*_{C=O}$					
3	290.2		2	288.6	$\pi *_{O-C=O}$		
4	291.9	σ* <sub>C-C</sub>	3	294.1	$\sigma^*_{C-C}$		
5	295.9	$\sigma^*_{C=O}$	2	298.0	$\sigma^*_{C=O}$		
O 1s							
1	532.3	$O 1s(C=\underline{O}) \rightarrow \pi^*_{C=O}$	1	532.2	$\pi^*_{C=O}$		
2	535.2	$O 1s(\underline{O}-C=O) \rightarrow \pi^*_{C=O}$	2	534.9	σ* <sub>C-O</sub>		
3	540.3	σ* <sub>C=0</sub>	3	539.6	σ* <sub>C=O</sub>		

**Table S2** Energies and tentative assignments of features in the C 1s and O 1s spectra of unexposed and 30 min UV/air damaged polystyrene (PMMA).



**Figure S8** X-ray absorption spectra of (a) undamaged and (b) 30 min UV/air damaged PMMA in the C 1s and O 1s regions fit to OD/h curves, where h = 31 nm for undamaged PMMA (C<sub>5</sub>O<sub>2</sub>H<sub>8</sub>, d=1.18 g/mL) and h = 11 nm for 30 min UV/air damaged PMMA (C<sub>5</sub>O<sub>4</sub>H<sub>8</sub>, d=1.18). The elemental composition for the damaged PMMA was derived as outlined in the main paper.

Spectral assignment for PFSA sample is shown in Table S3 and the raw UV-SR data as a function of exposure time is shown in Figure S9. The raw spectra are consistently similar as the exposure time increases, indicating that PFSA is not sensitive to the same UV radiation as PS and PMMA.

	undamaged		
#	Energy (eV)	Assignment	
C 1s			
1	289.1	$\sigma *_{C=O}$	
2	292.4	$\sigma *_{C\text{-}F} \bot$	
3	295.5	$\sigma *_{C-F} (//)$	
4	298.6	$\sigma^*_{C-C}$	
5	307	σ* <sub>C-C</sub>	

**Table S3** Energies and tentative assignments of features in the C 1s and F 1s spectra of perfluoro-sulfonic acid (PFSA).

 $^{(a)}$  MS = multiple scattering



**PFSA** 

**Figure S9** Reflectance spectra recorded over time intervals between 0-30 m for a 52 nm thick PFSA film spun cast from a 2 wt% solution in an aqueous isopropanol mixture. The curves overlap within the noise level. This is the raw data used in determining the thicknesses reported in Figure 2.

#### S5. Correlating UV-SR and STXM thickness measurements

The linear correlation analysis between UV-SR and STXM thickness for PS, PMMA and PFSA films from Figure 9 is shown in Figure S10 with the values in Table S4.



**Figure S10** Absolute thicknesses (nm) of 3 polymeric thin films (PS, PMMA, PFSA spun coated and deposited on a 75 nm thick SiNx window) determined by UV-SR plotted against the thicknesses of the same areas determined by STXM (see Table 2 for numerical values), in both cases, using minimal exposure conditions. The straight lines are linear fits with the slopes and regression coefficients indicated in Supplemental Table S4.

**Table S4** Linear regression of the UV-SR and STXM thickness results presented graphically in

 Figure S9.

Sample Slope		Standard error of slope	$\mathbf{R}^2$
PS	0.885	0.0222	0.9969
PMMA	0.881	0.0038	0.9999
PFSA	0.967	0.0144	0.9995

# S6. Analysis of thickness decay data h(t) for PMMA and PS polymers

Part 1: obtaining phenomenological trends of all experimental data

Figure S11 represents the full raw data set obtained for different initial thicknesses

 $h_0 = h(t = 0)$  for both polymers PMMA and PS. Below we present an analysis aiming to find trends describing functionality of h(t) and its phenomenological parameters.



**Figure S11:** Raw h(t) data measured by UV-SR for different initial thicknesses  $h_0$  and different polymers (PMMA, PS) with respect to the UV radiation time applied:  $\bigcirc$  = method-ii PS 110nm (Fig. 4),  $\bigcirc$  = method-ii PS 40 nm (Fig. 2),  $\triangle$  = method-ii PS 42 nm,  $\blacklozenge$  = method-ii PS 49 nm (Fig. 4),  $\bigcirc$  = method-ii PS 49 nm (Fig. 4),  $\diamondsuit$  = method-ii PS 110 nm (Fig. 4),  $\bigcirc$  = method-ii PS 49 nm (Fig. 4),  $\circlearrowright$  = method-ii PS 110 nm (Fig. 2),  $\square$  = method-ii PS 126 nm,  $\bigcirc$  = method-ii PMMA 34 nm (Fig. 2),  $\square$  = method-ii PMMA 92 nm (Fig. 3),  $\bigcirc$  = method-i PMMA 91 nm (Fig. 3),  $\triangle$  = method-ii PMMA 49 nm (Fig. 3),  $\square$  = method-ii PMMA on Si (Fig. 5),  $\bigcirc$  = method-ii PMMA 54 nm.

Following the reviewer's suggestion, we tested all the data in Figure S11 against the following approximation function:

$$h(t) = h_0 e^{-bt},\tag{S1}$$

were  $h_0$  and b are some phenomenological parameters calculated for each given data set by applying the least square fit for S1 approximation. If the approximation S1 is satisfactory, then by introducing a new scale for Figure S11, all data points collapse making the obscured mathematical law of the exponential functionality look more pronounced. Figure S12 represents the same data in Figure S11 plotted with the new dimensionless axes X and Y scaled as: X = t \* *b* and  $Y = h(t)/h_0$ , respectively, where both  $h_0$  and *b* were found for each given data set by the least square fit of S1. Table S5 presents these parameters for a linear and exponential fit.

	Material	Method	h0*	h0 <sup>#</sup>	b*	b <sup>#</sup>
0	PS	ii	109.9	110.9	-0.613	-0.007
•	PS	i	111.2	112.1	-0.6125	-0.006
	PS/Si	ii	84.4	84.9	-0.959	-0.013
	PS	ii	126.2	127.1	-0.614	-0.006
٠	PS	i	49.6	49.9	-0.482	-0.011
0	PS	ii	49.0	49.3	-0.495	-0.012
Δ	PS	ii	41.5	42.0	-0.511	-0.015
0	PS	ii	40.7	42.9	-0.771	-0.029
	PMMA	i	89.3	92.2	-0.974	-0.015
	PMMA	ii	89.4	92.2	-0.955	-0.015
	PMMA/Si	i	78.2	82.2	-1.316	-0.025
	PMMA	i	47.5	48.1	-0.661	-0.018
Δ	PMMA	ii	48.3	49.1	-0.709	-0.019
0	PMMA	ii	33.2	33.8	-0.540	-0.022

**Table S5** Comparison of the phenomelogical parameters of a linear and exponentialapproximation for all PS and PMMA data points in Figure S11.

\* Linear approximation

# exponential approximation



**Figure S12** Same data as in Figure S11 plotted with new scaled coordinated X = t \* b and  $Y = h(t)/h_0$ , where coefficients  $h_0$  and b were found for each given data set as in Table S5 of Figure S11 by the least square fitting with S1 approximation. The slight exponential non-linearity is apparent.  $\bigcirc$  = method-ii PS 110nm (Fig. 4),  $\bigcirc$  = method-ii PS 40 nm (Fig. 2),  $\blacklozenge$  = method-i PS 49 nm (Fig. 4),  $\bigcirc$  = method-ii PS 110 nm (Fig. 4),  $\bigcirc$  = method-ii PS 110 nm (Fig. 4),  $\bigcirc$  = method-ii PMMA 34 nm (Fig. 2),  $\square$  = method-ii PMMA 92 nm (Fig. 3),  $\square$  = method-ii PMMA 49 nm (Fig. 3),  $\triangle$  = method-ii PMMA 49 nm (Fig. 3),  $\square$  = method-ii PMMA 49 nm (Fig. 5),  $\square$  = method-ii PMMA 54 nm.

The natural logarithm is applied to Y axis in Figure S12 and is shown in Figure 10. The overall trend looks more linear than in Figure S12, confirming that the natural logarithm function is the appropriate experimental approximation.

With the given intervals of X and Y, the collapsed exponential trend looks very similar to a linear approximation (due to the small values of phenomenological coefficient *b*, b\*t<1, where time *t* is large and change in the interval (0,3600 s) as shown in Table S5.

#### Part 2: Theoretical analysis of experimental trends

We assume that all data points in Figure S11 is a monotonous decaying data.

The speed of the thickness decay can be written as: dh(t)/dt. This could be named as the rate of the thickness decay and denoted by R:

$$\frac{dh(t)}{dt} = R, \text{ where } R < 0 \tag{S2}$$

Which type of functionality of R describes the data in Figure S11? The data in Figure S11 is presented as a function of h(t), which is a particular solution of the S2 differential equation. Therefore, the function R must be constructed such that the solution of S2 will give us the exact h(t) functionality discovered in Part1.

In the Part1 we found that from experimental point of view, the exponent with a negative power  $h_0e^{-bt}$  is a good approximation of the experimental h(t). At the same time, we noticed that *b* is small and another type of approximation – a linear approximation  $h(t) = h_0 - at$  - is also reasonable.

Here both cases are considered. First, the differential equation S2 is solved for R = -a and then for R = -h(t)b.

The rate R is a constant:

$$\frac{dh(t)}{dt} = -a. \tag{S3}$$

Integrating and finding the constant of integration for a linear model of h(t):

$$h(t) = h_0 - at$$
, where  $h_0 = h(t = 0)$ . (S4)

The rate R is proportional to the thickness:

$$\frac{dh(t)}{dt} = -h(t)b \tag{S5}$$

Integrating and finding the constant of integration for the exponential model of h(t):

 $h(t) = h_0 e^{-bt}$ , with similar  $h_0 = h(t = 0)$ . (S6)

From the analysis of the experimental data, *a* is between ~0.5 and ~1, while *b* is between ~0.006 and ~0.03, i.e. *b*<<1. Therefore, we could represent a solution for equation S5 as a Taylor series with respect to the small parameter *b*:

$$h(t) = h_0 e^{-bt} = h_0 \left( 1 - bt + \frac{b^2 t^2}{2} + O(b^2) \right),$$
 (S7)

where  $O(b^2)$  is a second order residue. With the first order accuracy, the exact solution S6 can be replaced with;

$$h(t) \approx h_0 (1 - bt). \tag{S8}$$

There are two different types of the decay rate: R = -a and R = -h(t)b, which produce different equations and thus different particular solutions: linear S4 and exponential S6,

respectively. The exponential solution S6 due to given experimental conditions ( $b \le 1$ ) can be further reduced to the linear equation S8. Comparing S4 and S8:

$$a = h_0 b. \tag{S9}$$

where *a* is a constant rate of the thickness decay and its dimension is [length/time]. Parameter *b* is a reciprocal of time; thus,  $\tau = 1/b$  and its dimension is [time]. Now S9 can be rewritten as the rate for both models of R:

$$a = h_0 / \tau. \tag{S10}$$

# *Part3: analysis of relationship for phenomenological parameters a,* $h_0$ *, and b*

Differential equations S3 and S5 describe dynamics of the change of thickness decay rate depending on the implemented model of R. The solutions S4 and S6 gives us two evolutions of how the thickness may decay with respect to the time. These two solutions depend on a few coefficients: a,  $h_0$  and b (the last one is  $1/\tau$ ), which are the phenomenological parameters for the experimental data. Is there a particular relationship between these parameters, with respect to the raw data obtained in Figure S11? Are there additional relationships related to equations S9 and S10?

Figure S13 shows  $h_0$  and  $\tau$  (which is 1/*b*) calculated for each dataset of Figure S11 for PMMA and PS. In Figure S13 there are two distinct correlations of characteristic time of the decay,  $\tau$ , with respect to the initial thickness of the layer,  $h_0$ .



**Figure S13** Least square fit coefficients  $h_0$  and  $\tau = 1/b$  obtained for the thickness decay rate model R = -h(t)b with solution  $h(t) = h_0 e^{-bt}$  for all data sets presented in Figure S11 where • denotes all PMMA and • all PS samples.

Both correlations PMMA and PS overlap when  $h_0 \rightarrow 0$  giving the characteristic time  $\tau \approx 15$  min, which is *independent from the material*. The same data as in Figure S13 can be replotted in terms of the characteristic decay rate *a* (S9, S10).

Similar to Figure S13 both correlations for PMMA and PS overlap when  $h_0 \rightarrow 0$  giving a characteristic decay rate  $a \approx 0.5$  nm/min which is *independent on the material*. The data in Figure S13 and Figure S14 are inverted with respect to the polymer material, indicating that the lower characteristic time corresponds to higher decay rate.



**Figure S14** Same data as in Figure S13 re-plotted against the characteristic decay rate  $a = h_0 b$  (S9) where  $\bullet$  denotes all PMMA and  $\bullet$  all PS samples.

# References

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