

Characterization of Parylene-N and Parylene-C Photooxidation

K. G. PRUDEN,¹ K. SINCLAIR,² S. BEAUDOIN¹

¹Department of Chemical and Materials Engineering, Arizona State University, Box 876006, Tempe, Arizona 85287-6006

²Department of Chemical Engineering, Washington University, Campus Box 1198, One Brookings Drive, St. Louis, Missouri 63130-4899

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ABSTRACT: Parylene-N and parylene-C are polymers of interest for microelectronic and medical coating applications. Modifications for improved surface properties could make them even more useful in such applications. Parylene-N and parylene-C films were exposed to ultraviolet light in the presence of oxygen and analyzed with Rutherford backscattering spectrometry, secondary-ion mass spectroscopy, X-ray photoelectron spectroscopy, and infrared spectroscopy. This study shows that such exposure results in the formation of aldehyde and carboxylic acid groups near the surface of the films. At the maximum exposure dose, the concentration of oxygen in both parylene-N and parylene-C is about 13% at the film surface, and it decreases exponentially with increasing depth. Further modeling and optimization of this process would allow it to be used to tailor the surface concentration of oxygenated species in parylene for the optimization of adhesion and wettability or for the chemical binding of other moieties. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 1486–1496, 2003

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INTRODUCTION

The microelectronics industry's ongoing pursuit of faster, higher performance devices is driving the development of novel materials with improved chemical, electrical, mechanical, and thermal properties. The inclusion of microelectronic devices in nontraditional applications, such as medical devices, places additional restrictions on the properties of these materials. In particular, the need for biocompatible devices has driven the reconsideration of many of the polymeric species currently used for packaging applications. Parylenes are good candidates for use as packag-

ing materials, and this is especially true for medical applications involving an interface with living tissue. The ideal structures of parylene-N and parylene-C are shown in Figure 1. Parylene-C is one of the most bioinactive polymers that has been examined by researchers.^{1–3} The surface modification of parylenes to help them resist protein adsorption can improve the biocompatibility of these films. Moreover, it is often useful to functionalize the surfaces of such polymers so that desired moieties may be attached chemically.

Polymer surfaces can be modified with a spectrum of techniques. Some common examples of surface modification techniques include chemical grafting, plasma treatment, and photochemical modification.^{4–15} Such modifications can result in changes to the wettability, adhesion to other surfaces, roughness, crystallinity (which impacts the transport of materials through the polymers), and

Correspondence to: S. Beaudoin (E-mail: steve.beaudoin@asu.edu)

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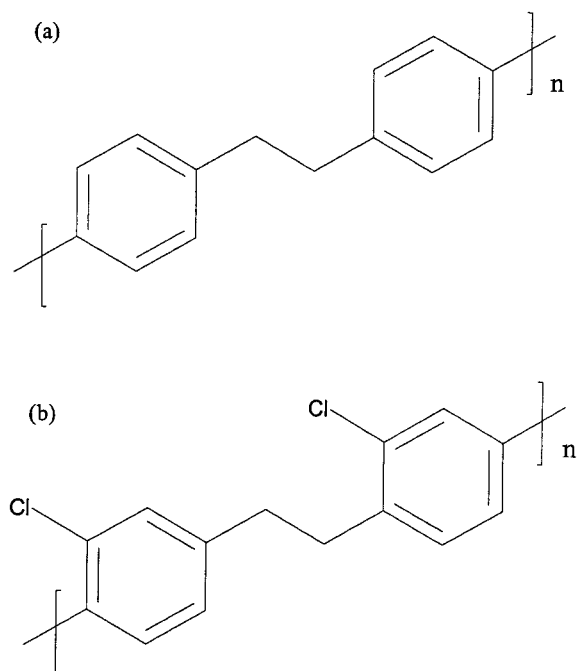


Figure 1. Structures of (a) parylene-N and (b) parylene-C.

biocompatibility. By selecting the appropriate modification technique for a particular material and by adjusting the operating parameters used in this technique, we can control the depth of the modified region, the type and concentration of chemical groups created, and the type and degree of physical modification of the surface.

Several studies have already been performed on the photochemical modification of parylene-N and parylene-C with ultraviolet (UV) light. UV irradiation in the presence of air resulted in the oxidation of the parylene films. These studies were conducted with the purpose of facilitating the selective removal of parylene-N by rendering undesirable sections soluble in basic aqueous solutions via photooxidation.^{13,14,16} Subsequent studies were conducted with the goal of assessing the stability of parylenes at wavelengths found in sunlight through the qualitative assessment of chemical changes that occur because of photooxidation.^{17,18} Other recent studies have assessed key mechanical and electrical property changes that occur with the photooxidation of parylenes.^{18,19} This study is meant to assess both the qualitative and quantitative chemical changes that occur when parylenes are exposed to short-wavelength UV light. Specifically, thin films of parylene-N and parylene-C were exposed to UV light in an oxy-

gen-containing environment to induce photooxidation. As demonstrated later, photooxidation occurred as a result of oxygen molecule attack at radical sites that were created by UV photoinitiation. The degree of photooxidation was measured as a function of the UV dose and film depth.

EXPERIMENTAL

Overview

Photooxidation was induced by the exposure of parylene-coated silicon wafer coupons to UV light in the presence of oxygen. Atomic oxygen incorporation into the films was measured with Rutherford backscattering spectrometry (RBS) and secondary-ion mass spectrometry (SIMS). X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy were used to determine the chemical structures of the oxygenated films.

Materials

Silicon wafers were coated with parylene-N and parylene-C by Paratronix (Attleboro, MA). The film thicknesses, as measured by a Filmetrics film thickness measurement system, were 3 and 3.1 μm , respectively. The as-deposited film composition was checked with RBS. For the parylene-N samples, the carbon/hydrogen ratio was 1:1, and they can be considered ideal in structure. For the chlorinated polymer, only three out of every five monomers contained chlorine (i.e., 60% of the chlorine expected in the ideal structure).

UV Exposure

Sample coupons were exposed in a 51 cm \times 51 cm \times 23 cm exposure chamber. Air was the ambient for these exposures. The chamber was equipped with an 8-W UV germicidal lamp (General Electric G8T5), the primary output of which was 254 nm. The light intensity was measured with a Minolta UV radiometer and was 0.63 mW/cm² on average at the sample surface. The UV dose was controlled by changes in the exposure time. Exposure times ranged from 13 min for a dose of 500 mJ/cm² to 4 h and 15 min for a dose of 10,000 mJ/cm². The 500 mJ/cm² dose was about 4 times higher than doses typically used in industrial photolithography during integrated circuit manufacturing. The doses used here were chosen so that

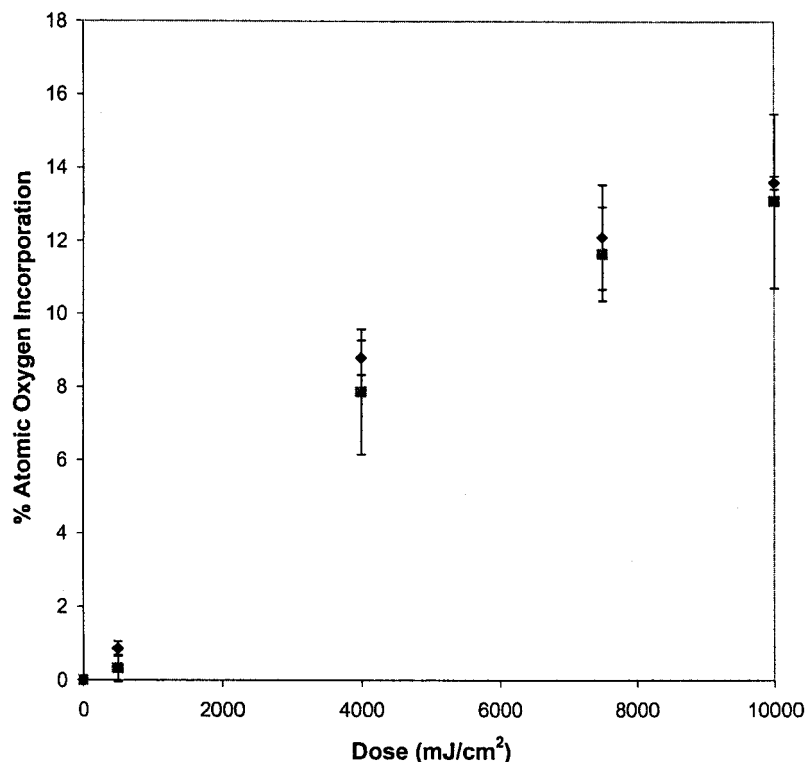


Figure 2. Atomic oxygen incorporation in (♦) parylene-N and (■) parylene-C film surfaces (top 5%) as a function of dose.

we could examine the range of photooxidative behaviors occurring over this dose interval.

Characterization

A Cameca IMS 3f ion microscope (with Cs^+ as the primary ion beam) was used to generate SIMS depth profiles from gold-coated samples. The Cs^+ ion beam had a beam current of 150 nA and an energy of 10 keV. Conventional RBS was performed with a 2.8-MeV He^{2+} ion beam with an incident angle of 7° . This technique was used to analyze the as-deposited compositions of parylene films and to generate quantitative atomic composition values, against which SIMS data were calibrated. XPS was performed with a Kratos XSAM800 system with an Mg $K\alpha$ line X-ray source at 1.25 keV and a takeoff angle of 90° . This technique was used to identify bonding states in the products of parylene photooxidation. A Split-Pea horizontal attenuated total reflectance accessory (Harrick Scientific, Inc., Ossining, NY) was used on a Nicolet Nexus 470 FT-IR spectrometer so that we could examine bonding in the parylene samples. Finally, a Rame-Hart goniometer was

used to measure the contact angle (with water as a probe fluid) on the exposed samples.

RESULTS

Overview

Our results indicate that the exposure of parylene-N and parylene-C to 254-nm UV light in the presence of air causes photooxidation. The incorporation of oxygen caused by this exposure has been studied as a function of the exposure dose and film depth, and the identities of products formed from these reactions have been investigated with several characterization techniques.

Oxygen Incorporation as a Function of Dose

Experiments were performed at target doses of 500, 4000, 7500, and 10,000 mJ/cm^2 . The atomic oxygen incorporation was measured at the surface of the parylene films (top 5%) with RBS and was plotted as a function of dose, as shown in Figure 2. Atomic oxygen incorporation into the

Table 1. Contact-Angle Summary

Dose (mJ/cm ²)	Contact Angle	
	Parylene-N	Parylene-C
0	80.73 ± 3.86°	89.71 ± 0.81°
500	85.24 ± 2.76°	89.73 ± 0.97°
4,000	78.48 ± 4.11°	92.69 ± 3.25°
7,500	67.48 ± 11.87°	65.25 ± 7.50°
10,000	56.52 ± 13.33°	58.37 ± 0.90°

parylene films increased linearly as a function of dose at low doses (4000 mJ/cm² or less). At higher doses (7500 mJ/cm² or greater), the degree to which atomic oxygen incorporation changed with increasing dose was reduced in comparison with the low-dose conditions. These profiles were similar for both parylene-N and parylene-C. Each point is the average of three to five samples, and a total of 32 samples were characterized.

Goniometer measurements are summarized in Table 1. These indicate that, for both parylene-N and parylene-C, the contact angle does not change

significantly until the sample has been exposed to a dose higher than 4000 mJ/cm². This effect is due to the lack of polar groups at the surface of as-deposited parylene films. The contact angle decreases for both parylene types upon exposure to high doses of UV light because of the incorporation of polar oxygen groups.

Oxygen Incorporation as a Function of Depth

RBS was used in conjunction with SIMS to determine a quantitative depth profile of oxygen throughout the film.²⁰ Figure 3 shows the results of this approach and indicates that for samples exposed at a dose of 10,000 mJ/cm², atomic oxygen is incorporated mainly in the top 25% of the film. Also, the atomic oxygen concentration reaches a maximum near, but not at, the surface of the film.

Photooxidation Product Identification

IR

IR spectroscopy was performed on parylene-N samples (exposed at doses of 500, 2000, 4000,

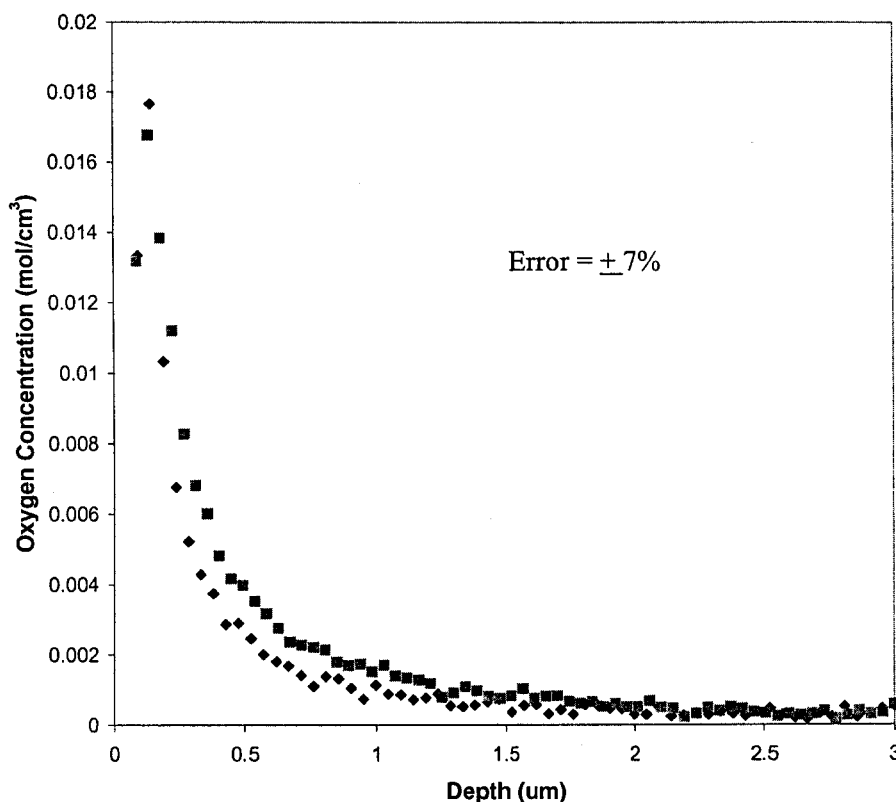


Figure 3. Atomic oxygen incorporation in (◆) parylene-N and (■) parylene-C as a function of depth.

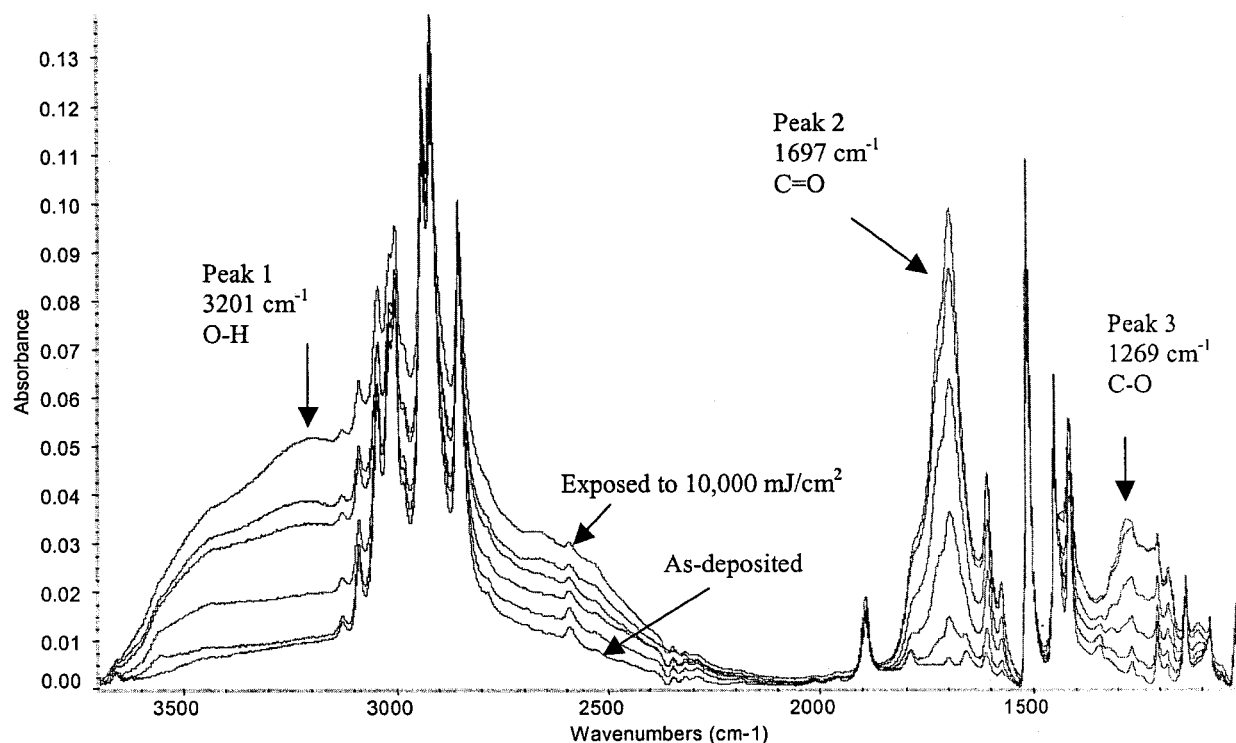


Figure 4. IR spectra of as-deposited and UV-exposed parylene-N.

7500, and 10,000 mJ/cm^2). These spectra are shown in Figure 4. IR spectroscopy was used to determine what oxygen-containing structures were formed as a result of photooxidation. A peak at 1697 cm^{-1} in the exposed spectrum can be attributed to carbonyl groups ($\text{C}=\text{O}$). This peak appears at a wave number that is low for a $\text{C}=\text{O}$ bond; this means that it probably is indicative of an aldehyde or carboxylic acid. A peak formed at 1269 cm^{-1} can be attributed to a $\text{C}-\text{O}$ bond, which is also indicative of a carboxylic acid. A broad peak in the region greater than 3100 cm^{-1} is characteristic of the formation of $\text{O}-\text{H}$ bonds.²¹ A peak appears here at higher doses. The peak ratios (relative to as-deposited parylene-N) of the $\text{C}=\text{O}$, $\text{C}-\text{O}$, and $\text{O}-\text{H}$ peaks as a function of dose are shown in Figure 5. The combination of $\text{C}=\text{O}$, $\text{C}-\text{O}$, and $\text{O}-\text{H}$ bonds indicates that carboxylic acids are formed in parylene-N as a result of photooxidation with UV light. The IR spectra for UV-exposed and as-deposited parylene-C are similar and imply the same results.

It is not clear from these IR results if oxygen incorporation is occurring at chain carbons or at ring carbons. None of the aromatic or aliphatic carbon peak ratios follow a significant trend as a function of dose, so the IR data are inconclusive on this point.

XPS

The XPS spectra for as-deposited parylene-N and parylene-C are shown in Figure 6. Figure 7 shows XPS spectra of parylene-N and parylene-C exposed to UV light at a dose of 10,000 mJ/cm^2 .

Consistent with the XPS spectra of parylene from the literature, the aromatic and chain carbon peaks are irresolvable.^{16,22,23} Peaks representing carbon attached to oxygen appear at higher binding energies, and hydrocarbon contamination appears at lower binding energies. XPS was also performed on both parylene-N and parylene-C exposed to 500, 4000, and 7500 mJ/cm^2 . At a dose of 4000 mJ/cm^2 , a new peak appeared, representing $\text{C}-\text{O}$ or $\text{C}=\text{O}$ groups. This peak was also present in samples exposed to doses of 7500 and 10,000 mJ/cm^2 . Moreover, in samples exposed to doses of 7500 and 10,000 mJ/cm^2 , an additional peak appeared, representing $\text{O}-\text{C}=\text{O}$ groups. This peak was indicative of carboxylic acid formation.

It is not clear from the XPS data whether the oxygen-containing groups are being formed from chain carbons or ring carbons. This is due to the fact that the peaks that are typically attributed to both the chain carbons and ring carbons are not

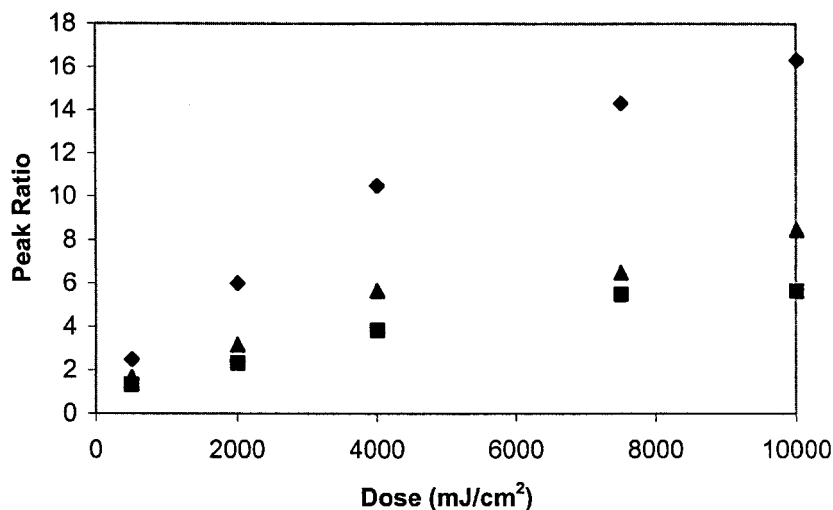


Figure 5. IR peak ratios (relative to as-deposited parylene-N) for peaks (▲) 1, (◆) 2, and (■) 3 as a function of dose. Peak numbers refer to the peak labels in Figure 4.

individually identifiable because only their summation peak is easily resolved.

Feasible Reaction Products: Limiting Case Calculations

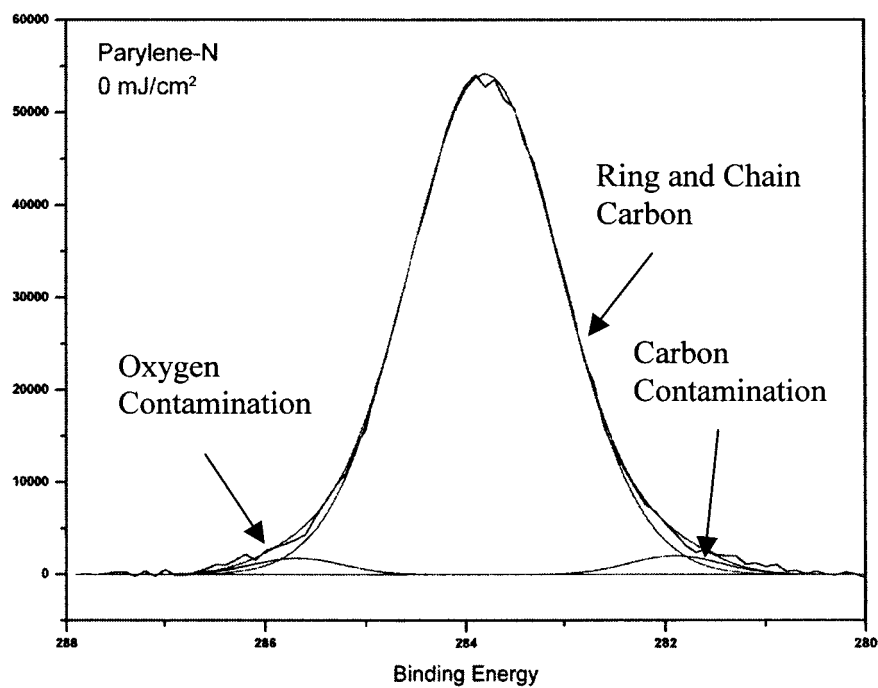
The quantification of atomic oxygen incorporation (% atomic oxygen) can also elucidate which products are being formed. According to the RBS results, the percentage of atomic oxygen incorporation reaches a value of $13.6 \pm 0.2\%$ for parylene-N and $13.1 \pm 2.4\%$ for parylene-C after the samples have been exposed to the maximum dose of 10,000 mJ/cm². Table 2 shows some expected products, with their respective atomic oxygen percentages. A limiting case study was performed with different combinations of these products to determine if they can account for the measured atomic oxygen percentage values. This limiting case study was performed with the assumption of ideal monomers for simplicity. The hypothesized products shown in Table 2 were paired so that all possible pair combinations were considered. Then, the proportion of each product was calculated so that the average atomic oxygen percentage matched that measured with RBS. This was done with a weighted average of the theoretical atomic oxygen percentages for each pair of products. Weighted averages that resulted in one product's proportion equaling less than 0 or greater than 100% were determined to be not physically realizable. This study is summarized in Table 3. The analysis shows that the combinations of disubstituted aldehyde and disubstituted carboxylic acid and di-

substituted aldehyde and aldehyde/carboxylic acid are reasonable within the context of the measured atomic oxygen percentages.

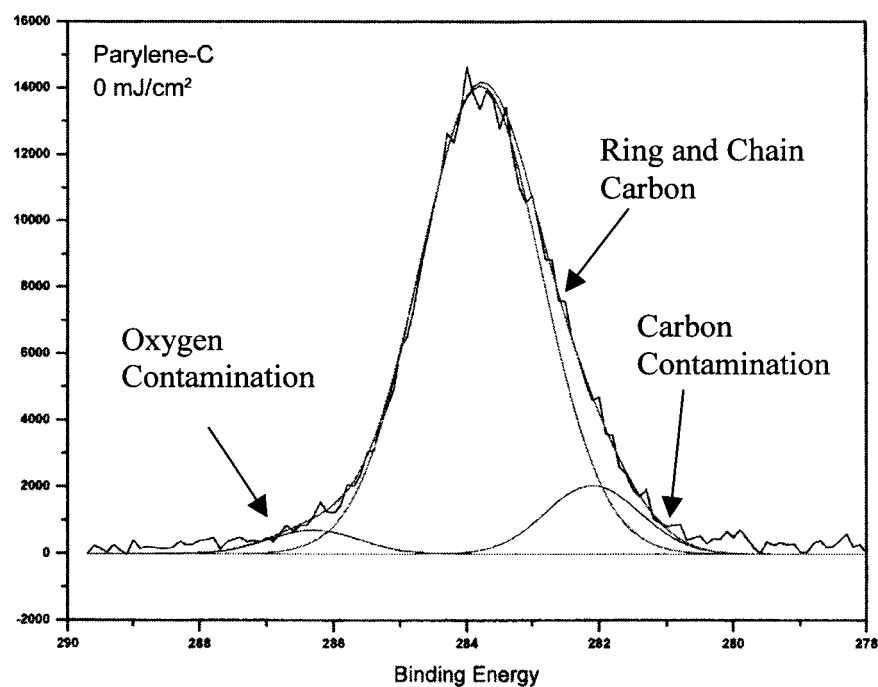
As discussed earlier, the parylene-C samples used here consisted of nonideal monomers; this was determined from the RBS analysis of as-deposited parylene-C samples. Instead of each parylene-C monomer containing a Cl atom, only 60% of the monomers contained a Cl atom. The aforementioned study was repeated under the assumption of nonideal parylene-C (i.e., with only 60% of the ideal Cl content). Although the percentages of aldehyde and carboxylic acid groups differed slightly, the overall conclusions about which product combinations may form did not change.

DISCUSSION

The results indicate that the overall oxidation reaction results from a molecular oxygen reaction with a radical site, which is most likely formed because of photolytic scission of a chain C—H bond.²⁴ Given that the concentration of available C—H bonds is finite, the consumption of these radical sites may be one explanation for the fact that the change in the atomic oxygen incorporation as a function of dose decreases as the dose increases. This has also been hypothesized for the thermal oxidation mechanism of parylene, which exhibits the same behavior.²⁵ The XPS data indicate that the initial products of this reaction are

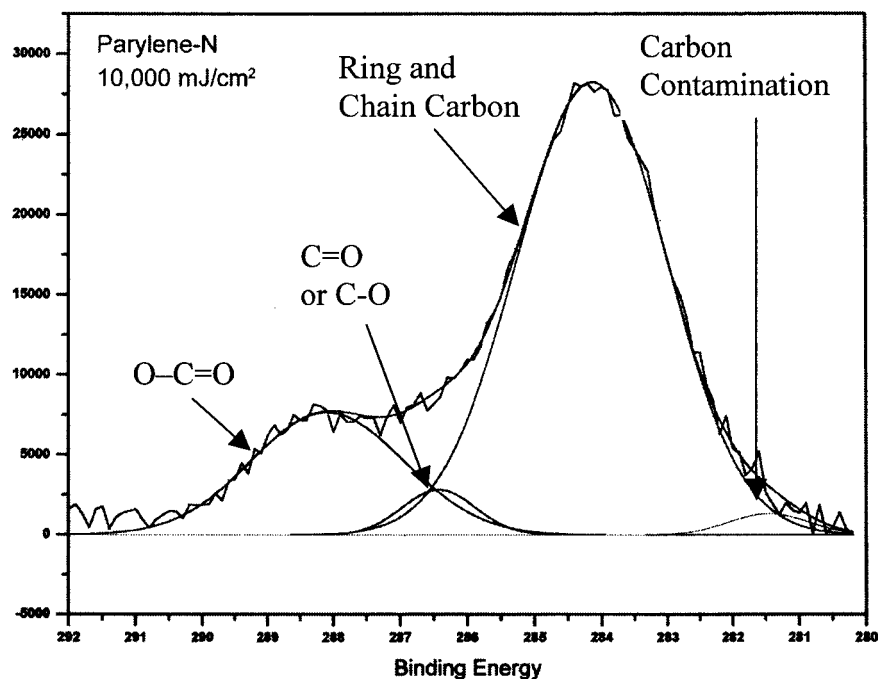


(a)

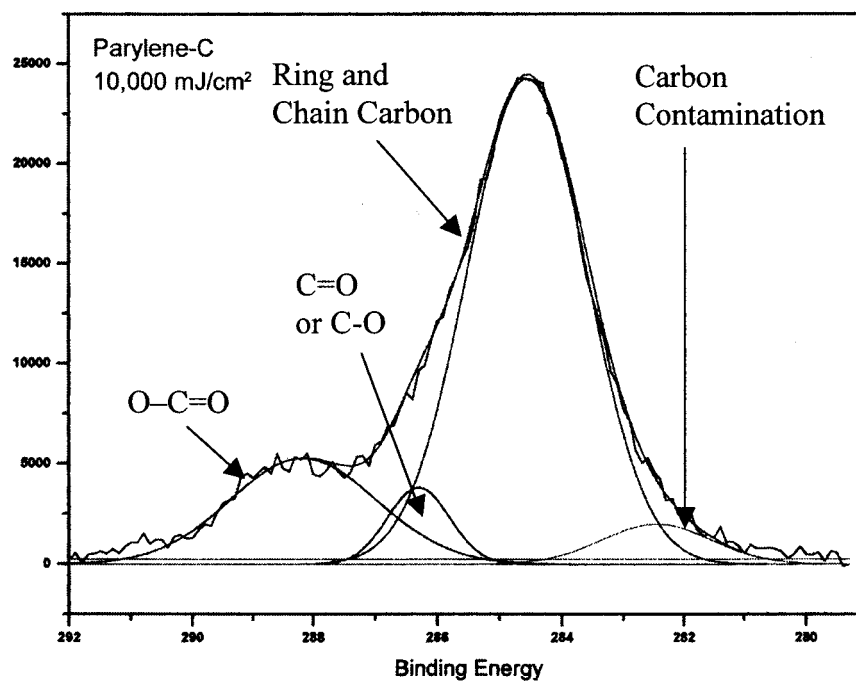


(b)

Figure 6. XPS spectra of as-deposited (a) parylene-N and (b) parylene-C.



(a)



(b)

Figure 7. XPS spectra of (a) parylene-N and (b) parylene-C after exposure at a dose of 10,000 mJ/cm².

Table 2. Expected Photooxidation Products

Parylene-N Structure	Formula	Parylene-C Structure	Formula	Atomic Oxygen (%)
	C_8H_8		C_8H_7Cl	0
	C_8H_7O		C_8H_6ClO	6.25
	$C_8H_6O_2$		$C_8H_5ClO_2$	12.5
	$C_8H_7O_2$		$C_8H_6ClO_2$	11.76
	$C_8H_6O_3$		$C_8H_5ClO_3$	17.6
	$C_8H_6O_4$		$C_8H_5ClO_4$	22.2

Table 3. Atomic Oxygen Percentage Limiting Case Study Results

Product Combination	Parylene-N		Parylene-C	
	Oxygenated Groups That Are Aldehyde (%)	Oxygenated Groups That Are Carboxylic Acid (%)	Oxygenated Groups That Are Aldehyde (%)	Oxygenated Groups That Are Carboxylic Acid (%)
Both disubstituted	89	11	94	6
Both monosubstituted		Not physically realistic		
Disubstituted aldehyde and aldehyde/carboxylic acid	78	22	88	12
Disubstituted carboxylic acid and aldehyde/carboxylic acid		Not physically realistic		

aldehydes, as evidenced by the presence of a peak attributable to C=O only. At higher doses, carboxylic acids form in addition to aldehydes. This is supported by the appearance of an XPS peak attributable to O—C=O and the IR spectra of parylene-N at the different exposure doses, which show a C=O peak, a C—O peak, and an O—H peak (appearing at higher doses). The decrease in the contact angle, as shown by the goniometry results, also supports the incorporation of polar groups at higher doses.

Studies of the photooxidation of other polymers have shown a subsurface atomic oxygen concentration maximum similar to the one observed in parylene-N and parylene-C in this study. Other researchers have hypothesized that this peak is due to competitive reactions between radicals. At very high doses (e.g., at the immediate film surface), photolytic scission is very efficient, creating a large concentration of polymer radicals and hydrogen radicals. Therefore, near the surface of the film, the recombination of radicals is the dominant reaction. Deeper into the film, recombination becomes less significant, and the net oxidation reaction becomes more significant. The maximum oxygen content would occur at the point at which the reaction switches from being recombination-dominated to oxidation-dominated.²⁶ In the parylene films studied here, it is clear that significant chemical changes occur near the surfaces of the films. These changes also may impact the diffusion of oxygen into the films, the structure of the films near the surface, or the absorbance of UV light. Any of these factors may also contribute to the near-surface peak in oxygen concentration observed in this work.

It is still unclear whether the ring carbons are participating in the observed reactions. The IR analysis performed in this study does not necessarily support ring opening, as peaks attributable to ring carbons should decrease and peaks attributable to chain carbons should increase in this case. Likewise, the XPS data are inconclusive on this point. Early literature on parylene photooxidation predicts that oxidation only occurs at chain carbons. The oxidation of chain carbons in parylene is thought to result in the production of terminating carboxylic acids. Because carboxylic acids are highly soluble in basic solutions, and the oxidization of parylene results in its solubility in basic solutions, it is thought that this oxidation occurs primarily at the chain carbons.^{13,14,16} Recently, Fortin and Lu¹⁹ examined the degradation of UV-treated samples. Using IR spectroscopy,

they found that UV treatment at a wavelength of 253.7 nm and at a dose of 13,000 mJ/cm² did not change the spectrum significantly; this suggested that ring opening did not occur. However, Bera et al.¹⁸ did predict that parylene photooxidation would result in ring opening on the basis of an IR spectroscopy analysis of photooxidation experiments. Their experiments showed that the carboxylic acids that formed during exposure for 110 h ($\lambda > 300$ nm) at 60 °C were both aliphatic and aromatic.

CONCLUSIONS

The photooxidation of parylene-N and parylene-C by exposure to 254-nm UV light in ambient air has been studied. Characterization shows that the reaction begins with aldehyde production at low doses. At higher doses, carboxylic acid groups form, in addition to the aldehyde groups. For the conditions studied here, the top 25% of the film is chemically altered by this reaction, with most of the reaction occurring in the top 5%.

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