Plasma- and Vacuum-ultraviolet (VUV) Photo-polymerisation of Bioactive Organic Coatings: Stability in Polar Solvents and in Air

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Abstract: We have investigated amine- ([–NH$_2$])-rich coatings in various cell-culture applications for several years, depositing films by plasma polymerisation from ethylene (C$_2$H$_4$)-N$_2$ or C$_2$H$_4$–NH$_3$ mixtures, respectively. More recently, vacuum-ultraviolet- (VUV, $\lambda < 200$ nm) assisted photo-polymerisation has proven highly advantageous: Employing quasi-monochromatic Kr and Xe VUV sources, we have found the latter to possess particularly high [-NH$_2$] values, presumably due to more specific and selective reactions induced by mono-energetic photons rather than by "hot" electrons, which are characterised by Maxwell-Boltzmann-like energy distributions. However, high concentration of [–NH$_2$] groups and very low solubility in aqueous media tend to be mutually exclusive; for the best possible compromise, we select appropriate precursor gas-mixture ratios.

We have now extended our investigations to O-containing organic deposits, again comparing photo- and plasma-assisted polymerisation from C$_2$H$_4$–N$_2$O, or C$_2$H$_4$–O$_2$ (10% O$_2$, diluted in Argon) gas mixtures, to verify that selective reaction pathways favouring high concentrations of the "desirable" –COOH or –OH functionalities exist, here too. All deposit types were characterised by XPS, FTIR, SEM and AFM, concentrations of particular functional groups being quantified via chemical derivatization, by reaction of toluidine blue O (TBO) with –COOH, and trifluoroacetic anhydride (TFAA) with -OH. As in the case of (–NH$_2$), where the derivatizing reagent is 4-(trifluoromethyl)benzaldehyde (TFBA), experimental results tend to confirm that more selective reactions occur via the VUV route.

1. Introduction

Recent review articles [1] bear witness to the extensive and rapidly-growing literature on the use of plasma-chemistry for creating bio-active polymer surfaces for the immobilisation of living cells or bio-molecules. From those articles it is clear that nitrogen (N)- or oxygen (O)-containing functional groups are particularly advantageous, more specifically primary amines (-NH$_2$), or carboxylic acid (-COOH) or hydroxyl (-OH) functionalities, respectively. This laboratory has for a number of years investigated N-rich polymer surfaces for various biomedical and cell-culture applications,[2] surfaces that were prepared by depositing N-rich organic thin films using atmospheric-pressure- or low-pressure plasma polymerisation of ethylene (C$_2$H$_4$)-N$_2$ or C$_2$H$_4$–NH$_3$ mixtures;[3] or, most recently, by vacuum-ultraviolet- (VUV, $\lambda < 200$ nm) assisted photo-polymerisation of such gas mixtures using quasi-monochromatic VUV sources.[3] We have compared the chemical structures of films prepared by (low-pressure) plasma- and VUV-assisted deposition, and have found the latter to possess particularly high -NH$_2$ concentrations, [-NH$_2$], presumably due to more specific and selective

reactions that may be achievable with mono-energetic photons rather than with "hot" electrons, which are responsible for plasma chemistry and which are characterised by "Maxwell-Boltzmann-like" energy. The purpose of the present research has been to extend those investigations to O-containing organic thin film materials, that is, to also compare photo- and plasma-assisted polymerisation of C_2H_4–nitrous oxide, N_2O, or C_2H_4–$(Ar+O_2)$ gas mixtures for possible selective reaction pathways that favour high concentrations of the "desirable" –COOH or –OH functionalities. In order to facilitate those comparisons, we again present data relating to (C_2H_4-NH_3) mixtures, as well.

2. Experimental Methodology

The experimental set-up used for VUV photochemical experiments was described and illustrated in detail elsewhere.[2,3] Briefly, it consists of a stainless steel "cross" chamber, which was first evacuated to a base pressure of about 5×10^{-6} Torr (~7 × 10^{-4} Pa) using a combination of turbo-molecular and rotary vacuum pumps. In the present VUV photo-polymerisation experiments, similar to our earlier ones, we irradiated flows of binary gas mixtures comprising C_2H_4 and NH_3, C_2H_4 and N_2O, or C_2H_4 and $(Ar+O_2)$ at low pressure, typically 100 mTorr (13.3 Pa). N_2O is employed in plasma chemistry as an oxidizer; $Ar+O_2$ mixture (90/10) was also used here, in order to completely avoid any incorporation of bound nitrogen in the deposits. The flow rate ratios, R (= F_{NH3}/F_{C2H4} or F_{N2O}/F_{C2H4}), were varied between 0 and 1; in the case of $(Ar+O_2)$, we resorted to much smaller R values, on account of the high reactivity of the O_2 molecule. Those conditions had been found to lead to the highest values of deposition rates, r, in this particular reactor. The coatings resulting from the photochemical reactions, henceforth designated "UV-PE:N" and "UV-PE:O" (for "ultraviolet-polymerised, nitrided or oxidised ethylene"), were deposited on glass slides with a thin (~ 100 nm) Ag coating. Two non-coherent VUV sources were used (Resonance Ltd., Barrie ON, Canada), based on electrodeless r.f. discharges in noble gases at low pressure, Krypton (Kr) and

Xenon (Xe). These (monochromatic) lamps and their resonant spectral characteristics (λ = 123.6 nm and 147.0 nm for Kr and Xe, respectively) were described in further detail elsewhere.[2,3]

For comparison, we have also used low-pressure plasma to deposit thin plasma polymer films with the same gas mixtures, henceforth designated "plasma-polymerised, nitrided (or oxidised) ethylene", PPE:N (or PPE:O). Under the conditions used, films had the desired maximum [N] (or [O]), and [–NH_2] ([–COOH] or [-OH]) concentrations. All deposits were characterised by XPS analyses, and by Fourier Transform (reflection-absorption) infrared (FTIR) spectroscopy. Concentrations of primary amines, [NH_2], and of hydroxyl groups, [OH], were determined by chemical derivatization reactions with 4-(trifluoromethyl)benzaldehyde (TFBA) and trifluoroacetic anhydride (TFAA), respectively, followed by XPS.[2,3]

FTIR spectra were obtained in the reflection mode, with the silver coating acting as the reflector. A blank silver coated microscope slide was used to acquire background spectra. In order to compare the intensity of the bands in a semi-quantitative manner, the thickness of organic coatings was maintained constant at about 650 nm and 1000 nm for the C_2H_4 - N_2O and C_2H_4 - (O_2+Ar) systems, respectively. Finally, as described elsewhere,[3] we examine the stability (solubility) of deposits by loss of thickness after immersion in aqueous solvents.

3. Results and Discussion

In order to optimise the deposition rate, r, and N- or O-incorporation into these organic films, one must judiciously select the wavelength, λ, of the VUV source, so that maximum absorption of photons and maximum photo-dissociation can be achieved.[4] At λ = 123.6 nm and 147.0 nm, the values of absorption coefficients, k, are quite high for both C_2H_4 and NH_3, as well as for N_2O and O_2.[4] High k values indicate efficient absorption of the photons, which possess energies of 10.3 eV and 8.7 eV for the Kr and Xe lamps, respectively. These greatly exceed bond energies of the molecules, and therefore readily

enable photo-dissociation reactions, often accompanied by redistribution of excess energy to the resulting fragments. The reader is referred to ref. [4] for primary processes relating to the molecules in question.
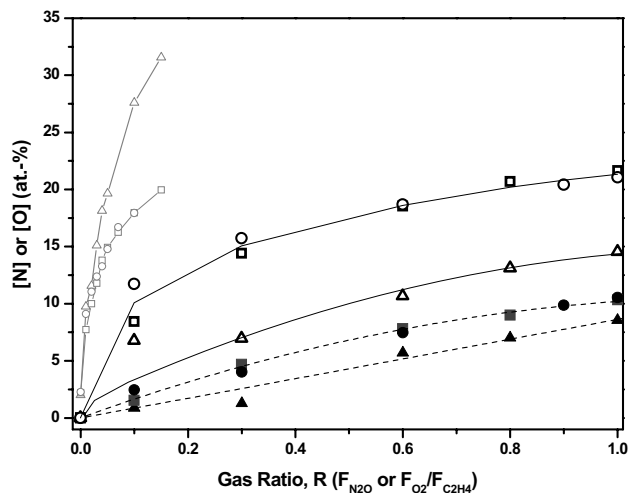

Figure 1. Surface concentrations of oxygen, [O], and nitrogen, [N] (in at.%), as a function of R of N_2O/C_2H_4 (black continuous lines) or O_2/C_2H_4 (gray continuous lines) gas mixtures: [O] for UV-PE:O films, deposited using the Kr (□) and Xe (○) lamps; and for PPE:O deposits (△). The corresponding values of [N] for the N_2O/C_2H_4 mixture are represented by the full symbols and dotted lines. Data for NH_3-based coatings are not shown, in order to avoid overcrowding.

Figure 1 shows the near-surface nitrogen [N], and oxygen [O], concentrations from broad-scan XPS measurements, for the three types of coatings obtained from C_2H_4-N_2O, as well as those corresponding to the C_2H_4-(Ar+O_2) mixtures. In all cases, [O] is seen to increase markedly with rising R, with no apparent distinction between the two photo-polymerised film types, but with significantly higher values than in the case of PPE:O: the highest [O] values, for R=1, are about 23 and 11 at.% for UV-PE:O and PPE:O, respectively, in the case of N_2O oxidiser. However, when O_2 was used as the oxidiser, the [O] values are seen to be reversed: 32 at.% and 20 at.% for PPE:O and UV-PE:O, respectively, at R=0.15. Now, Figure 1 also shows that significant concentrations of N are chemically bonded within the N_2O-based deposits, both in the UV-PE:O and in the PPE:O films. This is not unexpected, because atomic nitrogen is generated and it is very reactive; [N] values corresponding to

the two VUV lamps are indistinguishable, but only slightly higher than for PPE:O. In spite of the fact that [N]/[O] = 2 in the (N_2O) precursor molecule, this ratio is only about 0.6 in UV-PE:O, and slightly higher in PPE:O; this would suggest that the incorporation of oxygen dominates both in the photo- and the plasma-activated reactions. In other words, it is not surprising that the [N]/[O] ratio of the feed gas is not conserved in the deposits, especially in the PPE:O case, where molecular fragmentation by the plasma is well known. What *is* somewhat unexpected is the fact that N is incorporated less than one-third as "efficiently" as O. As to be expected, no N-incorporation took place when O_2 was the oxidiser, and its reactivity was vastly greater; this is manifested by the fact that at R=0.15 [O] had reached its highest practical values: For still higher R, the deposition rate became impractically low; in other words, etching reactions tended to dominate over deposition.

Figure 2(a) shows FTIR reflection-absorption spectra for a set of UV-PE:O films of nominally equal thickness, 650 nm, that had been prepared using the Kr VUV lamp; the three spectra shown correspond to different gas mixture ratios, namely R = 0 (pure ethylene), 0.6, and 1.0. Roman numerals I to V, shown below the main spectral features, refer to the broad bands that comprise overlaps of many different types of IR-active molecular motions. Clearly, I, III and IV are due to O- and N-containing moieties, since they are not visible on the R = 0 spectrum. In 2(b) we plot the amplitudes of bands I and III versus R, both for the UV-PE:O samples from (a) (and others corresponding to different values of R), as well as for the family of PPE:O samples. Focusing on O-bearing functional groups, band III deserves our particular attention since it represents stretching vibrations of carbonyl-containing groups, which include carboxylic acids, one of the functionalities of most interest in this present study: Supposing that the distributions of carbonyl-containing functional groups are similar in both types of films, the UV-PE:O films are quite obviously much richer in –COOH than their PPE:O counterparts, but it is not possible to estimate concentrations on the basis of the data we present

here. Nevertheless, XPS (Fig. 1) indicates at least 40% higher [O] content in the former. Our derivatization experiments using TFAA greatly assist in answering these questions.

Finally, Figs. 2(c) and (d) pertain to FTIR reflection-absorption spectra of UV-PE:O and PPE:O films deposited from C_2H_4-$(Ar+O_2)$ mixtures; (c) represents spectra of both film types, corresponding to R=0.1 and 1000 nm thickness. Not surprisingly, we note the very same spectral features as those in (a), except that band IV at 2150 cm^{-1} (assigned to C≡N stretching vibrations) is absent from the N-free samples in (c). In (d), we have again plotted the amplitudes of bands I and III versus R for both the UV-PE:O and the PPE:O samples from (c), along with others corresponding to different values of R. As in (b), we noted that the amplitude of the band near 2900 cm^{-1} varied little compared with those of I and III, so that the plotted data for the latter two represent *normalized* relative amplitudes. The major difference between (b) and (d), of course, is that in (d) it is the "P"-films that had higher [O] values than their "UV" counterparts, as we had pointed out in Fig. 1, hence the reversed trends of the continuous and dotted curves through the data points. Indeed, the main purpose in presenting these plots, (b) and (d), is to show that major, systematic structural differences exist between PPE:O and UV-PE:O deposits, as in the case of their N-containing counterparts. By way of a single rough example, the ratios of relative COOH to OH band amplitudes corresponding to R=0.1 in (d) are found to have numerical values of ~ 6 and ~ 1.8 for UV-PE:O and PPE:O, respectively, suggesting higher selectivity for the COOH functionality in the case of VUV photo-polymerized deposits. However, we underline that these data are the subject to much further ongoing research, and that the contribution of carbonyl-containing functional groups to band III has been considered constant in all films, for simplicity.

For lack of space we were not able to address the issue of stability in this text, but for some details about methodology and results relating to PPE:N and UV-PE:N films the reader may consult ref. [3]. PPE:O and UV-PE:O are inherently more stable in air, for obvious reasons.
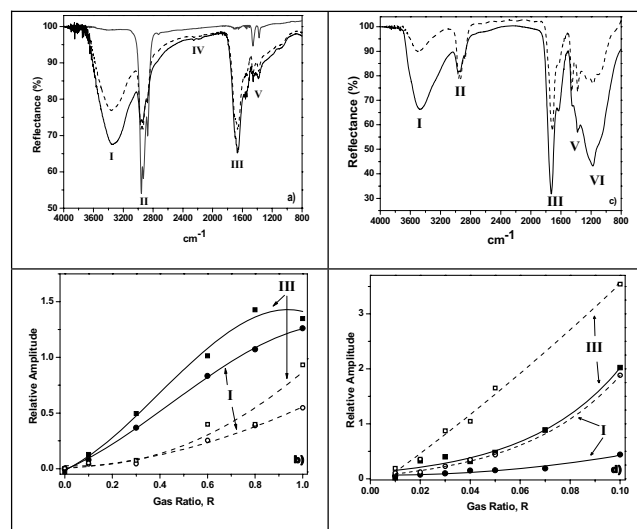

Figure 2. (a) FTIR reflectance spectra of 650 nm-thick UV-PE:O films, obtained with N_2O/C_2H_4 mixtures and the Kr lamp (λ= 123.6 nm); the three spectra correspond to $R = 0$ (—), 0.6 (----) and 1.0 (—). (b) Plot of relative amplitudes of bands "I" and "III" [see 2(a)] versus R, for UV-PE:O films (full symbols and continuous curves); for comparison, corresponding data for PPE:O deposits are also shown (open symbols, dashed curves). (c) FTIR reflectance spectra of 1000 nm-thick PPE:O (—) and UV-PE:O (---- KrL) films obtained by using the same O_2/C_2H_4 gas mixture ratio ($R = 0.10$). (d) Plot of relative amplitudes of bands "I" and "III" [see 2(c)] versus R, for UV-PE:O films (full symbols and continuous curves); for comparison, corresponding data for PPE:O deposits are also shown (open symbols, dashed curves).

Acknowledgements

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